ESRF	**Experiment title:** Magnetism in charge transfer metal-organic coordination structures at surfaces	**Experiment number**: HE-3271
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Report:

Aim of the experiment was to investigate the magnetic properties of fully coordinated Mn-TCNQ networks on Ag(100) and Au(111) surfaces. The overall metal-to-molecule ratio is 1:1 and each cyano group of the molecule is engaged in coordination bonding to a Mn atom. In addition, it was expected that on the Au(111) surface lateral charge transfer between the ligands and metal adatoms takes place. The purpose of the measurements was to obtain insight into the electronic state of the metal centers as well as the molecular ligands and to find a potential magnetic coupling between the metal centers.

We succeeded in preparing highly ordered Mn-TCNQ networks on the Au(111) surface. In addition we prepared and investigated Ni-TCNQ networks on Ag(100) and Au(111) surfaces. While the Ni-TCNQ networks are nearly identical to the previously investigated Mn-TCNQ networks on Ag(100), the Ni-TCNQ structures on Au(111) exhibit a somewhat distorted coordination structure with respect to Mn. All structures were successfully studied by XAS and XMCD spectroscopy. The results are summarized in figures 1-4.

The nitrogen *K*-edge XAS contains information about the molecule substrate interaction and possible charge transfer. As reported in Ref. [1] TCNQ adsorbed on Cu(100) receives at least one electron from the surface. A similar scenario was found on Ag(100). During these measurements and as reported also for the experiment HE2836 there is only little change upon coordination of the cyano groups to metal adatoms. In figure 1 (a) and (b) the nitrogen XAS spectra for TCNQ adsorbed on Au(111) and Mn-TCNQ on Au(111) are shown, respectively. The pure molecular layer shows features that are very similar to the neutral TCNQ powder with a strong linear dichroism resulting from the homogeneous orientation of the molecules. Upon coordination to Mn adatoms the spectrum changes significantly and resembles the spectra obtained for pure and coordinated TCNQ on the Cu and Ag surfaces. We interpret this as the signature of lateral charge transfer. A similar result was found for the Ni-TCNQ networks on Au(111).

The XAS and XMCD spectra for the Ni- and Mn-TCNQ networks on Au(111) are shown in figure 2. In addition we measured Ni adatom impurities on Au(111) (figure 2(a)) and Ag(100) (figure 3(a,c)) deposited on a cold substrate directly at the magnet chamber. The Ni adatom impurities do not show a sizable XMCD signal and appear to be mainly non-magnetic. This is in agreement with earlier observations by scanning tunneling spectroscopy measurements [2]. Ni adatoms hybridize strongly with the surface metal states and are interpreted to assume a spin-quenched mixed-valence state. However, in the networks as shown in figure 2(b,c) the Ni centers recover their magnetic moment. The lineshape analysis suggests a mixed valence configuration with d^8 and d^9 character. The anisotropic XAS and XMCD is a result of the square-planar coordination geometry of the Ni centers. The spectral features are also different from the Ni adatoms with a

more pronounced L_2 edge and a multiplet fine structure at the L_3. A sharp and well-defined XAS multiplet structure was also observed for the Mn-TCNQ networks on Au(111), see figure 2(c,e). The spectral lineshape suggest a d^5 configuration with little differences compared to the Mn XAS observed for the networks on Cu and Ag surfaces (see report HE2836). In fact the line shape is very similar to the 1:1 Mn-TCNQ network on Ag(100) (this experiment) and the 1:2 Mn-$TCNQ_2$ structure on Cu(100) (HE2836). Interestingly, the sum rule analysis for the Mn centers on Au(111) shows a sizable orbital moment while on the other surfaces a nearly zero orbital moment was found.

