



Experiment title:

Magnetic properties of CuPc vs CoPc and FePc ordered arrays on Au(110): influence of 3d metal-substrate interaction

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HE-3626

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15

Local contact(s): Dr. Julio Criginski CEZAR

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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. Valdis Corradini*, CNR-NANO, Modena, Italy

Report:

Aim of the proposed experiment is to extend to CuPc the investigation of the spin and orbital configuration of a single layer (SL) of metal-phthalocyanine (MPc) chains deposited on the Au(110) reconstructed channels. The comparison of CuPc with FePc and CoPc (HE3394-ID08) will unravel the interrelation between the orbital and spin state of the adsorbed molecules and the molecular orbitals involved in the interaction with the Au surface and how this is related to the orbital symmetry and interface hybridisation of these molecules.

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

The single layers were grown by sublimating MPc 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 MPc's 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.

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).¹

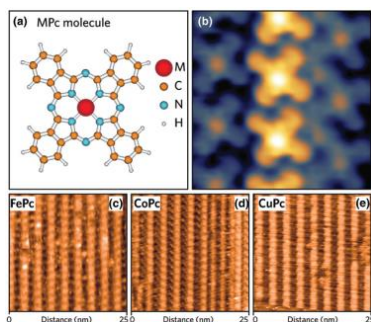
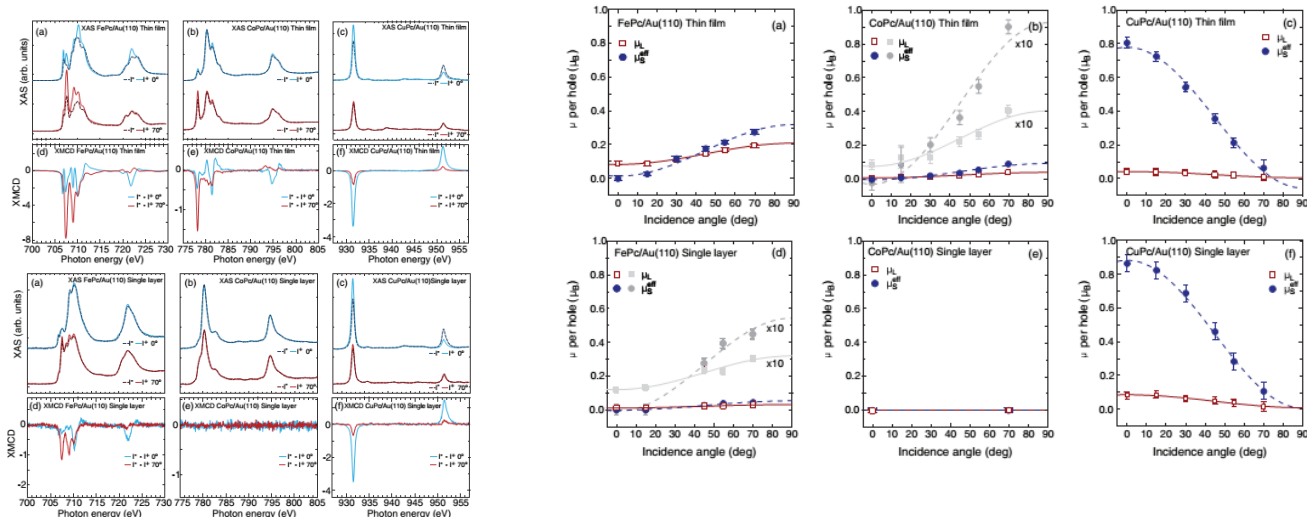


Figure 1: STM image of the MPc/Au(110) single layer.

The magnetic characterization was performed exploiting the x-ray magnetic circular dichroism (XMCD) technique at the $L_{2,3}$ edges of Cu, Fe and Co atoms. 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 conclusion this experiment has been successful in determining the Cu, Fe and Co magnetic moments and their angular dependence for long-range ordered arrays on Au(110) and for the corresponding multi-layers. The results of the present study demonstrate that, by adsorption of organometallic complexes on gold (110), a naturally nanostructured template surface, it is indeed possible to create ordered arrays of TM atoms with electronic and magnetic configuration determined by the rehybridization of MOs involving metallic states from the substrate. Both the experimental and the theoretical analyses show that the orbital and spin configuration of FePc, CoPc, and CuPc chains are strongly modified upon adsorption on the Au(110) surface if the orbitals responsible of the magnetic moments are involved in the interaction process. The insight gained by this joint approach makes it possible to understand the interface charge mixing and its direct consequences to the orbital filling and symmetry reduction of the molecular states located perpendicular to the molecular plane. The resulting adsorbed layer magnetic properties are “single molecule properties” meaning that the relevant interaction is between the TM central atom and the substrate, rather than “layer” properties dominated by the molecular interactions within the compact layer. This is a prerequisite for making it possible to address localized magnetic perturbations and responses, e.g., to use the adsorbed molecules as individual magnetic-sensitive blocks. By choosing suitable MPc and by tuning the amount of orbital occupation (for example, by doping the substrate surface or the molecular SL with electrons or holes) a tuning of the molecular magnetic moment and of its anisotropy with respect to the surface normal could be obtained. These experiments remain to be performed, but the evidence of the MO perturbation and symmetry lowering by interface bonding are supporting the feasibility of such “fine tuning” approach. Furthermore, new possibilities to tailor the interface molecular magnetism can be explored regarding proximity effects with ferromagnetic instead of paramagnetic substrate surfaces. In such case the interface hybridization can imply spin polarization transfer and allow exchange coupling and magnetic order at room temperature.

These results have been published in:

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Spin and orbital configuration of metal phthalocyanine chains assembled on the Au(110) surface

Pierluigi Gargiani,^{1,*} Giorgio Rossi,^{2,3} Roberto Biagi,^{4,5} Valdis Corradini,⁵ Maddalena Pedio,³ Sara Fortuna,⁶ Arrigo Calzolari,³ Stefano Fabris,⁶ Julio Criginski Cezar,⁷ N. B. Brookes,⁷ and Maria Grazia Betti¹

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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)