



	Experiment title: Magnetism in highly-ordered metal-organic coordination structures by XMCD and STM at beamline ID08	Experiment number: HE 2836
Beamline: ID08	Date of experiment: from: 28/01/2009 to: 03/02/2009	Date of report: 10/08/2009
Shifts: 18	Local contact(s): Dr. J. C. Cezar	<i>Received at ESRF:</i>
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Report:

The aim of the experiment HE2836 was the investigation of the spin state and magnetic coupling in two-dimensional metal-organic charge transfer networks, in particular $\text{Mn}(\text{TCNQ})_x$ structures, at surfaces. Those compounds have been reported to exhibit relatively high Curie-temperatures in bulk samples (~ 50 K) and in case of $\text{Ni}_2(\text{TCNQ})$ even ferromagnetic transition temperatures beyond room temperature have been reported [1]. While it is believed that ferromagnetic order in the bulk samples arises due to exchange coupling via the TCNQ ligands it is an open question if such coupling could exist in planar structures adsorbed on a metal surface. The purpose of the measurements was to obtain insight into the electronic state of the metal centers as well as the molecular ligands.

After finishing the measurement series on the $\text{Mn}(\text{TCNQ})_2$ structures we continued the beam time by XMCD measurements on $\text{Tb}(\text{Pc})_2$ molecules on a $\text{Cu}(100)$ surface, since the proposed $\text{Fe}(\text{TCNQ})_2$ networks turned out to be significantly less ordered than the $\text{Mn}(\text{TCNQ})_2$ networks. The measurements on the $\text{Tb}(\text{Pc})_2$ are a continuation of the experiment HE2106. $\text{Tb}(\text{Pc})_2$ molecules represent a novel class of single-molecule magnets where a single Terbium ion is located between two phthalocyanine (Pc) units. The aim of this experiment was the determination of the magnetic anisotropy and the observation of magnetic hysteresis in such highly oriented surface supported systems since the blocking temperature of $\text{Tb}(\text{Pc})_2$ has been determined to be higher than 40K [2].

Results have been obtained on $\text{Mn}(\text{TCNQ})_2$ structures on the $\text{Cu}(100)$ and $\text{Ag}(100)$ surfaces as well as Mn impurities on the $\text{Cu}(100)$ surface for comparison. The preparation of the $\text{Mn}(\text{TCNQ})_2$ compounds was carried out in-situ at the ESRF taking advantage of the dedicated STM chamber connected to the high-field magnet of the ID08 beamline. Figure 1 shows a summary of the morphological characterization of the samples. LEED and STM, acquired at different positions on the samples, were employed prior to the XAS measurements to ensure the homogeneity of the samples. The coverage was kept low enough to provide the necessary space and mobility for the adsorbates to form fully reticulated networks. The Mn-to-TCNQ concentration ratio was carefully adjusted to avoid the formation of Mn metal clusters and surface alloying.

Temperature and magnetic field dependent XAS and XMCD spectra were recorded at the $L_{2,3}$ Mn-edges and K N-edge in total electron yield mode using circular and linear polarized light at angles between normal (0°) and grazing (70°) incidence. We report on a number of significant results: (1) The Mn atoms in the network structures exhibit sharp XAS and XMCD spectral features and a strong natural linear dichroism signifying the strong interaction between the Mn atoms and the TCNQ molecules. (2) There is a noticeable difference in XAS lineshape between the structurally similar networks on the $\text{Cu}(100)$ and $\text{Ag}(100)$ surfaces. (3) On both surfaces the Mn spectra are consistent with a high-spin d^5 configuration [3]. (4) The N-edge spectra for both systems reveal signatures of charge transfer to the molecule compared to spectra of

multilayer TCNQ films [4]. (5) There is no significant magnetic anisotropy in the Mn centers. (6) The magnetization curves vs. temperature and field do not give evidence for magnetic coupling between the Mn atoms. (7) There is no magnetic dichroism at the N-edge of the molecules detectable.