In addition to the proposed experiments we managed to prepare also Ni-TCNQ networks with different coordination ratios on a Ag(100) surface. The results for the Ni adatom impurities and the Ni-$TCNQ_2$ network are summarized in figure 3. The Ni-$TCNQ_x$ networks are structurally nearly identical to the previously studied Mn-$TCNQ_x$ networks. They only differ strongly in their 1:1 structures with the Ni networks being much better ordered than their Mn counterpart. The Ni XAS and XMCD lineshape differs strongly from the networks on Au(111) surface. From the XAS lineshape we infer that the Ni has a predominant d^9 electronic configuration. Similarly to the structures on Au(111), Ni recovers it magnetic moment when incorporated in the organic coordination networks. The spectral satellite features indicate significant configurational mixing of d^8 and d^9 states in this case as well.

The magnetization curves obtained for the various structures are presented in figure 4. The curves have been obtained as the L_3 XMCD intensity vs. applied magnetic field. All curves are normalized to 1 at B = 5 T for comparison. In addition, also the Brillouin function with S=5/2 and S=1, ½ were added and represent the paramagnetic case for the Mn and Ni spin centers, respectively. The Mn magnetization curves (left panel in figure 4) follow closely the Brillouin function expected for a high-spin center with d^5 configuration. The little deviation for some networks could indicate small antiferromagnetic interaction but could be also a result of a somewhat higher measurement temperature. For the Ni magnetization curves on the other hand we find a significant stronger s-shaped curve than would be expected from paramagnetic S=1 or S=1/2 centers (right panel of figure 4). This is a clear indication for ferromagnetic coupling between the Ni centers that is more pronounced for the structures on Au(111). The effect cannot be attributed to a sizable orbital moment. The magnetization curve can be fitted by Monte-Carlo simulations assuming S=1 centers with a ferromagnetic exchange coupling of about 0.3 meV. This relative small value does not favor either a ligand or surface electron (RKKY) mediated coupling scheme.

At the time of writing, the analysis of the data together with the XAS simulations is still in progress. The XAS simulations using ligand field multiplet calculations will provide a deeper understanding of the present charge transfer channels and spin states of the metal centers. Two manuscripts are currently in preparation that describe the magnetism and chemical bonding of Mn-TCNQ networks on Cu, Ag and Au surfaces as well as the magnetic coupling observed in the Ni-TCNQ networks on Au(111).

References

[1] T.-C. Tseng et al., *Nature Chemistry* **2,** 374 (2010).

[2] T. Jamneala, V. Madhavan, W. Chen, and M. F. Crommie, *Phys. Rev. B* **61**, 9990 (2000).

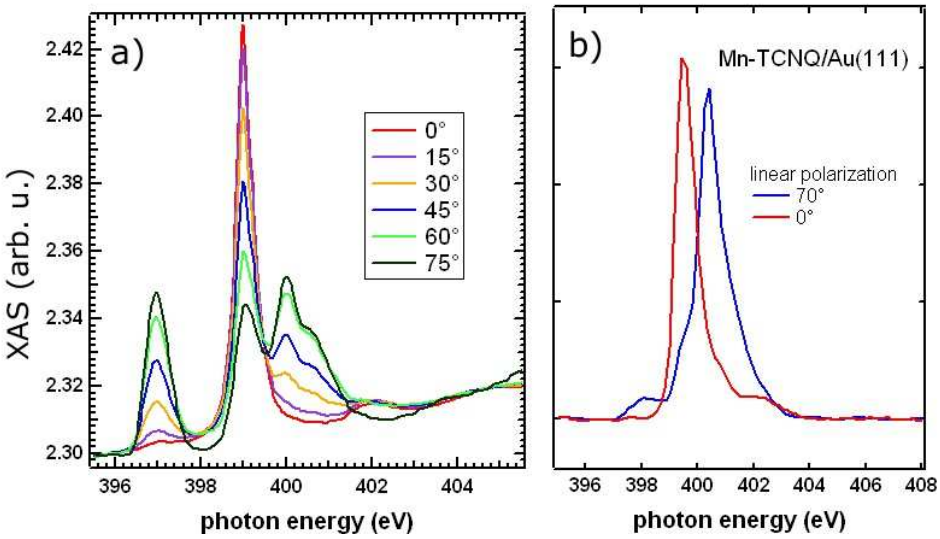

Figure 1: N-edge spectra with linear polarized light for (a) TCNQ on Au(111) and (b) Mn-TCNQ on Au(111). The spectrum of the pure TCNQ layer is very similar to spectra obtained for neutral TCNQ in powder form [1]. Upon coordination the first peak vanishes due to charge transfer and the second peak splits in energy.

