On-surface coordination chemistry of planar molecular spin systems: Novel magnetochemical effects induced by axial ligands

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Paramagnetic transition-metal complexes assembled on surfaces are of great interest for potential applications in organic spintronics. The magnetochemical interactions of the spin of the metal centers with both ferromagnetic surfaces and optional axial ligands are yet to be understood. We use a combination of X-ray magnetic circular dichroism (XMCD) and quantum-chemical simulations based on density functional theory (DFT+U) to investigate these metal-organic interfaces with chemically tunable magnetization. The interplay between an optional axial ligand (NO, spin $S=1/2$ or NH_3 , $S=0$) and Ni and Co ferromagnetic surfaces affecting the spin of Co(II) tetraphenylporphyrin (d^7 , $S=1/2$), Fe(II) tetraphenylporphyrin (d^6 , $S=1$), Mn(II) tetraphenylporphyrin (d^5 , $S=5/2$) and Mn(II) phthalocyanine (d^5 , $S=3/2$) is studied. We find that the structural *trans* effect on the surface rules the molecular spin state as well as the sign and strength of the exchange interaction with the substrate. We refer to this observation as the surface spin-*trans* effect.

Introduction

A large portfolio of concepts in coordination chemistry of porphyrin and phthalocyanine based metallo-organic complexes has been developed to rationalize the broad spectrum of physico-chemical functionalities¹. Recently, coordination chemistry on the surface is being explored^{2–6}. In the specific case of competitive coordination which is usually referred to as the *trans* effect⁷, the ligand on one side of a metallo-organic complex is affecting the ground state energy or the bonding/unbonding kinetics with the second ligand on the opposite side. To understand coordination chemistry with the surface acting as a ligand^{8–10}, square-planar complexes and their reaction with axial ligands like NO, CO, NH_3 affecting the molecule-substrate bonding, have been monitored experimentally.

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This has been performed by measurements of the spectral characteristics in X-ray photoelectron spectroscopy (XPS)^{9,11,10}, in UV photoelectron spectroscopy (UPS)^{9,10} and in scanning tunneling microscopy/spectroscopy (STM/STS)^{10,6}. The term surface *trans* effect has recently been introduced to describe the observed reduction in bonding with the ‘surface-ligand’¹⁰.

Magnetochemical interactions of spin-bearing, square-planar transition metal complexes like porphyrins and phthalocyanines with ferromagnetic surfaces offer a unique platform to fabricate metal-organic interfaces with stable magnetization at room temperature that are of great interest for organic spintronics. The search for gaining control over the magnetic properties of these interfaces has revealed a number of important findings: paramagnetic complexes on surfaces may be magnetized by their specific bonding interactions with the ferromagnetic (FM) surface^{12–20}. Also, the coordination of surface-ligands to paramagnetic metallo-porphyrins and phthalocyanines often results in a significant hybridization and/or charge transfer^{21–26}. Furthermore, it has been demonstrated that the spin state in cobalt porphyrin adsorbed on a ferromagnetic Ni substrate can be controlled by axial coordination on the open site, e.g. by NO²⁷. The present work aims at answering the fundamentally important question arising from the above findings: to what extent can classical coordination chemistry concepts, which do not consider the surface specific molecule-substrate interaction, be used to understand the on-surface magnetochemistry of metallo-organic complexes?

We show that the effect of axial coordination onto the spin of planar coordination complexes like porphyrins and phthalocyanines supported on FM substrates can only be understood by inclusion of the surface-ligand into the