Figure 2 shows a summary of the XAS and XMCD characterization of the Mn atoms. Mn impurities (<0.01 ML) deposited on Cu(100) held at 8 K exhibit rather isotropic XAS spectra, see figure 2 (c). Upon incorporation of Mn into the supramolecular networks the XAS lineshape changes significantly and exhibits a strong natural linear dichroism as can be seen in figure 2 (a) and (b) also for the spectra recorded with circular polarized light. This signifies the formation of strong coordination bonds to the TCNQ molecules where the Mn centers are subjected to a C_4 symmetry crystal-field environment giving rise to the natural linear dichroism. The binding to the ligands does not change the d^5 character of the Mn atoms and the metal centers remain in the high-spin state, supported by the sizable XMCD intensity and the XAS branching ratio. The absence of significant magnetic anisotropy further supports the d^5 high-spin scenario with no orbital moment present. Although the structure on the Cu and Ag surfaces are found to be very similar significant distinct spectral features are observed for the two systems. We ascribe this to the differences in the adsorbate-substrate hybridization competing with the coordination bonding. However, for both surfaces we find no evidence for magnetic coupling between the Mn centers from the analysis of temperature dependent XMCD spectra and magnetization curves recorded at the L_3 -edge, example shown for the Mn(TCNQ)₂ network on Cu(100) in figure 3 (b). The fitting of the magnetization curve with a Brillouin function suggests independent paramagnetic Mn atoms.

Figure 3 (a) shows the XAS spectra at the N-edge recorded with linear polarization at grazing incidence for the Mn(TCNQ)₂ on Ag(100). The lineshape is in agreement with molecules adsorbed parallel to the surface. Moreover, the spectra signify charge transfer to the molecule [4], which is also present at the absence of Mn atoms. No XMCD intensity was observed at the N-edge rendering the molecules non-magnetic. The same result is valid for the Cu(100) surface. The strong hybridization of the ligands with the surface could quench potential magnetic interactions between the Mn centers.

Figure 4 shows a summary of the results obtained for the Tb(Pc)₂ molecules on Cu(100). We succeeded in the thermal evaporation and deposition of integer Tb(Pc)₂ molecules on the Cu(100) surface as shown in figure 4 (a). On this surface the molecules are isolated on the surface due to the strong interaction of one of the Pc units in close contact with the copper surface. The XAS and XMCD measurements show that we can obtain XAS spectra of only very little amount of isolated SMMs on a Cu(100) surface as can be seen in figure 4 (b). Spectra were taken at the Tb $M_{4,5}$ edge as well as the K N-edge for the phthalocyanine molecules in magnetic fields of 5T and temperature of 8K. Moreover, we have measured the pristine powders of Tb(Pc)₂ and Dy(Pc)₂ to check the integrity of the molecule samples and provide a comparison between the electronic and magnetic behavior of the molecules in bulk polycrystalline environments and coupled to a metal surface.

Neither the powder samples nor the surface supported molecules showed magnetic hysteresis, confirming results obtained during a previous experiment HE2106. The strong natural linear dichroism shown in figure 4(b), demonstrates that the 4f shell is subjected to an appreciable crystal-field environment. Furthermore, the magnetization curves, shown in figure 4(c), exhibit a giant anisotropy of the magnetic moments which reflects the strong anisotropy of the orbital moment at the Tb ions. At the moment the data is further analyzed by atomic multiplet calculations. Potential charge transfer between molecules and surface could give rise to strong deviations of magnetic properties compared to bulk samples.

At the time of writing, the analysis of the data together with the XAS simulations is still in progress. At the moment we are carrying out STM and tunneling electron spectroscopy on metal-TCNQ structures adsorbed on a Au(111) surface. The measurements clearly demonstrate that the TCNQ does not undergo charge transfer upon adsorption. Only molecules in coordination networks are charged. This lateral charge transfer could give rise to magnetic coupling between the metal centers.