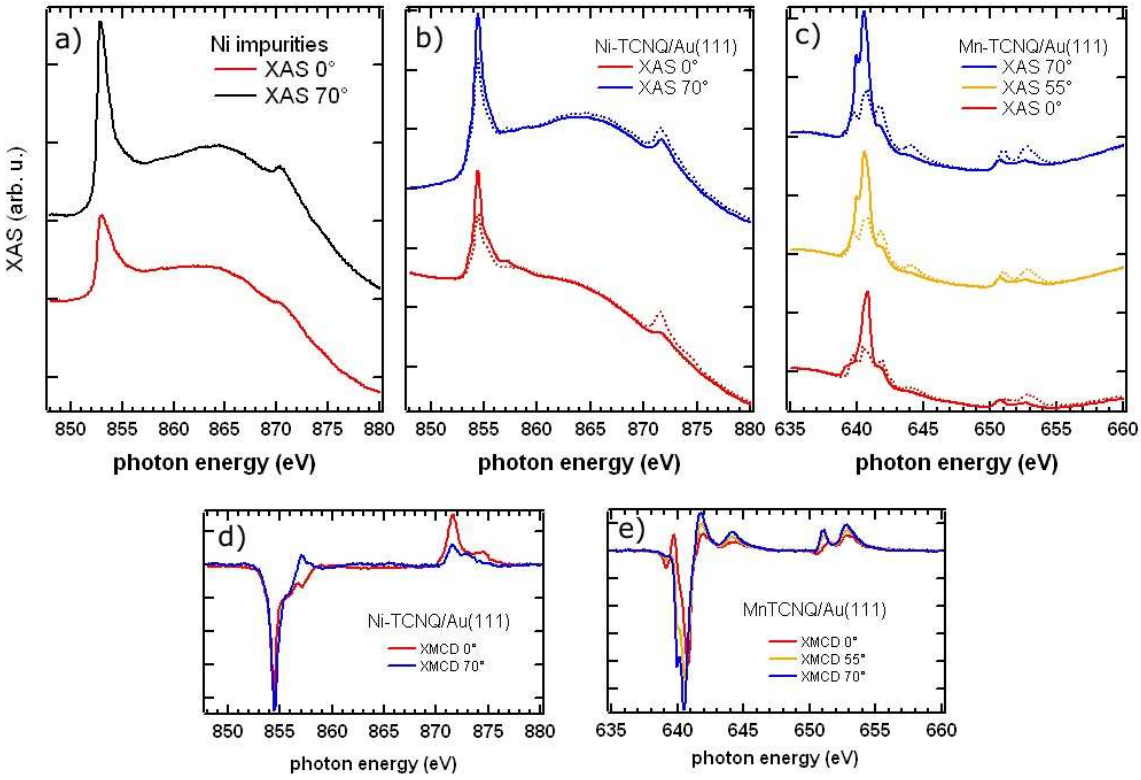

Figure 2: XAS and XMCD spectra for (a) single Ni adatom impurities on Au(111), (b,d) Ni-TCNQ network on Au(111) and (c,e) Mn-TCNQ network on Au(111). The Ni impurities on Au(111) as well as Ag(100) do not exhibit a sizable XMCD signal. (a-c) Solid and dotted lines indicate XAS spectra obtained with right and left circularly polarized light, respectively.

