Enhanced Magnetic Anisotropy in Low Dimensional Metal-Organic Layers Deposited on Graphene/Ir(111)

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Abstract

Graphene (Gr) interaction with metal surfaces and with magnetic atoms is of great technological importance not only because of widely demonstrated large-scale productions of high-quality Gr on metal substrates, but also for the preparation of spin-polarized contacts in Gr-based devices and spintronic units. A fascinating perspective is to study arrays of size-selected magnetic molecular systems comprising a single magnetic atom embedded in an organic frame in interaction with the Gr-metal support. Self-assembling of nanosized magnetic architectures is attractive for basic investigations as well as for device applications, when the magnetic anisotropy can be controlled. Gr grown on transition metal (TM) surfaces presents different degrees of interaction and a long-scale ordered moiré reconstruction at the nanoscale [1]. The Ir(111) surface allows to have a supported Gr layer and a low interaction, leaving almost unchanged its intrinsic electronic properties, while granting samples of high quality and stability with a small moiré corrugation [1]. Thus, Gr/Ir can be used as an efficient buffer layer, allowing ordered molecular self-assembly [2-3] and electronic decoupling between the adsorbate and the underlying Ir metal [4].

TM magnetic atoms deposited on Gr generally assemble in clusters [5, 6], while when they are embedded into an organic cage can be assembled as a regular array of magnetic centers at the nanoscale [2-3]. The metal-phthalocyanines (MPcs, $M-C_{32}H_{16}N_8$) are organo-metallic molecules with a metal atom embedded in the center of an organic environment, in a nearly D4h symmetry (Fig.1). The organic environment allows self-assembling on metal-supported Gr, with the formation of planar ordered layers [2-3, 7]. The central TM atom in the free molecule presents a bonding with transfer of two electrons to the surrounding N atoms, with incomplete non-degenerate d-shell, due to the symmetry lowering imposed by the D4h ligand field (Fig.1). The Hund's rule is broken for this configuration and the spin and orbital moments can be heavily quenched. However, this is not the case for FePc, where the spin and orbital magnetic moments are still present [8].

We present an experimental study of the spin and orbital configuration of a single-layer (SL) of FePc grown on Gr/Ir(111), by X-ray magnetic circular dichroism (XMCD). The sample is kept in a high magnetic field (5T) at liquid helium temperature. Near-edge absorption fine-structure (NEXAFS) measurements are taken at the Fe-$L_{2,3}$ edges, by means of circularly polarized X-ray radiation with helicity parallel or antiparallel to the magnetic field. The resulting spectra can be related, via suitable sum rules, to the effective spin and orbital moments of the initial state of the system [9]. We explored the dependence on the X-ray incidence angle to shed light on the spatial localization of the magnetic moments of the FePc SL. The FePc single layer is long range ordered on the Gr sheet and the interaction with the Gr slightly influences the electronic molecular states [6]. The Gr results a buffer layer and the FePc are uncoupled with the underlying Ir surface [6]. The orbital and effective spin magnetic moments of the central Fe ion are unquenched (Fig. 2). Furthermore, the effective spin and orbital spatial anisotropy results enhanced with respect to those of a FePc thick film. Due to the relation between orbital moment and magnetic anisotropy and the long-range order, this configuration allows to the formation of a spin network with a preferential magnetic axis parallel to the molecular plane.

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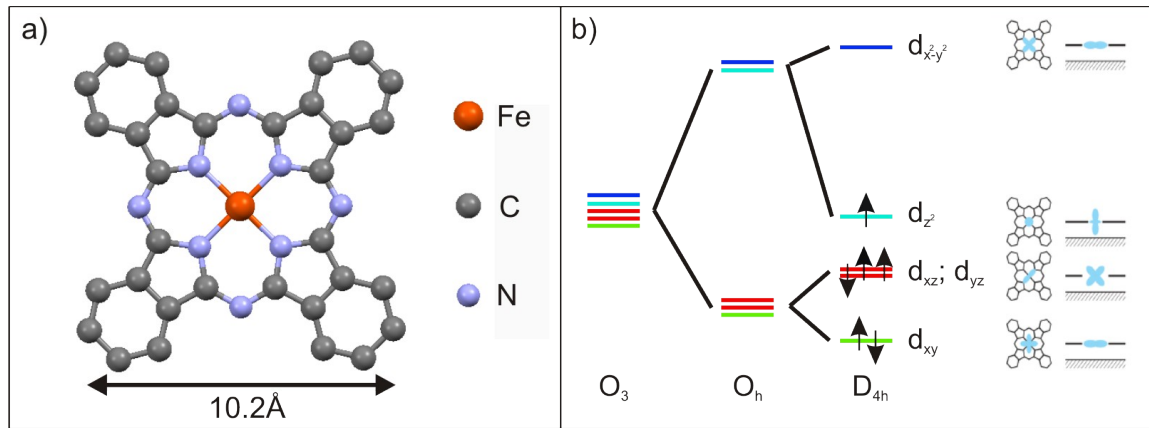
Figures

