Experimental Report proposal 27271, ID08

"Magnetic properties of FePc ordered single-layer on the moiré superlattice of graphene on Ir", by C. Mariani, P. Gargiani, M. Scardamaglia, and Maria Grazia Betti

In this experiment, we aim at determining the spin and orbital configuration of the Fe *d*-orbital of iron-phthalocyanine (FePc, Fe-$C_{32}N_8H_{18}$) molecules adsorbed on a graphene sheet grown on the Ir(111) surface, by X-ray magnetic circular dichroism (XMCD). Graphene/Ir(111) has been chosen because of its nanostructured long-range ordered moiré structure with 2.5 nm surface periodicity, offering a suitable template for growth of ordered FePc layer.

Prior to the XMCD experiment, we prepared *in-situ* and characterized by x-ray linear dichroism (XLD) (i) the graphene single-layer and (ii) the FePc ordered layer on the graphene sheet.

(i) Graphene on Ir(111) was grown in-situ at the ID-08 experimental chamber, by several cycles of thermal decomposition of ethylene (C_2H_4) dosed at room temperature (RT), followed by annealing up to 1500 K. The graphene quality was checked by LEED and STM, verifying the correct formation of the moiré pattern.

(ii) FePc has been UHV purified and deposited on graphene at RT, from less than a single-layer (SL) up to 8-nm-thick thin-film (TF).

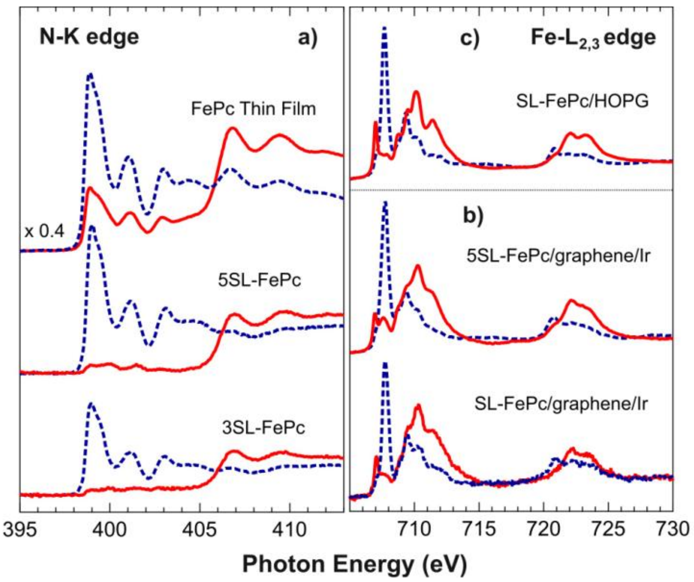

Fig.1: XLD data across the N-K edge (left, a)) and the Fe-$L_{2,3}$ edges (right), for FePc-graphene/Ir(111) at increasing FePc coverage (b)). Data for the Fe-$L_{2,3}$ edge at FePc/HOPG is also reported (c)), for comparison. Grazing incidence (70°) with linearly polarized radiation: total in-plane polarization (continuous red line); mostly out-of-plane polarization (blue dots).

The molecular orientation on the graphene sheet was determined via XLD at the N-K and Fe-$L_{2,3}$ edges (shown in **Fig. 1**): the FePc SL is in a definite flat-lying configuration, maintained up to 18 Å thickness (about 5 SL), while the 8 nm-thick TF does not show a preferential orientation, in agreement with the three-dimensional Stranski-Krastanov growth mode observed in a recent work.[1] The FePc molecules are also lying flat when the SL is adsorbed on a highly-oriented pyrolitic-graphite (HOPG) substrate (panel **c)**).

More information on the electronic structure of the FePc layer resides in the XLD Fe-$L_{2,3}$ lineshape (panel **b)**): the first intense peak for the out-of-plane polarization 707.7 eV is mainly due to the excitation to empty Fe-d_z^2 states (a_{1g} in the free molecule), while higher lying structures are due to contributions from mixed (e_g at about 707.0 eV and 709.3 eV) and in-plane states (b_{1g} at about 710.3 eV). The narrow pre-edge peak at 707 eV and the main peak at 707.7 eV are narrower and more resolved structures in the FePc SL than in the molecular multi-layer. Furthermore, the main absorption peak at 707.7 eV, despite being narrower, presents a lower normalized intensity for the SL than for the multi-layer. Finally, all peaks appear as narrower for the SL FePc adsorbed on HOPG: in this latter case, the absence of other interaction than purely dipolar forces, leads to an XLD spectrum definitely closer to that of an isolated FePc molecule.

The FePc interaction at the SL is lower than on Au(110),[2] but higher than on HOPG. The N K-edge lineshape measured in all coverage phases is unaffected by the interaction process. The Fe $L_{2,3}$ lineshape for the FePc-SL presents an intensity reduction of the out-of-plane states, comparing with a flat-lying FePc thin-film.[3] The Fe-related in-plane *d*-states are less involved in the interaction.

