

COMMUNICATION

Investigating magneto-chemical interactions at molecule-substrate interfaces by X-ray photo-emission electron microscopy

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The magneto-chemical interaction of spin-bearing molecules with substrates is interesting from a coordination chemistry point of view and relevant for spintronics. Unprecedented insight is provided by X-ray photo-emission electron microscopy combined with X-ray magnetic circular dichroism spectroscopy. Here the coupling of a Mn-porphyrin ad-layer to the ferromagnetic Co substrate through suitably modified interfaces is analyzed.

Spin-bearing metal-organic molecules like porphyrins and phthalocyanines on magnetic substrates have recently received increasing attention.¹ This trend is driven by the perspective to fabricate spin-interfaces with controllable properties for applications in molecular spintronics.² X-ray photo-emission electron microscopy (PEEM), an imaging technique, reveals spatially resolved maps of the local X-ray absorption cross section. It thus provides a chemically-sensitive tool for spectro-microscopy investigations revealing both electronic and magnetic properties with nanometer scale chemical specificity if combined with X-ray magnetic circular dichroism (XMCD) and X-ray absorption (XA) spectroscopy. While being well established for studying magnetic nano-structures, down to the level of single nanoparticles,³ PEEM has not yet been used to investigate molecule-substrate spin-interfaces. Here, we employ X-ray PEEM (Fig. 1a) to study the chemical and magnetic interaction of adsorbed manganese(III) tetraphenylporphyrin chloride (MnTPP(Cl)) (Fig. 1b) with the native metallic and oxygen covered Co substrate as well as with Co substrates modified by a wedge shaped Cr spacer underneath the molecular layer.

The magnetic domain pattern of the substrate is analyzed by excitation of the Co thin films with circularly polarized X-rays in PEEM. The XMCD effect gives rise to a spatial intensity variation which scales with the projection of the local magnetic moment \vec{m} onto the X-ray propagation vector \vec{k} . Tuning the

photon energy to the Co L_3 absorption edge (~ 778 eV) therefore reveals the individual magnetic domains of the Co(001) substrate (Fig. 1a, left inset). Magnetic domains of the substrate imaged white (black) [grey] correspond to a magnetization vector \vec{m} aligned parallel (antiparallel) [perpendicular] with the incident photons.

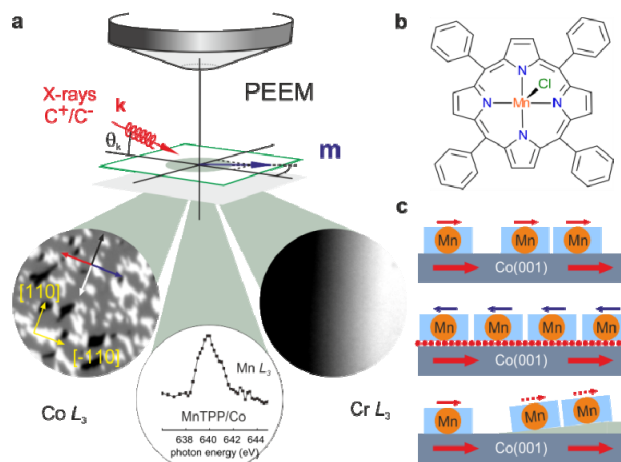


Fig. 1. (a) Sketch of the experimental setup: *Bottom left*: magnetic contrast image of a bare Co film, bright (dark) areas denote a magnetization parallel (antiparallel) to the X-ray beam propagating along \vec{k} direction, grey areas reveal a magnetization perpendicular to the X-rays; *center*, Mn L_3 edge XA spectrum recorded on the MnTPP/Co system; magnetic anisotropy directions i.e. $\langle 110 \rangle$ marked yellow. *right*; X-ray absorption contrast (elemental contrast) of a Cr-wedge on Co. (b) Chemical structure of MnTPP(Cl). (c) Cartoon of MnTPP(Cl) molecules and their magnetization on the different samples investigated; Co (*top*), oxygen-covered Co (*center*) and a Cr-wedge layer on Co (*bottom*).