References

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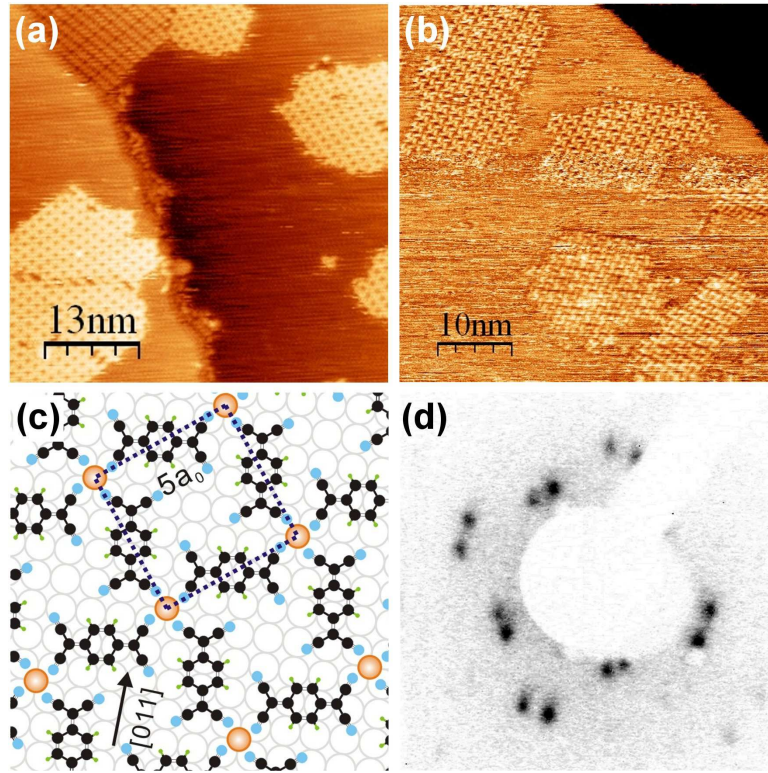


Figure 1: STM images of $\text{Mn}(\text{TCNQ})_2$ structures on $\text{Cu}(100)$ (a) and $\text{Ag}(100)$ (b) surface taken at ESRF prior to XAS measurements. (a) In upper left corner a patch of pure TCNQ phase is visible. (c) Structure model of the $\text{Mn}(\text{TCNQ})_2$ phase on $\text{Cu}(100)$. A similar structure is identified on $\text{Ag}(100)$ with different relative orientation of the network with respect to the registry of the surface. (d) LEED image taken at ESRF of the $\text{Mn}(\text{TCNQ})_2$ network on $\text{Ag}(100)$. Two slightly different oriented square structures can be identified.

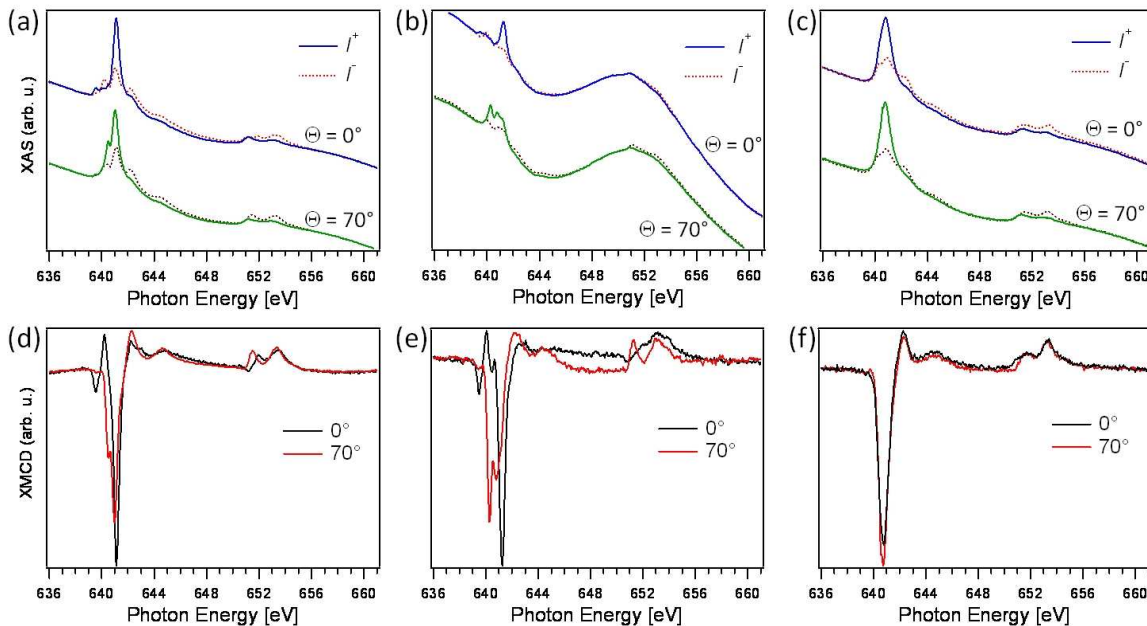


Figure 2: (a)-(c) XAS spectra at the Mn $L_{3,2}$ -edge with right I^+ and left I^- circularly polarized light taken at $B=5\text{T}$ and $T=8\text{K}$ for x-ray normal ($\theta=0^\circ$) and grazing incidence ($\theta=70^\circ$) angles. (a) $\text{Mn}(\text{TCNQ})_2$ on $\text{Cu}(100)$, (b) $\text{Mn}(\text{TCNQ})_2$ on $\text{Ag}(100)$, and (c) Mn impurities on $\text{Cu}(100)$. (d)-(f) Corresponding XMCD spectra for the spectra shown in (a)-(c), respectively. Note that the non-linear background in (a)-(c) arises from the Cu and Ag EXAFS.

