**Magnetic exchange coupling of a synthetic Co(II)-complex to a ferromagnetic Ni substrate**

Christian Wäckerlin, Pablo Maldonado, Lena Arnold, Aneliia Shchyrba, Jan Girovsky, Jan Nowakowski, Md. Ehesan Ali, Tatjana Hählen, Milos Baljovic, Dorota Siewert, Armin Kleibert, Klaus Müllen, Peter M. Oppeneer, Thomas A. Jung* and Nirmalya Ballav*

Magnetic exchange coupling of a synthetic porphyrin-related complex of Co(II) with C_{2v} symmetry to a ferromagnetic Ni substrate.

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On-surface assembly of a spin-bearing and non-aromatic porphyrin-related synthetic Co(II)-complex on a ferromagnetic Ni thin film substrate and subsequent magnetic exchange interaction across the interface were studied by scanning tunnelling microscopy (STM), X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) and density functional theory +U (DFT + U) calculations.

Magnetochemical interactions across hybrid molecule-substrate interfaces are of eminent interest for potential applications in molecular spintronics.¹ In particular, it has been shown that a ferromagnetic substrate can exhibit magnetic exchange coupling with various paramagnetic transition-metal complexes and thereby introduce a magnetic moment in the first monolayer of these complexes even at room temperature.² Furthermore, on-surface coordination chemistry has recently been employed to modify this induced molecular magnetic moment as well as the strength and sign of the magnetic exchange interaction between molecules and the substrate.³⁻⁷ However, to the best of our knowledge, the exchange-coupling to ferromagnetic substrates has been reported in the literature only for metallo-porphyrins, metallo-phthalocyanines and rare-earth-metal double-decker phthalocyanine complexes.^{2,3,8-23} A major question is, whether the magnetic exchange interaction can also be obtained for structurally different synthetic complexes. If confirmed, this could open access to a much wider range of magnetically-tuneable on-surface complexes. Here we show that a structurally different porphyrin-related synthetic complex containing a Co(II) ion (designated as complex **1** or simply Co-complex; *cf.* sketch in Fig. 1a)²⁴ exhibits an

induced-magnetic moment upon exchange coupling with a ferromagnetic Ni substrate. In this Co-complex, the pyrrolenine and pyrrole units of the porphyrin have been replaced by pyridine and carbazole groups, respectively. Notably, in contrast to porphyrins and phthalocyanines, the macrocycle under study is inherently non-planar, non-aromatic, and has a lower (C_{2v}) symmetry (Fig. 1b). The electronic, magnetic and structural properties of an on-surface configuration have been investigated by combining X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), scanning tunnelling microscopy (STM), and density functional theory calculations taking additional Hubbard interactions into account (DFT + U).

The Co-complex (*cf.* ref. 24 for synthetic details and characterization) was sublimed under ultra-high vacuum onto a ferromagnetic Ni(001) thin film grown on a Cu(001) single crystal^{3,4} (sketched in Fig. 1c). STM data, obtained after sublimation of the carefully degassed molecules onto Ni(001),

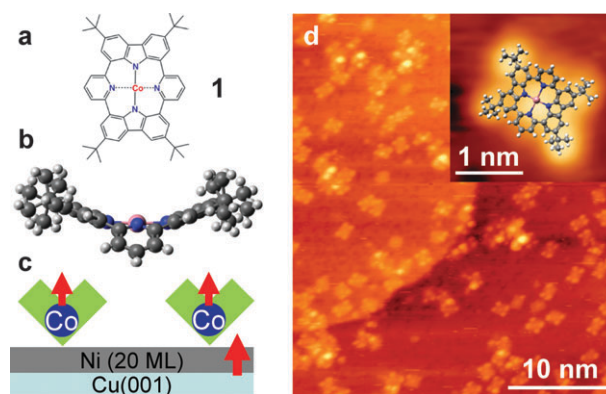


Fig. 1 (a) Molecular scheme of the porphyrin-related complex **1**, (b) side view based on the crystal structure,²⁴ (c) sketch of the investigated system: the Co-complex adsorbed on a ferromagnetic Ni(001) thin-film grown on Cu(001). (d) Scanning tunnelling microscopy (STM) data of the Co-complex on Ni(001) (−1.2 V, 20 pA, 300 K). Single molecules adsorbed on the Ni(001) surface are observed with their macrocyclic core parallel to the substrate.

