

Supplementary Information

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

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Experimental: PEEM and XMCD experiments were performed at the SIM beamline of the Swiss Light Source, Switzerland (cf. Ref. 3a, 3b). Samples were prepared in a preparation chamber attached to the microscope with a base pressure below 5×10^{-10} mbar. The clean Cu(001) crystal was prepared by sputtering with Ar ions and subsequent annealing to ~ 800 K. Co thin films (approx. 20 atomic layers) and the Cr-wedge (by using a shutter) were deposited onto the prepared substrates by means of e-beam evaporation. The thickness of the Co thin films, the Cr-wedges as well as the molecular coverage of MnTPPCI was controlled by means of a quartz crystal microbalance. The latter was calibrated in independent scanning tunneling microscopy experiments. The full wedge from 0 to nominally 8 atomic monolayer thicknesses was prepared in steps of equal width and one nominal monolayer height over the total wedge extension of about 3 mm. Half of the sample remained uncovered by Cr, such that PEEM allows for a direct comparison of the molecular coupling to the bare Co and the Cr covered part of the sample. The cleanliness of the substrates was monitored by low energy electron diffraction. An oxygen reconstructed Co(001) substrate was prepared according to the protocol given in Ref. 1f. During the deposition of the MnTPPCI molecules (purity 98%; Sigma-Aldrich), the substrates were kept at room temperature. All samples were demagnetized by means of applying an ac-magnetic field before transferring them into the PEEM chamber where measurements were performed at room temperature.

The deposition of the Mn(III)TPPCI molecules on the oxygen reconstructed cobalt substrate leads to an AFM coupling of the manganese ion. The chemical state of the manganese ion is therefore not changed due to the retention of the chlorine ligand attached to the MnTPPCI molecules (Ref. 1f). This is also confirmed by measuring X-ray absorption spectra at the Mn L_3 edge using PEEM. The shape and position of the L_3 peak (~ 641.5 eV) are similar to those in spectra acquired with the standard XAS experiments referred in ref. 1f. Therefore we conclude that manganese is in the Mn(III) oxidation state (see Fig. S1 g).

In Fig. S1 we show the magnetic contrast when tuning the photon energy to the Mn L_2 edge. The contrast reversal compared to the Mn L_3 edge (cf. Fig. 2 b and d) confirms the magnetic origin of the signal.

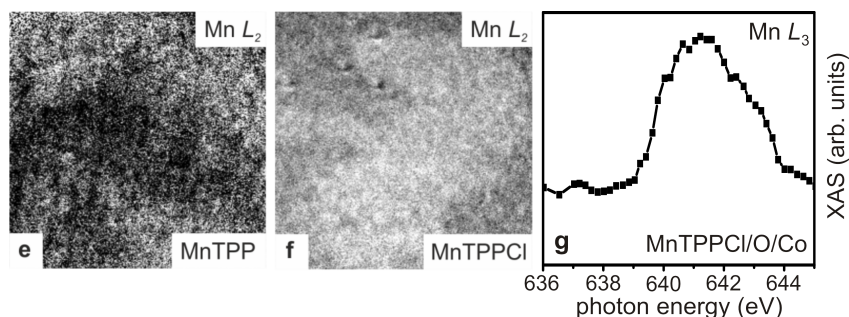


Figure S1. PEEM images acquired at the Mn L_2 edge of the MnTPP(Cl) molecules on Co(001) (e) and O/Co(001) (f), show an inverse magnetic contrast when compared to the Mn L_3 edge (Figure 2b,d) and thus confirm the magnetic origin of this signal. (g) XA spectra acquired at the Mn L_3 edge of the MnTPP(Cl) molecules deposited on the oxygen reconstructed cobalt substrate.

Fig. S2 compares data taken at the same spot of the sample, but with the photon energy tuned to the L_3 edges of Cr, Co, and Mn, respectively. All data show the onset region of the Cr wedge, similar to Fig. 3a and 3b but at another place on the sample. Fig. S2 a shows the chemical contrast of the Cr layer. Note that the Cr rich regions appear bright. The Cr coverage ranges from zero in the upper right corner to nominally one monolayer in the lower left part. The magnetic domain pattern of the Co substrate is shown in Fig. S2 b. No influence of the Cr wedge on the domain pattern is seen. Fig. S2 c presents the magnetic contrast of the Cr layer as found at low coverage. The magnetic domain pattern resembles that of the Co substrate, which confirms the ferromagnetic polarization of the Cr as found in metallic tri-layers Co/Cr/Fe (cf. Ref. 5(b) of the main text). Note that the magnetic contrast in Fig. S2 c stems mainly from the Cr $3d$ electrons. The coupling between bottom and top layer in the metallic Co/Cr/Fe tri-layer is also mediated by the spin-polarized conduction electrons (cf. e.g. page 292 ff. in Ref. 3(d) of the main text). Despite the detectable polarization of the $3d$ electrons in the Cr layer, the molecular ad-layer exhibits no magnetic polarization when being in contact with the Cr, cf. Fig. S2 d.

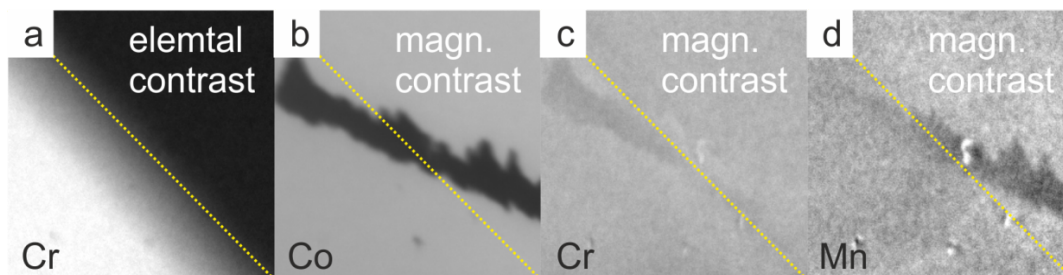


Figure S2. Magneto-chemical contrast of MnTPP(Cl) on a Cr-wedge on a Co(001) substrate. (a) XA elemental contrast of the Cr-wedge. (b)-(d): Magnetic contrast image recorded at the same spot with the photon energy tuned to the Co L_3 edge in (b), to the Cr L_3 edge in (c), and to the Mn L_3 edge in (d).