The element-specific sensitivity of PEEM to the magnetic moment induced in a single MnTPP(Cl) layer on Co(001) is demonstrated in Fig. 2a and b by tuning the photon energy to the Co and Mn L_3 edge, respectively. Note that upon adsorption

onto the Co substrate the molecular species [Mn(III)TPPCI] is reactively modified to Mn(II)TPP by loss of the Cl ligand.^{1f} The magnetic domain pattern of the Co substrate is shown in Fig. 2a. By tuning the photon energy to the Mn L_3 edge (~ 640.4 eV) we obtain the magnetic contrast image for the molecular ad-layer (Fig. 2b). The latter (Mn) image reproduces the domain pattern of the Co film thereby providing evidence for a ferromagnetic (FM) coupling of the molecules to the substrate. Such coupling has also been found in previous XMCD experiments^{1a,1f}; DFT+U calculations on similar systems revealed that the magnetic interaction of the metal-center's spin with that of the Co substrate can be due to an indirect exchange coupling mediated by the N- p_z electrons, which are spin-polarized due to hybridization with Co substrate orbitals.^{1c, 1j, 1l} The magnetic contrast in our PEEM experiment is confirmed by the contrast reversal of the domain patterns when tuning the photon energy to the Mn L_2 edge (see Figure S1 in the ESI). The XMCD contrast in Fig. 2b amounts to about one to two percent of the total signal, and hence is similar to the spectroscopic findings reported in earlier work.^{1a, 1f, 1j, 1l}

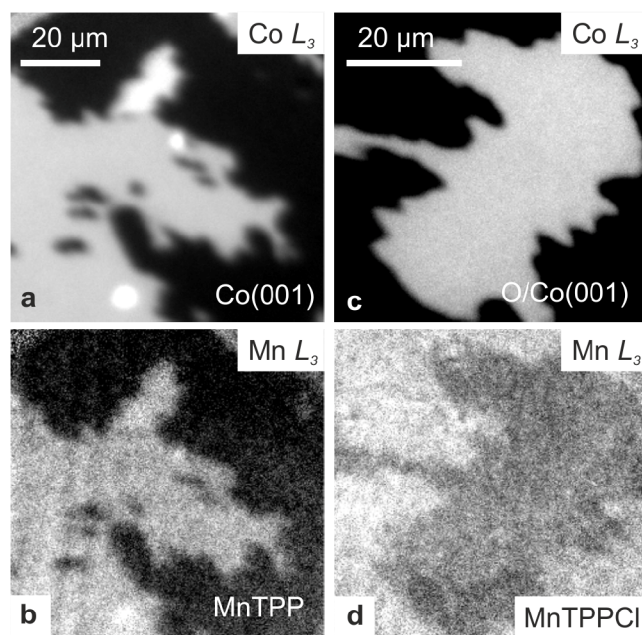


Fig. 2. Magnetic contrast images obtained at the Co L_3 edge (a,c) and at the Mn L_3 edge (b,d) of the MnTPP(Cl) molecules on Co(001) and O/Co(001), respectively.

In comparison we investigate, MnTPPCI layers on oxygen-covered Co substrates (O/Co(001)) where Mn ions couple antiferromagnetically to the Co substrate due to superexchange via the O atoms, in analogy to bulk antiferromagnets.^{1d, 1f} XA spectroscopy (see ESI) and complementary X-ray photoelectron spectroscopy^{1f} additionally demonstrate that the chemical species is actually Mn(III)TPPCI (i.e. the Cl ligand remains). The domain pattern of the Co substrate is shown in Fig. 2c and, indeed, when tuning the photon energy to the Mn L_3 edge (~ 641.0 eV), we find that the

MnTPPCI molecules display an inverse magnetic contrast compared to that of the Co substrate (see Fig. 2d and ESI).

The magnetic exchange coupling of a monolayer of MnTPP to the Co substrate is studied in dependence of the thickness of a Cr spacer layer in the form of a wedge (cf. Fig. 1c and ESI). Cr is known to promote a strong interlayer coupling in magnetic multilayers, such as Fe/Cr/Fe.⁴ The onset region of the Cr-wedge on the sample is detected when recording an intensity image with the photon energy set first to the Cr L_3 edge (578.0 eV) and then to the pre-edge energy at 572.0 eV. Pixelwise division of both images reveals the Cr wedge in the field of view as shown in the right side of Fig. 1a (Cr rich regions appear bright).