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1 visualize the on-surface species (Fig. 1d). The adsorbed
 molecules randomly distributed on the surface with their
 macrocyclic core parallel to the substrate and most of the
 ad-molecules are imaged as rectangular objects. The four *tert*-
 5 butyl substituents are imaged as bright protrusions.²⁵ This
 adsorption behaviour corresponds well to results obtained for
 Mn, Fe, Co and Ni porphyrins adsorbed on Co(001) and Ni(001)
 thin films.^{3–5,14} In the case of the stacking of two complexes
 onto each other, as observed for a small fraction, the over-
 10 lapping parts are imaged as brighter protrusions.

The magnetic and electronic properties of the ad-complexes
 are studied by XAS and XMCD spectroscopies. The XMCD
 technique measures the difference in the absorption cross
 section of circularly polarized X-rays with opposite helicities.
 15 Tuning the photon energy to the $L_{3,2}$ -adsorption edges of the
 respective 3d transition-metal ions, XMCD provides element-
 specific information on the magnetisation of both the substrate
 and the adsorbed transition-metal complexes separately.²⁶ For
 the Co-complex on Ni(001), the XAS/XMCD measurements
 20 (*cf.* Fig. 2) were carried out at 300 K at normal incidence of
 the X-rays. In this geometry XMCD is sensitive to the out-of-
 plane magnetic moments of the sample. For the measurements
 the Ni films were magnetized perpendicular to the film plane,
i.e. parallel to their easy axis of magnetization and retained this
 25 magnetisation in remanence, due to the ferromagnetism of the
 thin film.³

The XAS and XMCD spectra of the Ni $L_{3,2}$ edges of the
 substrate (Fig. 2a and b) correspond to the magnetic moment in
 the substrate. The respective XAS and XMCD signals of Co $L_{3,2}$
 30 provide direct evidence for an induced magnetic moment in the
 Co ion in the molecule (Fig. 2c and d). The same sign of the
 respective Ni and Co ions of the XMCD spectra (Fig. 2b and d)
 reveals that the ad-complex's magnetic moment is ferromagne-
 tically (FM) coupled to the magnetization of the substrate.
 35 Notably, these results tally well with our XMCD measurements
 performed on different Co-porphyrins on Ni(001).^{3,4} The XAS
 of the currently studied Co-complex shows a substructure at the
 Co L_3 absorption edge. Compared to the Co-porphyrin on Ni,^{3,4}
 40 the Co-complex's spectra show a narrower signal at 779.4 eV
 and a reduced side-peak at 781.3 eV (Fig. 2c). We tentatively
 explain this difference by the different electronic structure of

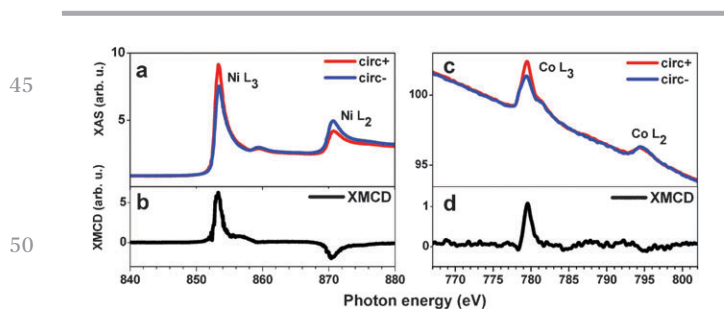


Fig. 2 X-ray absorption (XAS) and X-ray magnetic circular dichroism (XMCD) data of the ferromagnetic Ni substrate (a and b) measured in remanence, after magnetisation, and of the Co-complex (c and d). Co $L_{3,2}$ and XMCD of the Co-complex adsorbed on the Ni thin film. The dichroic signal measured at room temperature provides clear evidence for an induced magnetic moment in the on-surface complex and its ferromagnetic coupling to the substrate.

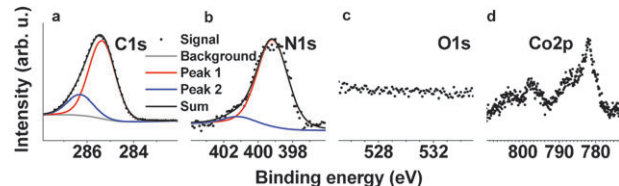


Fig. 3 X-ray photoelectron spectroscopy (XPS) data obtained on a multilayer of the Co-complex on Ag(111). The C1s (a) and N1s (b) signals are consistent with the chemical structure of the complex and the absence of any O1s (c) signal shows that the complex is sublimed without the THF and H₂O ligands present in the crystalline compound. The Co2p_{3/2} peak (d) is significantly narrower than the respective data obtained on the molecular crystals.²⁴

the Co-complex *vs.* the Co-porphyrin on-surface species as discussed in the context of the DFT + *U* calculations (*vide infra*).