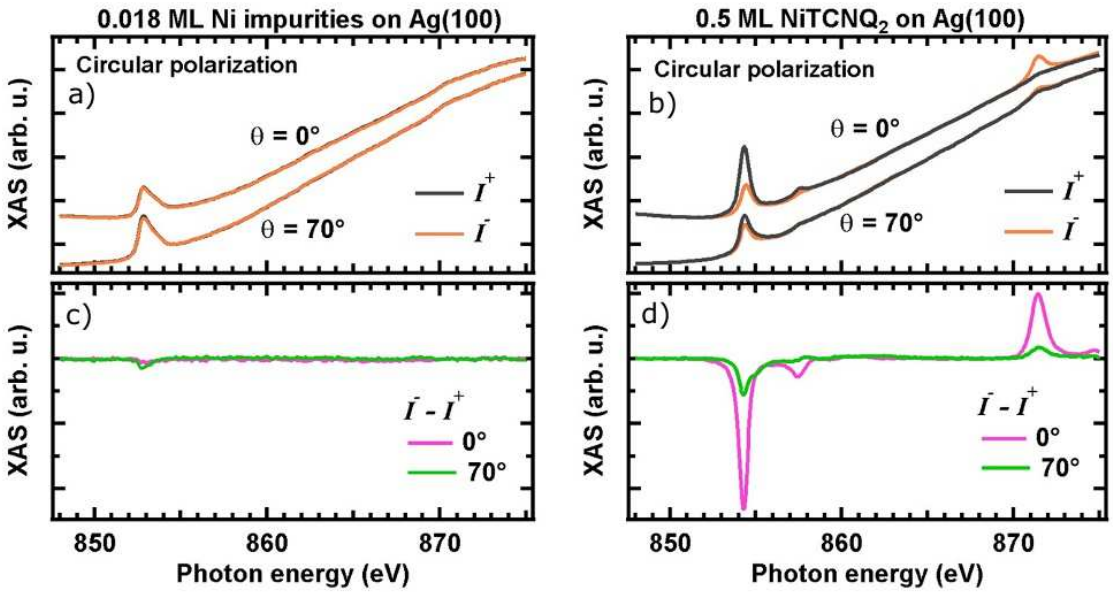

Figure 3: XAS and XMCD spectra of (a,c) Ni adatom impurities and (b,d) Ni-$TCNQ_2$ networks on Ag(100). The Ni-TCNQ structures with ratio 1:1 show a similar spectra lineshape.

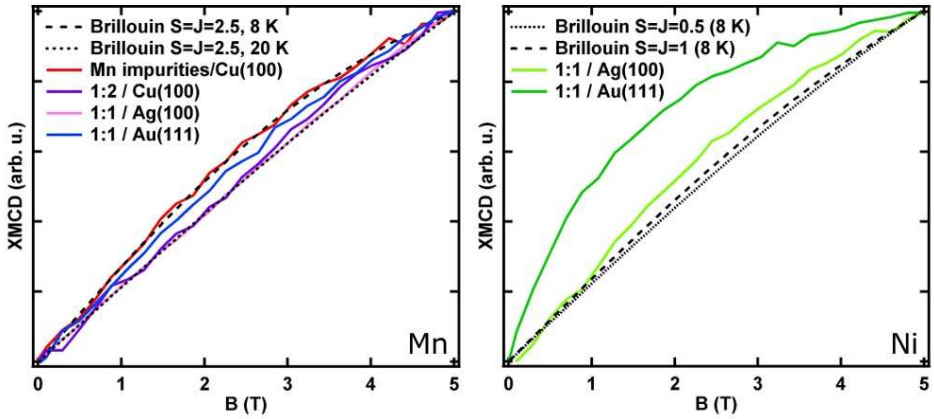

Figure 4: Magnetization curves for (left panel) Mn structures and (right panel) Ni networks. For comparison Brillouin functions with different moments and temperatures have been added. All curves were normalized to 1 at B = 5 T.