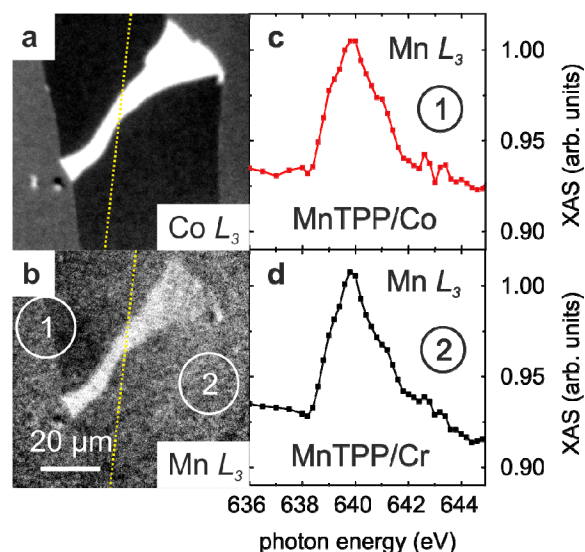


Fig. 3. (a) Magnetic domains of the cobalt substrate at the onset of the Cr-wedge as seen when tuning the photon energy to the Co L_3 edge. (b) Magnetic contrast of the molecular layer detected with the photon energy set to the Mn L_3 taken at the same sample spot like (a). The yellow dashed lines in (a) and (b) denote the onset of the Cr-wedge with the Cr thickness increasing to the right. Local XAS spectra recorded at the Mn L_3 edge of MnTPP on the bare Co(001) surface (c) and on the Cr-wedge (d). The spectra were obtained in the marked areas (white circles) on the left or right from the yellow dashed line, respectively.

Fig. 3a (3b) show the magnetic contrast images of the Co substrate (MnTPP layer) at the same spot as in the right side of Fig. 1a. Across the investigated coverage range of the Cr wedge no influence on the underlying magnetic domain pattern of the Co is found. However, the presence of Cr significantly alters the magnetic contrast detected from the MnTPP molecules across the wedge: The MnTPP molecules on the bare Co surface (left side of Fig. 3b) show magnetic contrast with FM coupling (cf. Fig. 2). With increasing Cr coverage the Mn contrast decreases (Fig. 3b, right hand side) and for even higher Cr thickness no magnetic contrast in the MnTPP molecules is found (cf. ESI). XA spectra acquired at the Mn L_3 edge reveal the same spectral signature on Co or at any position of the PEEM image of the Cr wedge (Fig. 3c and d, respectively). These spectra match with previously reported data on Mn(II)TPP on Co^{1f}, thus, the oxidation state of the Mn ion is the same on Co and on Cr (cf. also ESI). The gradual loss of

magnetic contrast in the molecules at the onset of the Cr wedge is unexpected when compared to the findings for tri-layer structures such as Co/Cr/Fe.⁵ In such systems the ferromagnetic substrate gives rise to a thickness-dependent spin polarization in the Cr spacer layer, which induces a magnetization coupling to the top-layer film which is determined by the magnetization of the bottom substrate layer. In analogy to the top-layer in the inorganic system, the MnTPP molecules are expected to magnetically interact with the bottom substrate via the spin-polarized electrons of the Cr layer either directly via hybridization with the Mn d-electrons or indirectly via the N p_z electrons (see also ESI). The gradual loss of a detectable effect suggests that this interaction mechanism via Cr is too weak to result in a stable coupling at room temperature. Notably, the inter-layer coupling of paramagnetic MnTPP molecules through a Cr spacer differs from the corresponding case of only inorganic magnets in multilayers e.g. Fe/Cr/Fe in that the ad-molecules (which are paramagnetic in their bulk form) in the layer do not interact with each other^{1a}, but only with the underlying substrate. Thus, the absence of inter-molecular interactions at elevated temperatures (>300 K) may be responsible for the absence of a stable coupling of the molecules to the Co substrate via the Cr wedge.

In conclusion, we have demonstrated chemically-sensitive X-ray PEEM in combination with spin-sensitive XMCD to detect molecule-surface magneto-chemical interactions down to the single monolayer coverage. This spatially resolving spectro-microscopy technique is expected to be particularly advantageous when studying coupling phenomena on electronically complex and as well as on patterned substrates. Furthermore, wedged samples enable a direct comparison of various interfaces in one measurement under identical conditions. Importantly, as a microscopy technique PEEM goes beyond the established photo-absorption spectroscopy in that it allows for the investigation of on-surface coordination chemistry and on-surface magneto-chemistry in real time and space.

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