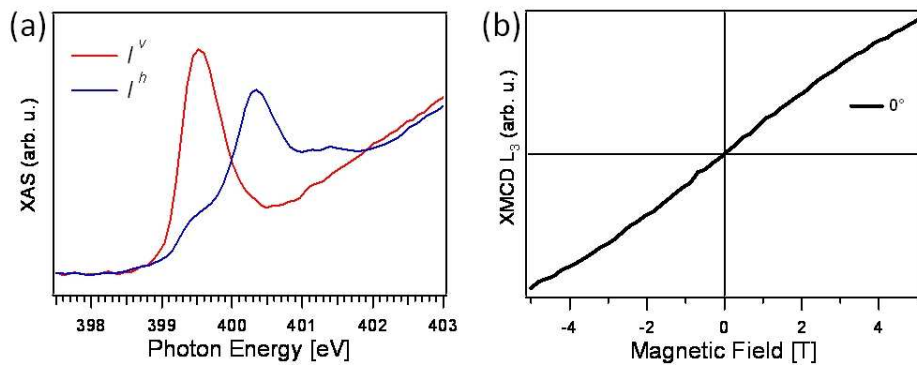


Figure 3: (a) XAS spectra taken at the N-edge with linear polarized light at grazing x-ray incidence for the $\text{Mn}(\text{TCNQ})_2$ network on $\text{Ag}(100)$. (b) XMCD L_3 intensity plotted vs. magnetic field for the $\text{Mn}(\text{TCNQ})_2$ network on $\text{Cu}(100)$.

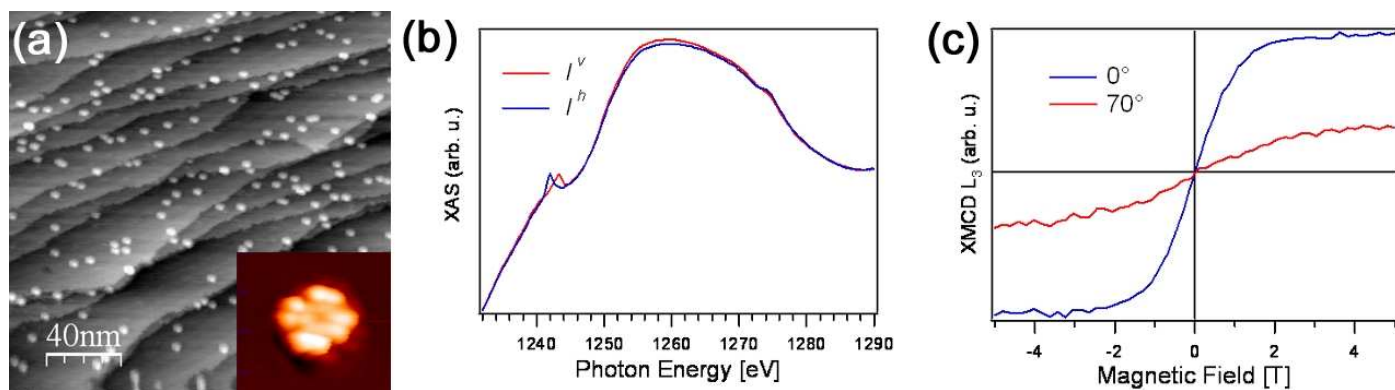


Figure 4: (a) STM image of a low coverage of Tb-DD molecules (white protrusions) deposited onto a $\text{Cu}(100)$ surface via sublimation from a powder sample. (Image taken at the ID-08 beamline prior to XAS measurements.) The inset shows a detailed view of the DD with a similar lobe structure as observed at cryogenic temperatures [5]. (Image taken in Stuttgart at substrate temperature of 300K.) (b) Absorption spectra of Tb using in- and out of plane polarized light. The strong non-linear background is a result of the Cu EXAFS. (c) Magnetization curves of the Tb-DD. The plot shows the normalized M_5 XMCD peak height.