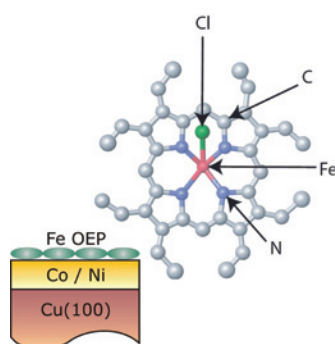




## The digital octopus – or dual career for porphyrins

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**Fig. 1:** Schematic representation of Fe octaethylporphyrin (OEP) chloride and the sample setup.

It's not only that they look like molecular octopuses – they also have 'their tentacles everywhere': the Fe-porphyrins investigated here have eight legs as their counterpart in the fauna. Fascinatingly, porphyrins are parts of numerous biologically active molecules. A member of this family with magnesium in the centre is chlorophyll – the green colour of leaves – which insures that plants can use sun light to store energy. In haemoglobin Fe-porphyrins take care of the oxygen transport in our blood. The latter have aroused the interest of physicists, since with iron in the centre these molecules act as tiny magnets, a prerequisite on the way to achieve molecular spintronics. This technology utilizes the electron spin additionally to its charge. To make the porphyrin useful for spintronics, it is essential to investigate the interaction of the porphyrin with surfaces and, even more challenging, to manipulate or switch its iron spin direction.

In this experiment we studied a single layer (monolayer: ML) of porphyrins on epitaxially grown ferromagnetic cobalt and nickel layers on Cu(100) [1,2]. From our measurements we observe that the Fe-porphyrins adsorb flat on the surface like octopuses 'accidentally' reaching the beach and drying in the sun. We find that the Fe spin of the porphyrins couples ferromagnetically to magnetic films (the beach in our picture). The promising result for spintronics is that the iron centres of the porphyrins can be switched by changing the magnetic direction of the underlying magnetic film. This might be used in the future for spin-dependent electric transport through biomolecular devices.

The results were obtained with X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at the beamline UE56/2-PGM2. Thereby we were able to discriminate the magnetic effects of all the key players in this game. The samples were prepared by sublimating Fe-octaethylporphyrin chloride (OEP) under UHV conditions on a 5 ML Co film and a 15 ML Ni film epitaxially grown on Cu(100) (schematic representation in Fig. 1). One advantage of the X-ray absorption spectroscopy is that the information on the electronic structure and the magnetism can be gained in an element-specific manner

by tuning the photon energy to the absorption edges of the elements in the molecule (e.g. Fe, N, C) and the underlying film (Co or Ni) (see labels in Fig. 1).

To determine the orientation 'of the octopus on the beach' we analyzed the Near-Edge X-ray Absorption Fine Structure (NEXAFS) at the nitrogen K-edge versus the incidence angle of the incoming light with linear polarization [1]. These spectra exhibit a prominent angular dependence (Fig. 2). This reveals a well defined orientation of the molecules on the surface. The detailed fine structures can be assigned to typical molecular electronic structures – the antibonding  $\pi^*$ - and  $\sigma^*$ -resonances (labelled in Fig. 2). The  $\sigma^*$ -resonances are scattering resonances probing the antibonding states oriented in direct connection from atom to atom. For the case of the N K-edge these are the N-Fe and N-C  $\sigma^*$ -states. Since the  $\sigma^*$ -resonances are strong at normal X-ray incidence and the  $\pi^*$ -resonances dominate at grazing X-ray incidence it can be safely concluded that the octopus is basically lying flat on the beach.

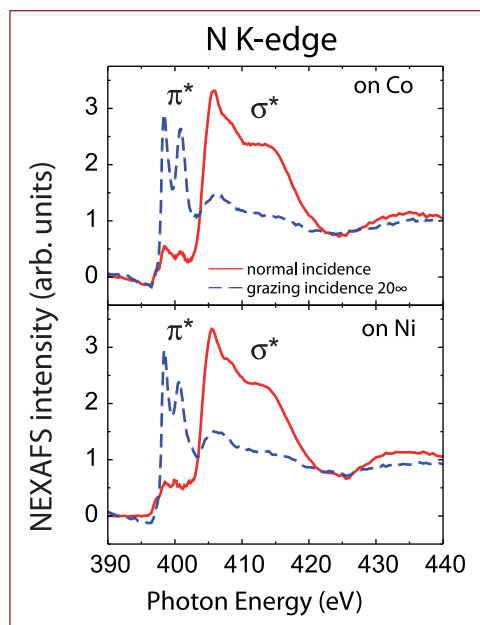
Next we tune the photon energy to the Fe  $L_{2,3}$  absorption edges to probe the magnetic properties (spin direction, magnetic moment) of the Fe atom in the molecule – the head of the octopus – in comparison to the magnetic properties of the Ni or Co film [1,2]. In Fig. 3 the Fe XAS and XMCD spectra are shown for the Ni film and Co film substrates. Since a 5 ML Co film exhibits an in-plane magnetization whereas that of a 15 ML Ni film is out-of-plane, the temperature-dependent measurements were carried out at grazing or normal X-ray incidence, respectively (see inset of Fig. 3). For both cases a clear XMCD signal can be seen at room temperature (Fig. 3 b, d) which demonstrates that the Fe spins in the porphyrins are ordered. Furthermore, it turns out that on the Co substrate all spins in the molecules are oriented in-plane whereas on the Ni film they are all oriented out-of-plane. A magnetic field of only  $\sim 10$  mT was applied to saturate the magnetic films, although at 300 K this field is far from being sufficient to order the paramagnetic Fe-porphyrin molecules. Hence, there must exist a further coupling mechanism of the spin in the molecule to the ferromagnetic films. Interestingly, there

