



	Experiment title: Magnetic properties of FePc and CoPc ordered arrays on Au(110): influence of 3d metal-substrate interaction	Experiment number: HE-3394
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Names and affiliations of applicants (* indicates experimentalists):

Dr. Roberto Biagi*, Dip. Fisica, Univ. Modena e Reggio Emilia and CNR NANO S3, Italy
 Prof. Maria Grazia Betti*, Dip. Fisica, Università di Roma La Sapienza, Italy
 Prof. Carlo Mariani*, Dip. Fisica, Università di Roma La Sapienza, Italy
 Dr. Pierluigi Gargiani*, Dip. Fisica, Università di Roma La Sapienza, Italy
 Prof. Giorgio Rossi*, Dip. Fisica, Univ. Modena e Reggio Emilia, Italy
 Dr. Maddalena Pedio*, IOM CNR, Basovizza, Italy
 Dr. Jun Fujii*, IOM CNR, Basovizza, Italy

Report:

In this experiment we have measured the x-ray magnetic circular dichroism (XMCD) of the transition metal absorption edges of FePc and CoPc molecules adsorbed on the Au(110) surface.

The single layers were grown by sublimating FePc and CoPc powders onto the Au(110) substrate kept at 450 K to favour the molecular ordering. Single-layers (SL) of FePc and CoPc deposited on Au(110) surface arrange in highly-ordered 2D arrays, as probed by LEED and STM equipments at ID-08 beamline. The STM image of the FePc single layer is reported in Fig. 1. The figure clearly shows the local order of the molecular chains arranged along the Au(110) reconstructed channels. The four-lobe structure of the single molecule can be well resolved within each molecular chain.

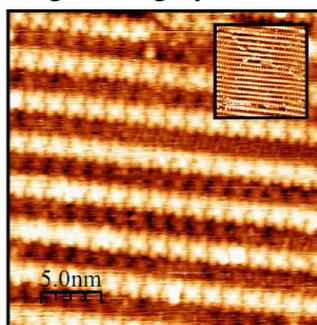


Figure 1: STM image of the FePc/Au(110) single layer.

The molecular orientation on the Au(110) surface was determined via the linear dichroism of the x-ray absorption (XLD) at the nitrogen K-edge, confirming the flat lying configuration on the Au(110) surface, both for single layers and for thick films (TF), as recently published.¹

The magnetic characterization was performed exploiting the x-ray magnetic circular dichroism (XMCD) technique at the $L_{2,3}$ edges of Fe and Co atoms for FePc and CoPc. The role of molecule/substrate interaction on the magnetic configuration of MPcs was singled out comparing the XMCD signal of the

single layer with the thick film one. The magnetic anisotropy has been investigated by measuring the XMCD signal as a function of the collinear impinging light and applied magnetic field direction ($H=5$ T, $0^\circ \div 70^\circ$ of incidence). The sample was kept at the lowest possible temperature (7K) during measurements.

In Fig. 2 (a-d) we report the absorption and XMCD spectra for FePc and CoPc, SLs and TFs acquired at 0° and 70° of incidence. Both the TFs (a,c) show a high magnetic dichroism, sign of the magnetic moment of Fe and Co atoms. Upon adsorption on the Au(110) surface, the out of plane components of the absorption