considerations. Our studies demonstrate that on-surface axial ligation can lead to i) spin states which are decisively changed by the interaction with the substrate, ii) a change in the spin alignment (sign of the exchange coupling: parallel or anti-parallel) or iii) a modification of the strength of the exchange coupling. These findings are based on X-ray magnetic circular dichroism (XMCD) spectroscopy and density functional theory calculations with additional Hubbard interaction taken into account (DFT+U). i) and ii) are revealed in the magnetochemistry of metallo-tetraphenylporphyrins (CoTPP, FeTPP and MnTPP) sandwiched between a FM surface (Co or Ni thin films) and the NO ligand. To demonstrate iii), we investigate the strongly chemisorbed²⁸ Mn-phthalocyanine/Co (MnPc/Co) system under the influence of the non-spin-bearing NH₃ ligand in comparison to the spin-bearing NO ligand. Therefore, the on-surface coordination of metallo-organic molecules is shown to lead to novel magnetochemical effects beyond those of classical coordination chemistry. Hence our observations classify as evidence for the surface spin-*trans* effect. Moreover, our data provide case studies for engineering magnetic metallo-organic interfaces in future spintronic applications.

Results

Research design

The electronic and magnetic properties of both the ad-molecules and the substrates are investigated by X-ray absorption spectroscopy (XAS) and XMCD spectroscopy (Fig. 1a). In the latter technique, circularly polarized X-rays from a synchrotron source with opposite helicities are used to perform the absorption experiments²⁹. XMCD, the difference of the XAS for opposite helicities, measured at the L_{2,3}-adsorption edges of the 3d transition metals provides information on the magnetization of both, the substrates and the adsorbed transition-metal complexes, separately, in an element-specific manner. Our experimental observations are complemented by density functional theory (DFT+U) calculations in order to reveal the effects of the axial ligation onto the electronic and spin states. In the DFT+U approach, the strong Coulomb interactions that are present within the open 3d-shell of the central metal ion are captured by the supplemented Hubbard U and exchange constant J. This approach has been shown to provide the correct spin state for free as well as substrate adsorbed metal-porphyrins^{15,17,30}. To manage computational efforts, we have carried out numerical calculations of the on-surface metallo-porphyrins (metal-P), *i.e.* without phenyl substitution^{13,31,16,17}.

Fig. 1 (a) Schematic representation of the X-ray magnetic circular dichroism (XMCD) experiment on metal-tetraphenylporphyrin (metal-TPP) adsorbed on a ferromagnetic thin film substrate. The magnetic moment of the transition metal centres which is induced by exchange interaction with the substrate is studied by XMCD before and after NO coordination. (b) Scanning tunneling microscopy (STM) of CoTPP on Ni showing that the molecules lie flat on the substrate. As a guide to the eye the chemical schemes have been superimposed in the STM data. (c-e) Molecular orbital (MO) diagrams depicting the reactions of Co, Fe and Mn TPPs with NO in absence of the surface-ligands.

In addition, scanning tunneling microscopy (STM) experiments provide insight into the 2D arrangement of the spin-bearing molecules at a molecular level and into the morphology of the samples in general (Figs. 1b and S1 in the ESI†). X-ray photoelectron spectroscopy (XPS) is primarily used to monitor the surface composition, *i.e.* substrate metal film thickness, molecular coverage and stoichiometry.

We have systematically studied the adsorption of d^7 , d^6 , and d^5 transition metallo-porphyrins (Co(II)TPP, Fe(II)TPP and Mn(II)TPP) onto the FM substrates. The spin of these square-planar complexes has been investigated with respect to the substrate-molecular bonding and the competitive axial ligation with NO. In the free molecules, the low-spin ($S=1/2$)⁹ and intermediate-spin ($S=1$)³² and high-spin ($S=5/2$)³³ states of CoTPP, FeTPP and MnTPP respectively are reconfigured to low-

spin ($S=0, 1/2, 0$)^{9,34–36} upon NO ($S=1/2$) coordination. As a basis for the discussion of the on-surface coordination in the focus of this paper, molecular orbital (MO) diagrams³⁷ illustrating the NO binding in absence of the surface-ligand are provided (Figs. 1c-e). XMCD experiments performed on the above spin-systems allow us to investigate the complex electronic and spin configurations which arise from the competitive interaction between the surface-ligand and the axial NO ligand. In addition to providing one unpaired electron, NO can undergo a non-innocent electron-transfer reaction³⁸. Thus, to assess the influence of the axial coordination onto the strength of the exchange coupling with the surface-ligand, we have chosen to study the strongly chemisorbed MnPc/Co system and its response to innocent³⁸ and non-spin-bearing NH_3 ($S=0$).