#### References:

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#### Acknowledgements:

We want to thank P.M. Panchmatia, B. Sanyal, P.M. Oppeneer and O. Eriksson (Uppsala University, Sweden) for their enlightening DFT+U calculations, which revealed the coupling mechanism. R.S. wishes to thank the DFG (SFB 658) for financial assistance and the University of Duisburg-Essen for hospitality and support. Supported by BMBF and DFG (SFB 658, Heisenberg-Programm).

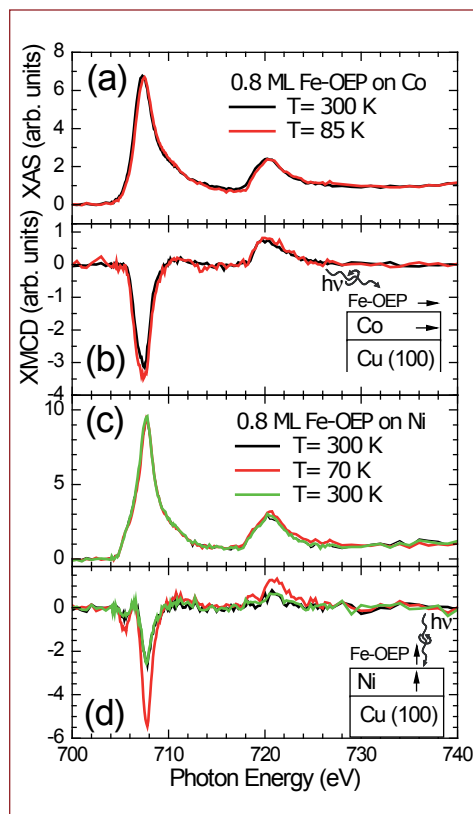


**Fig. 2:** Angular dependence of NEXAFS (linear polarization) of Fe-OEP at the N K-edge for the Co and Ni substrates. X-rays at normal and grazing incidence ( $20^\circ$ ) were applied to determine the molecule's orientation (Fig. taken from [1]).

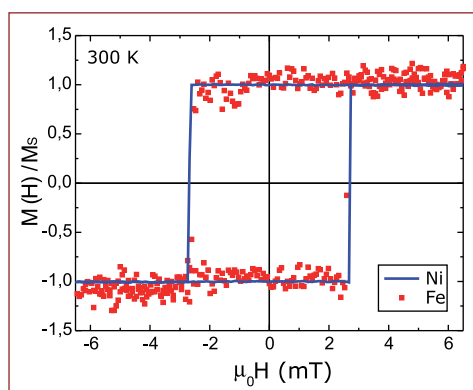
is hardly any change of the Fe XMCD intensity when cooling down the Co substrate to 85 K. However, when the Ni film is cooled down, a dramatic increase of the Fe XMCD signal can be seen in Fig. 3 (d). This reveals that the coupling of the Fe spins to the Ni film is considerably weaker than the one for Co [2].

What is the nature of this coupling phenomenon? To answer this question we collaborated with O. Eriksson and P.M. Oppeneer at Uppsala University, Sweden. Their density functional theory (DFT+U) calculations for the porphyrins on the Co film revealed that there is no direct hybridization between the Fe atom in the molecule and the Co film below [1]. However, the Fe-surrounding N atoms interact with the surface. By combining these results we conclude that a  $90^\circ$  indirect coupling mechanism is responsible for the observed phenomena [1].

To investigate the coupling in greater detail we measured element-specific hysteresis curves by tuning the photon energy to the Fe XMCD maximum or to the ones of the respective ferromagnetic films and swept the magnetic field. The result for the Ni substrate is presented in Fig. 4. The hysteresis curve of Fe in the molecule directly follows the one of the ferromagnetic film. This shows that the coupling is ferromagnetic. Even more fascinating is that the two hysteresis curves have the same shape, which demonstrates that the



**Fig. 3:** XAS and XMCD spectra (applied field 10 mT) for 0.8 ML Fe-OEP molecules on Co (a, b) recorded at 300 K and 85 K and on Ni (c, d) at 300, 70 and 300 K (Fig. taken from [2]).



**Fig. 4:** Element-specific hysteresis curves of the porphyrin Fe atom and the Ni film at the  $L_3$ -edge XMCD maximum of Fe OEP on Ni/Cu(100) at 300 K (Fig. taken from [1]).

Fe spin of the molecule directly follows the magnetization of the film. Hence, the spin of the molecule can be switched by reversing the magnetization of the film. The spin can point either left/right (as in the photograph) or up/down – a real digital octopus. The switching of the spin direction might open new possibilities for molecular devices for spintronics, where e.g. spin-dependent electric transport is utilized.

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