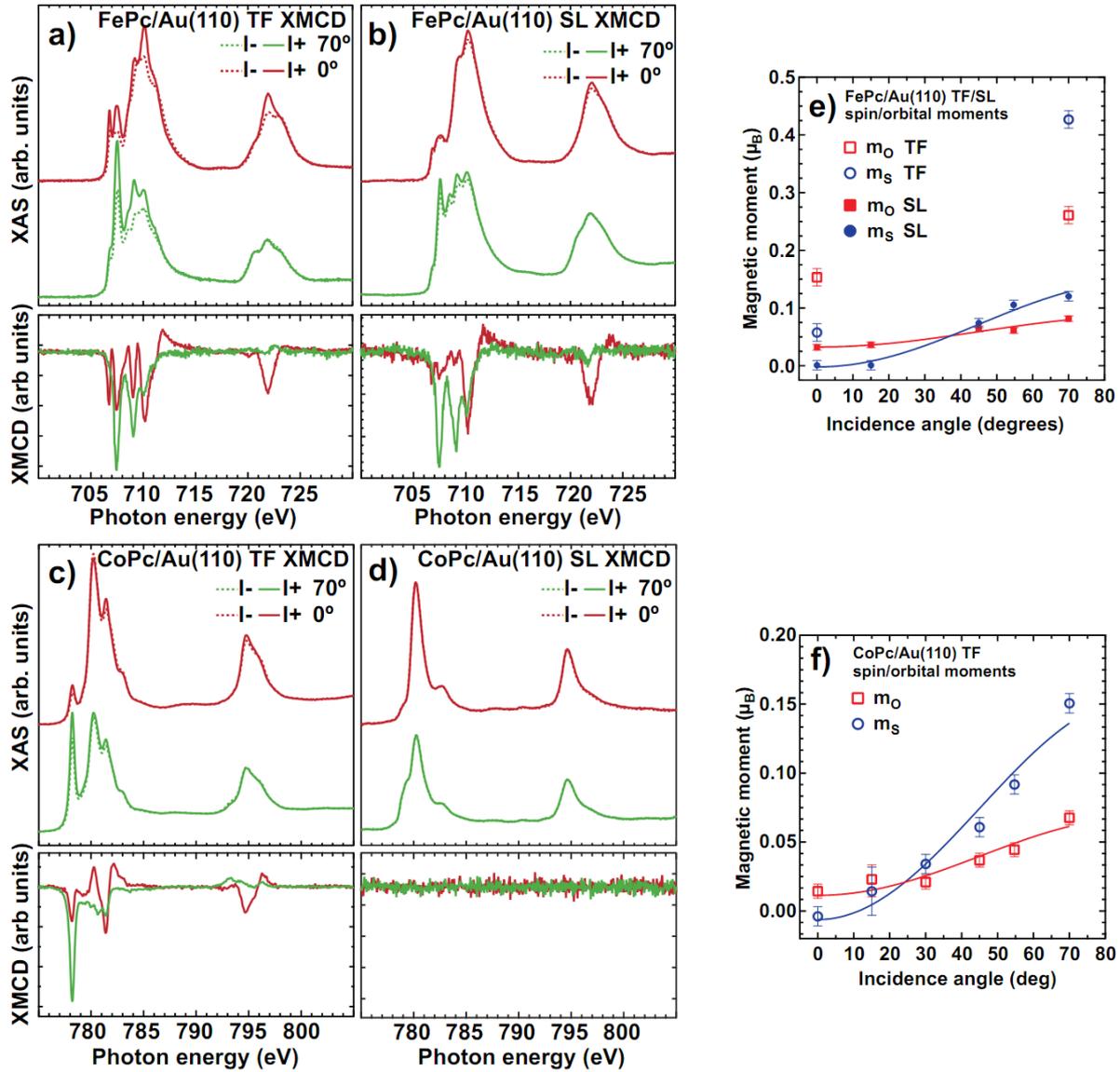


Figure 2: XMCD spectra for FePc/Au(110)-TF and SL (a and b) and CoPc/Au(110)-TF and SL (c and d). Orbital (m_o) and spin moments (m_s) as obtained from XMCD sum rules for FePc-SL and TF (e) and CoPc-TF (f).

spectra, enhanced at grazing incidence, are strongly reduced either in FePc and CoPc, indicating a strong hybridisation with the substrate involving the out-of-plane 3d-like empty orbitals¹. Such hybridisation determines a reduction of the magnetic dichroism in FePc and its complete quenching in CoPc, hence the magnetic moment is strongly affected by surface adsorption.

We have applied the XMCD sum rules to the XMCD signal to obtain the orbital and the effective spin component of the magnetic moments as a function of the impinging photon and magnetic field angle. Results are reported in Fig. 2 (e,f) for FePc TF and SL and CoPc TF, respectively. Both cobalt and iron atoms in the free molecules (represented by TF samples) are characterized by a strong anisotropy of the magnetization of easy-plane type. The FePc SL shows a reduced magnetic moment with respect to the TF although maintains the same magnetic anisotropy, while CoPc-SL magnetic moments are completely quenched. The charge transfer from the Au free electrons to Fe and Co orbitals determines a filling of the orbitals partially occupied in the free molecule, leading to a decrease of their total spin when interacting with the gold substrate. The residual magnetic moment at the FePc/Au(110) and the hybridization of the Fe 3d levels with the Au free electrons support our hypothesis of a Kondo resonance for this system. In fact a temperature dependent density of states at the Fermi level has been measured in our photoemission experiments on FePc/Au(110) SL.² CoPc does not show any sign of a Kondo resonance, in agreement with the total quenching of its magnetic moment. Furthermore, our XMCD results are also in agreement with theoretical results on the FePc and CoPc/Au(111) systems where a partial magnetic moment reduction and a total quenching was predicted for FePc and CoPc, respectively.³

We also obtained very preliminary results on the CuPc/Au(110) interface. The Cu ion seems to carry a significant magnetic moment after the adsorption process, in analogy with the CuPc/Ag(100).⁴ At variance with FePc and CoPc, this system has an easy axis of the magnetization along the molecule axis. If the results on CuPc could be confirmed, it would be an significant clue about the importance of the orbital symmetry of the spin carrying orbitals in determining the magnetic properties of the MPc/Au(110) interface.

In conclusion this experiment has been successful in determining the Fe and Co magnetic moments and their angular dependence for FePc and CoPc long-range ordered arrays on Au(110) and for the corresponding multi-layers. The partial (FePc) and total (CoPc) quenching of the SLs magnetization prove the expected strong interaction of the metal ion with the substrate. Very preliminary results obtained on SL-CuPc/Au(110) during this experiment suggest that the magnetic state of MPcs at the interface with a metal can be strictly related to the orbital symmetry of the spin-carrying orbitals.

¹ M.G. Betti, P. Gargiani, R. Frisenda, R. Biagi, A. Cossaro, A. Verdini, L. Floreano, and C.Mariani, J. Phys. Chem. C **114** 21638 (2010)

² Proposal of this experiment (HE3394)

³ Z. Hu, et al. J. Phys. Chem. C **112**, 13650 (2008)

⁴ S. Stepanow et al. Phys. Rev. B **82**, 1 (2010)