Fig. 2 XAS of CoTPP/Ni (a1), FeTPP/Ni (b1), MnTPP/Co (c1) and MnPc/Co (d1) measured at the respective L-edges, before and after exposure with the gaseous ligand (NO or NH_3). The corresponding XMCD spectra (a2–d2), clearly demonstrate an induced magnetic moment in the molecular spin systems. Positive dichroism at the L_3 edges corresponds to ferromagnetic exchange coupling with the substrate. NO ligation modifies the XAS peak shape. The XMCD spectra show the respective magnetic response of the spin bearing molecules: the magnetic moment in CoTPP/Ni is almost completely quenched, for FeTPP/Ni it is modified and reduced while for MnTPP/Co it is also reduced but the sign of the XMCD signal is inverted. This corresponds to an antiferromagnetically coupled magnetic moment. In the case of MnPc/Co (at low temperatures), the increased circular dichroism after NH_3 coordination indicates an increased spin. The magnetization density isosurface plots from the DFT+U calculation of the respective systems before (a3–d3) and after addition of the ligand (a4–d4) illustrate the spin density distribution and the bonding geometry. The light yellow isosurface denotes spin densities parallel to the substrate (ferromagnetic) and the light blue isosurface denotes spin densities antiparallel (antiferromagnetic) to the substrate spin.

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XAS and XMCD spectroscopy

Fig. 2 compares the Co, Fe and Mn $L_{2,3}$ -edges XAS and XMCD spectra recorded on CoTPP/Ni, FeTPP/Ni, MnTPP/Co and MnPc/Co systems. In the native state, *i.e.* before axial ligation, the observed energy positions of the L_3 -edge XAS signals appear at ~ 779.8 , ~ 709.2 , ~ 640.7 and ~ 640.0 eV, respectively, suggesting considerable electronic interaction of the central metal ion with the axial surface-ligand since the oxidation states of the respective central metal ions seem to be $\leq +2$ in comparison to the molecular bulk states^{27,13,18,28,39}. The XMCD signals clearly demonstrate that there is a stable magnetic moment of the ad-molecule. This magnetic order in the sub-monolayer regime of paramagnetic molecules on FM substrates originates from the considerable exchange interaction between the substrate and the ad-molecule^{7-9,10,13,16}. From the parallel orientations of the $L_{2,3}$ -edges XMCD signals of Co, Fe and Mn with respect to those of the substrates (Fig. S2 in the ESI†), a FM coupling is concluded in all native cases. Angular-dependent XMCD measurements reveal a collinear alignment of the molecular spins with the

substrate magnetization¹³. Notably, it is not always the case that the paramagnetic molecule retains its spin upon adsorption; as for example, for Co(II) phthalocyanine (CoPc)^{40-42,21,43} on Ni substrate we do not observe an XMCD signal (Fig. S3 in the ESI†).

NO coordination leads to almost complete quenching of the XMCD signal in CoTPP/Ni, while for FeTPP/Ni and for MnTPP/Co the XMCD signal is reduced but still present (Figs. 2a2-c2). Remarkably, the dichroic signal in NO-exposed MnTPP/Co is oriented antiparallel with respect to the substrate. Thus, the NO-CoTPP ($S=0$) and NO-FeTPP ($S=1/2$) in the on-surface configuration behave in first approximation as anticipated by MO theory (Figs. 1c and 1d). However, MO theory predicts a spin state ($S=0$) for NO-MnTPP (Fig. 1e), which is not seen in our experiment. Moreover, the reversed sign of the circular dichroism of NO-MnTPP, indicates an antiferromagnetic (AFM) coupling which is contrary to the usually observed FM coupling found in experiments on comparable systems^{12,13,27,28}.