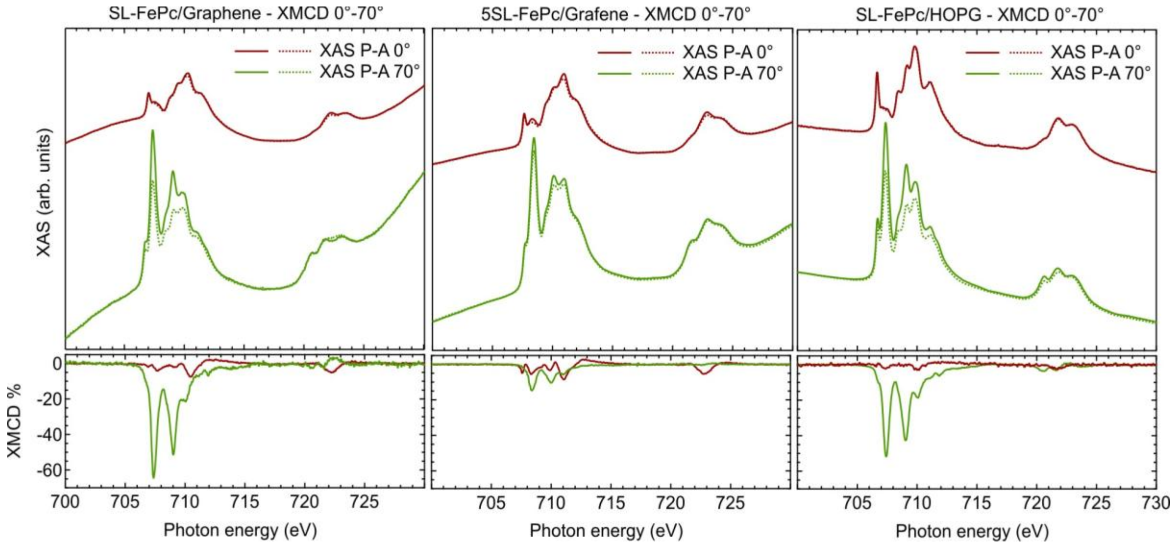

Fig. 2: (top panels) Fe-L$_{2,3}$ absorption data taken with circularly-polarized radiation parallel (red) or anti-parallel (blue-green) to the magnetic field, at 0° and 70° of incidence angle and H=5T; (bottom panels) XMCD signals at 0° and 70° of incidence angle and H=5T. From left to right panels: 1 SL FePc on graphene, 5 SL FePc on graphene, 1 SL FePc on HOPG.

The magnetic anisotropy of the FePc layer on graphene/Ir(111) has been investigated by measuring the XMCD signal as a function of the impinging circularly polarized radiation and of the applied magnetic field direction (H=5 T, 0°÷70° of incidence), with the sample kept at L-He temperature. In **Fig. 2**, we report the absorption data taken with circularly polarized radiation and the XMCD spectra for a selected set of data: the FePc-SL adsorbed on graphene/Ir(111), 5 FePc layers/graphene/Ir(111), and the SL FePc-HOPG (for comparison). For the FePc SL adsorbed on graphene (Fig. 2, left panels), there is clear evidence of a strong dichroism and a strong XMCD anisotropy, both heavily reduced for the flat 5 SL-thick FePc multi-layer on graphene (central panels) where a magnetic response is present in both directions (in-plane and out-of-plane). The quenching of the XMCD anisotropy for the flat FePc multi-layer on graphene has also been observed for flat-lying FePc thin-films (80 nm).[3] The dichroism decreases for the FePc SL adsorbed on HOPG, maintaining the anisotropy (right panels), suggesting a magnified in-plane magnetic moment for SL FePc interacting with graphene/Ir or HOPG.

A detailed analysis for quantifying the absolute value of magnetic moment along the different symmetry directions is still in progress. However, the first main results are an enhancement of the magnetic dichroism and of the in-plane/out-of-plane magnetic anisotropy for FePc/graphene/Ir at the SL completion, with respect to lower and higher coverage. A lower dichroism is observed on the FePc SL on the HOPG substrate. A strong coupling of Fe with graphene has been theoretically predicted,[4] though transition metals cluster on graphene,[5] while the use of FePc allows to cage and separate the Fe atoms for determining its coupling with graphene. The strong magnetic in-plane/out-of-plane anisotropy for the FePc SL/graphene claims for further experiments, using differently coordinated MPc, like CuPc where the isolated molecule presents a spin state associated only to in-plane states.

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[1] M. Scardamaglia, G. Forte, S. Lizzit, A. Baraldi, P. Lacovig, R. Larciprete, C. Mariani, M.G. Betti, J. Nanop. Res. **13**, 6013-6020 (2011).

[2] M.G. Betti, P. Gargiani, R. Frisenda, R. Biagi et al., J.Phys.Chem C **114**, 21638-21644 (2010).

[3] J. Bartolomé, F. Bartolomé, L. M. García, G. Filoti, T. Gredig, C. N. Colesniuc, I. K. Schuller, and J. C. Cezar, Physical Review B **81**, 195405 (2010).

[4] I. Zanella, S.B. Fagan, R. Mota, A. Fazzio, J.Phys.Chem C **112**, 9163 (2008).

[5] C. Vo-Van, S. Schumacher, J. Coraux, V. Sessi, O. Fruchart, N.B. Brookes, P. Ohresser, T. Michely, Appl. Phys. Lett. **99**, 142504 (2011).