Before discussing the magnetic properties of the on-surface complex on the basis of our DFT + *U* calculations, it is important to remark that the Co-complex in its crystalline form is axially ligated by tetrahydrofuran (THF) and H₂O ligands.²⁴ Our X-ray photoelectron spectroscopy (XPS) experiments (Fig. 3) performed on multilayer thin films on a Ag(111) surface show the respective C1s, N1s and Co2p XPS signals of the Co-complex and the complete absence of the THF and H₂O ligands (no O1s signal). We assign the absence of detectable oxygen to the dissociation of weakly bonded THF and H₂O ligands at or below the sublimation temperature. Moreover, the narrower Co2p signal for the thin-film produced by vacuum sublimation (Fig. 3d) compared to the complex in crystalline form²⁴ is an indication of a lower spin-state. Overall, the XPS results emphasise the importance to use complementary surface-analytical tools in order to unambiguously define the sublimed species.

To shed further light on the adsorption of the Co-complex on the ferromagnetic Ni(001) film substrate, DFT + *U* calculations (for details of the method see ref. 4 and 5) have been applied. Calculations were also performed for the free molecule as well as for its crystalline form. These simulations reproduced the experimental observations of a $S = 3/2$ high-spin (HS) state in the crystalline form²⁴ and showed a $S = 1/2$ low spin (LS) state for the molecule adsorbed on the Ni surface. We have studied different orientations and locations of the complex on the Ni(001) surface. Performing full geometrical optimisations, the most stable configuration was obtained when the Co atom was located in the hollow position, *i.e.* on top of a Ni atom of the 2nd surface layer, at a distance of 3.62 Å. The plane formed by Co and Ni ions of the molecule then lies 1.98 Å above the Ni surface. Besides, after the ionic relaxation, the two pyridine groups of the molecule are completely flattened, parallel to the Ni surface. Importantly, our calculations revealed the ferromagnetic coupling between the spins in the Co-complex and in the substrate, with the Co-complex being in the LS state, for the most favourable on-surface conformation. This is illustrated by the computed magnetization density, shown in Fig. 4a.

Two exchange paths contribute to the ferromagnetic coupling: direct Co–Ni exchange (distance of 2.53 Å) and super-exchange through the nitrogens. The latter is strongest for the pyridinic Ns (induced moment of $-0.02 \mu_B$). Note that this super-exchange interaction is also ferromagnetic, as the

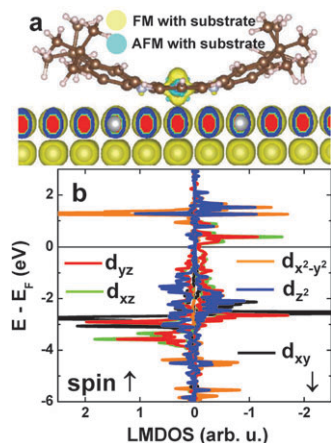


Fig. 4 Results of DFT + *U* calculations of the Co-complex on Ni(001) in its energetically most favourable arrangement. (a) Magnetization density isosurface plots. Bright yellow (bright blue) isosurface depicts positive (negative) spin densities. (b) Local magnetic density of states (LMDOS). The low-spin $S = 1/2$ magnetic moment in the Co ion is ferromagnetically coupled to magnetic moment of the Ni substrate.

Co–N–Ni bond angle is only 72° . The local magnetic density of states (LMDOS) projected on the Co 3d orbitals (Fig. 4b) illustrates that the Co 3d orbitals are appreciably broadened, exhibiting a hybridization with the Ni surface. The unpaired electron resides mainly in the d_{xz} and d_{yz} orbitals, and to a lesser extent in the d_z^2 orbital. In this respect the orbital population is different from that of for example the Co–porphyrin, where mainly the d_z^2 orbital is singly occupied. This result might give rise to the above-mentioned difference in the XAS of the Co–porphyrin adsorbed on Ni and the here studied adsorbed Co-complex. In the case of the minority of molecules which stack onto each other (*cf.* STM) we believe that the magnitude of the intermolecular exchange interaction is very weak (large Co–Co distance) to affect the overall strong molecule–substrate FM interaction.

In conclusion, we have provided convincing evidence for an exchange-stabilized magnetic moment in a synthetically designed, non-planar and non-aromatic Co(II)-complex adsorbed on a ferromagnetic Ni substrate. Our combined experimental and theoretical results suggest that the induced-magnetic moment, as previously only observed in the case of metallo-porphyrins and metallo-phthalocyanines, is a general effect not limited to these complexes. Complementary surface analytical tools were employed for the investigation of the magnetochemical interaction across the molecule–substrate interface. We anticipate our results to open-up new opportunities for the incorporation of spin-bearing transition metal ions other than Co(II) into the synthetic complex.

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