Fig. 3 The 3d orbital local magnetic density of states (LMDOS) is shown for CoP/Ni (a), NO-CoP/Ni (b), MnP/Co (c) and NO-MnP/Co (d) in the chemisorbed case. Without NO, both CoP and MnP are found to be ferromagnetically (FM) coupled with the respective substrates. The out of plane d_{z^2} and d_{π} orbitals of CoP and MnP are hybridized with the substrate as reflected in the broadening of the respective states. In case of CoP/Ni, the hybridization of d_{z^2} leads to a reduction of the spin below the initial value of $S=1/2$. The binding of NO onto the surface-supported CoP can be rationalized in the formation of a σ -bond with d_{z^2} of Co (depicted in the inset) as seen in the separation of the state. In case of MnP, a π -bond between d_{π} of Mn and π^* of NO is formed as depicted in the inset. The NO binding is found to weaken the hybridization of the d states with the substrate. The spin state of the on-surface NO-CoP is approximately zero ($S \approx 0$) in good agreement with considerations neglecting the substrate ($S=0$). In contrast, the spin state of the on-surface NO-MnP complex *can not* be rationalized in neglect of the surface where a spin state of $S=0$ is expected. Consistent with the experiments, a spin state between $S=1/2$ and $S=0$ is found to be antiferromagnetically coupled to the substrate.

The XAS of the transition metal centers are also significantly modified upon NO exposure (Figs. 2a1-c1): this modification can be primarily related to i) a change in the availability of empty states for the transition of 2p core electrons to the unoccupied 3d levels being excited by the X-ray photons, and/or ii) the change in the oxidation states of the metal ions after ligation with NO⁹⁻¹¹. The Co, Fe and Mn L₃-edge XAS signals are observed with their maxima at ~780.4, ~709.3 and ~640.9 eV, respectively after the NO ligation. The stronger shift of the X-ray absorption peak upon NO coordination for CoTPP (+0.4 eV) compared to NO-FeTPP (+0.1 eV) and NO-MnTPP (+0.2 eV) resembles the versatile coordination chemistry of NO which is related to the NO-central metal(M) bond angle. The NO-M bond is known to be bent (~120°) for NO-CoTPP and linear (~180°) in case of NO-MnTPP; NO-FeTPP is found to have an intermediate bond-angle⁴⁴. In the case of bent M-NO where back-bonding is less important, NO is sometimes described as the anionic π -ligand (NO⁻) with the tendency to withdraw charge from the metal center whereas with an efficient back-bonding in case of the linear (~180°) bond the increase of the metal oxidation state is smaller. The DFT+U calculations of the on-surface complexes reproduce these bond angles (Figs. 2a4-d4).

A surprisingly different system is given by MnPc/Co (intermediate spin state of S=3/2 in absence of the substrate⁴⁵) which strongly chemisorbes to the Co substrate²⁸. We have studied the strength of the magnetic coupling to the surface before and after NH₃ coordination by measuring the dependence of the XMCD/XAS ratio as a function of the temperature. NH₃ (S=0) was chosen since NO coordination with the d⁵ ion in NO-MnTPP/Co (Fig. 2c) leads to a low spin state, *i.e.* a smaller XMCD. For MnPc/Co (Figs. 2d1-d2) we find that the Mn XMCD/XAS ratio (Fig. S4 in the ESI†), *i.e.* the magnetization, exhibits almost no temperature dependence in the range of 45 – 373 K, thus providing evidence for a strong molecule-substrate magnetic coupling. After coordination with NH₃, the XMCD/XAS ratio shows a strong decrease when approaching room temperature (Fig. S4 in the ESI†), thus indicating a significantly weaker exchange coupling. However, while the exchange interaction is reduced, the data recorded at ~80 K indicate a sizeable increase of the spin after NH₃ coordination (Figs. 2d1-d2).

In the following, the experimental results of all four spin-systems are interpreted at a microscopic level by means of DFT+U calculations, as illustrated in the magnetization density plots (Figs. 2a3-d3 and 2a4-d4). The DFT+U calculations predict magnetization changes completely consistent with the XMCD measurements. This is further discussed in the next sections, evidencing towards the surface spin-*trans* effect.