Fig. 1*: a) Sketch of FePc molecule $C_{32}H_{16}FeN_8$ (hydrogen atoms omitted); b) Scheme of the ligand field effect, reducing the symmetry of the environment from spherical (O_3) to octahedral (O_h) and to square planar (D_{4h}), on the 3d orbitals of the central Fe ion. The subsequent occupation leads to a spin S=1 state.*
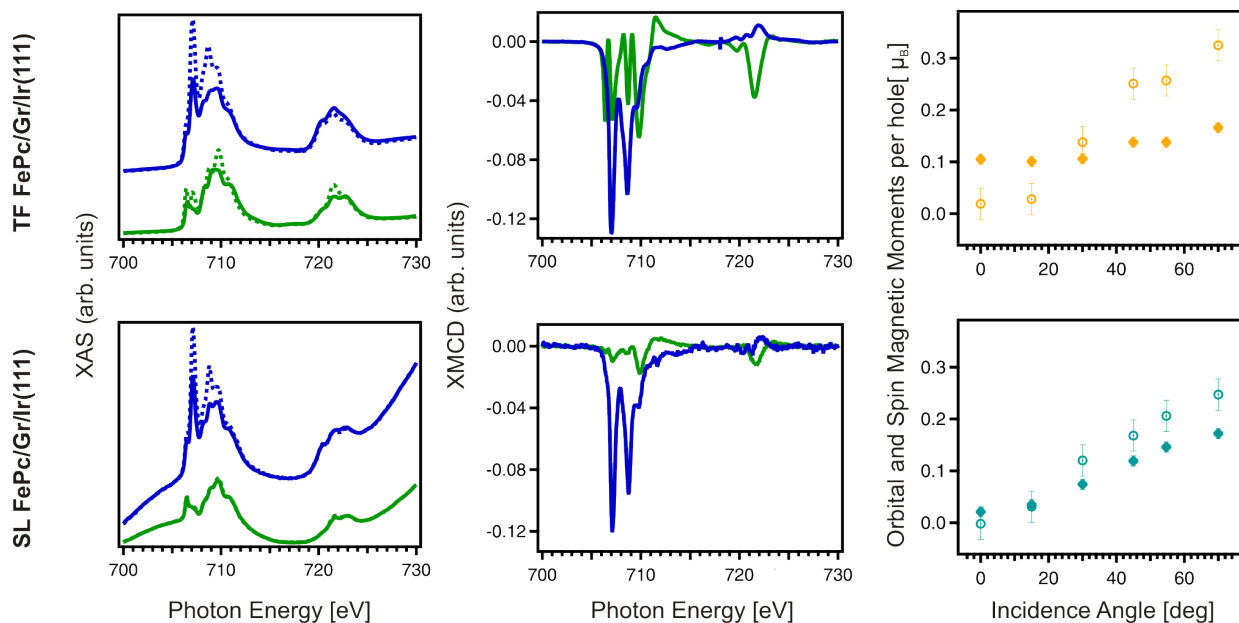

Fig. 2*: XAS (left) and XMCD (center) data of the Fe L_{23}-edges for TF FePc (top) and SL FePc on Gr/Ir(111) (bottom). Green lines label light with 0° incidence angle and blue lines label light with 70° incidence angle. Dotted lines correspond to parallel circularly polarized light and solid line to antiparallel circularly polarized light. The XMCD spectra are normalized to the integral of the sum signal resulting from parallel and atiparallel spectra for direct comparison with the sum rules [9]. Right: estimated orbital (solid circles) and effective spin (empty circles) magnetic moments as a function of the radiation incidence angle.*