Discussion

On-surface magnetochemistry in low-spin and high-spin metallo-porphyrins: NO coordination to CoP/Ni and MnP/Co

The mechanism of NO binding with low-spin d⁷ Co(II) and high-spin d⁵ Mn(II) porphyrin in the free molecule and the formation of low-spin (S=0) nitrosyl complexes^{9,36} can be rationalized by the MO diagrams shown earlier (Figs. 1c and 1e). In the low-spin Co(II) porphyrin, only the singly occupied d_{z²} is available for

bonding, thus the NO binding results in a σ -bond with the singly occupied π^* orbital of NO, whereas in the high-spin Mn(II) porphyrin the availability of singly occupied d _{π} orbitals (*i.e.* d_{xz} and d_{yz}) results in π -bonding with NO – schematically shown in the insets in Fig. 3. Our experimental and theoretical results on these two systems confirm that on the surface, NO binding proceeds in the same fashion. This is reflected in i) the higher electron affinity of σ -binding NO as confirmed in the observed stronger shift upon reaction with NO in Co XAS with respect to Mn XAS, ii) the calculated M-NO bond angles (Figs. 2a4 and 2c4) and iii) the hybridization of the d states with NO (Figs. 3b and 3d).

Recent DFT+U calculations showed that metallo-porphyrins can chemisorb or physisorb on metallic substrates³¹. In the case of chemisorbed metal-organic molecules Van der Waals interaction corrections can be neglected. In our DFT+U calculations for chemisorbed CoP/Ni (Fig. 3a), the hybridization of the singly occupied d_{z²} orbital with the substrate yields a reduced spin state of ~0.71 μ_B on Co. For the on surface NO-complex (Fig. 3b) we find a magnetic moment of ~0.04 μ_B on Co, *i.e.* the spin is almost completely quenched and the local magnetic density of states (LMDOS) is now equally distributed over the two spin-channels (spin $\uparrow$ and spin $\downarrow$). The quenching of the spin is in accordance to our experimental results (Figs. 2a1 and 2a2) and similar to the outcome for the free molecule (Fig. 1c). The hybridization of the d_{z²} with the substrate is reduced in favor of hybridization with NO and separation into bonding and antibonding states. Notably, the distance between the Co-ion and the substrate is increased only slightly (by 0.06 Å from initial 2.34 Å) thus reflecting that NO exerts here only a small structural *trans* effect^{7,44}. Notably, the observed reduction of the magnetic moment due to hybridization with the substrate is consistent with our XMCD data of Co-octaethylporphyrin/Ni (CoOEP/Ni) and CoPc/Ni systems, where we find that the magnetic moment is stronger reduced in CoOEP/Ni which has less bulky substituents than CoTPP and is even quenched in case of CoPc/Ni (Fig. S2 in the ESI†). In contrast to CoP/Ni, the influence of the surface-ligand onto the spin is clearly visible in MnP/Co (Figs. 3c and 3d): without NO, the spin state is slightly reduced to ~4.35 μ_B on Mn (between S=2 and 5/2, *c.f.* Ref. 31) NO binding affects all d-states and yields a significant structural *trans* effect as reflected in the increased distance (by 0.3 Å from initial from 2.11 Å) between the Mn-ion and the surface. This leads to a decreased hybridization between the substrate and d _{π} (now hybridized with NO and separated into bonding and antibonding states) and of d_{z²} (now mostly unoccupied orbitals of Mn). Importantly, while reducing the spin significantly towards a low-spin state (S=0), a magnetic moment of -0.49 μ_B remains AFM coupled with the substrate. In Mn-XMCD (Fig. 2c2), this is expressed by the inverted sign of the circular dichroism.

X-ray diffraction (XRD) data of NO-CoTPP in bulk shows a displacement of the Co ion from the center of 0.09 Å, as value which is slightly larger than the calculated Co lift-up on surface⁴⁶. The Co-N(NO) bond-length (1.83 Å) and angle ($\leq 128.5^\circ$) correspond very well with the calculated on-surface bond-length (1.82 Å) and angle (~123.6°). In case of NO-MnTPP in bulk, XRD data shows a Mn-N(NO) bond length of 1.64 Å and a linear (177.8°) Mn-N-O bond⁴⁷. This corresponds very well with the

calculated on-surface Mn-N(NO) bond length (1.63 Å) and angle (177.0°). The displacement of the Mn ion from the center (0.34 Å) is comparable to calculated value for the on-surface configuration. Overall, the *structural* characteristics of the calculated on-surface Co, Fe and Mn porphyrines correspond very closely with the XRD data of the bulk species. However, this is *not the case* for the spin states, the most remarkable feature being provided by the AFM coupled spin in the on-surface NO-MnTPP complex.

Fig. 4 The 3d LMDOS for MnPc/Co (a) and NH₃-MnPc/Co (b), in the chemisorbed case. Without NH₃, the out of plane d_z^2 and d_π orbitals are significantly hybridized with the substrate as recognized by their broadening. In the NH₃ complex, the hybridization with the substrate is weakened providing narrower d-states. In the calculated on-surface structure the Mn-ion is pulled out of the plane towards the NH₃ (Figure 2d4). The spin state of Mn is increased from approximately intermediate spin to approximately high-spin. This is experimentally observed in the increased XMCD/XAS ratio at low temperatures (Figure S4 in the ESI†). The weaker hybridization with the substrate is reflected in a strong reduction of the calculated magnetic coupling strength. This is confirmed by a stronger decrease of the XMCD/XAS ratio of the NH₃-complex in our experiments performed with increasingly higher temperature. A ferromagnetic coupling is found before and after NH₃ coordination.

On-surface magnetochemistry (FeP/Ni + NO): Tuning of the molecular spin

In contrast to d^7 Co and d^5 Mn porphyrins where a quenching of the magnetic moment is anticipated, the case of NO coordination with d^6 Fe porphyrin is expected to yield the low-spin $S=1/2$ complex³⁵ (Fig. 1d). The mechanism of NO binding to Fe porphyrin can be seen as an intermediate between the two previously discussed d^7 and d^5 complexes and is primarily reflected in a Fe-NO angle of $\sim 170^\circ$ for FeP – in between 120° (d^7) and 180° (d^5). Furthermore, the intermediate spin state ($S=1$) of Fe(II) porphyrin may change its spin state easily, e.g. the histidine-bound natural Fe-porphyrin is high-spin ($S=2$)⁴⁸. It is worth to mention that from all three on-surface metalloporphyrins reacting with the NO-ligand, it is the Fe-porphyrin

which shows the best reversibility upon heating. NO is completely desorbed from the FeTPP on-surface complex at $\sim 260^\circ\text{C}$ (Fig. S5 in the ESI†) thus at lower temperature than CoTPP ($\sim 340^\circ\text{C}$) and in contrast to MnTPP which is found to be irreversibly bound within the experimental range up to 400°C . This reflects the distinctive bonding fashion and strength between NO and Co, Fe and Mn ions.

Our DFT+U calculations (Fig. S7 in the ESI†) for FeP on the Ni surface have been performed for the molecule both being in physisorbed and chemisorbed conformation. The calculations yield spin states between $S=3/2$ and $S=2$ in case of physisorption ($\sim 3.73 \mu_B$) and chemisorption ($\sim 3.57 \mu_B$). For the physisorbed and chemisorbed NO-FeP complex we find spin states of $\sim 1.93 \mu_B$ and $\sim 3.49 \mu_B$, respectively. On the basis of the observed reduction of the Fe-XMCD signal (Figs. 2a and 2b) and the calculations suggesting that the exchange coupling strength is not reduced significantly (Fig. S6 in the ESI†), we favor the physisorbed FeP configuration which shows a significant reduction of the spin state.

On-surface magnetochemistry (MnPc/Co + NH₃): Tuning the exchange coupling.

We now discuss the on-surface magnetochemistry of the MnPc/Co system ($S=3/2$) and the subsequent effect induced by σ -donating axial NH₃ ligand. Without axial NH₃ ligand, our calculations for chemisorbed MnPc on Co (Fig. 4) find a magnetic moment of $\sim 3.25 \mu_B$ (spin state in between $S=3/2$ and $S=2$) and a strong hybridization between the surface and the out-of plane d-orbitals (d_z^2 and d_π). The calculations also yield a high coupling energy of ~ 189 meV. Experimentally, this is reflected in the nearly constant XMCD/XAS ratio as a function of temperature (Fig. S4 in the ESI†) which yields a lower limit for the exchange energy in the order of ~ 103 meV as discussed further in the Electronic Supplementary Information (ESI†).

In the calculations for MnPc/Co with axial NH₃, the ligand pulls the Mn-ion out of the phthalocyanine plane by ~ 0.42 Å from initially 2.30 Å and leads to an increased spin of $\sim 4.45 \mu_B$ (between $S=2$ and $S=5/2$). In the corresponding experimental data, the higher spin state is expressed by a higher XMCD/XAS ratio observed at lower temperatures (Figs. 2d1-d2). Remarkably, in our calculations the exchange coupling energy was found to be reduced to only ~ 4 meV. In the temperature dependent XAS/XMCD data, the reduction of the exchange energy is reflected in a significant decrease of the relative XMCD signal with increasing temperature (Fig. S4 in the ESI†). The data yield an accordingly reduced exchange energy of ~ 31 meV. Notably, a manipulation of the exchange energy has been claimed for Fe porphyrin, on the basis of the observed reduction of the circular dichroism after NO exposure⁴⁹, but the system has not been measured at different temperatures. We also note that the calculations and experiments for FeTPP/Ni and NO-FeTPP/Ni do not show significant differences in the exchange energy (Fig. S6 in the ESI†). The here presented MnPc/Co+NH₃ case unambiguously demonstrates the relation between axial coordination and exchange energy, i.e. surface spin-*trans* effect.

Conclusions

The presented data provide insight into the on-surface

magnetochemistry of spin-bearing square-planar complexes. The spins of the complexes (CoTPP, FeTPP, MnTPP and MnPc) are, before coordination with the optional axial ligand, found to be ferromagnetically coupled to the ferromagnetic substrate. The DFT+U calculations reveal a significant hybridization between the d-states in the transition-metal centers and the surface-ligand and show how the hybridization is affecting the spin states in the on-surface complexes. Subsequent axial coordination with the gaseous ligands (NO or NH₃) was found to lead i) to a rearrangement of the electronic structure in general agreement with coordination chemistry and ii) to induce a structural *trans* effect on the surface with a magnitude depending on the exact chemical species involved. The structural *trans* effect is deduced from the calculated increase of the distance between the transition-metal center and the substrate as well as the decrease of the hybridization with the surface-ligand. In the XMCD data of d⁷, d⁶, d⁵ porphyrins and NO this is reflected respectively by a quenching of the spin in CoTPP/Ni, a modification of the spin in FeTPP/Ni, and most notably a remaining magnetic moment in MnTPP/Co whose alignment with the substrate changed from FM to AFM by axial-ligation. The last system, namely MnPc/Co demonstrates that an axial ligand (here NH₃) may lead to a reduction of the exchange coupling strength. Hence, our data provide compelling evidence that on-surface axial-ligation leads to a *trans* effect, which influences the molecular spin state as well as the sign and strength of the exchange interaction. We therefore propose the term surface spin-*trans* effect for the consequences of the structural *trans* effect on the spin and the exchange coupling's sign and strength.

The surface spin-*trans* effect is anticipated to serve as a powerful concept in the design of tailor-made spin-tunable metal-organic interfaces, which may find applications in magnetochemical sensors, in components for future spintronic devices or quantum computing building-blocks. Our study underlines that on-surface magnetochemistry is emerging as a novel arena challenging the notions of classical coordination chemistry.

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