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## ABSTRACT

We propose the optimization of the magnetic remanence and the thermal stability of Mn phthalocyanine coupled with a ferromagnetic substrate, by exploiting interlayer exchange coupling within an advanced organic spin interface architecture, constituted by a FeCo film covered by a graphene membrane, hosting the MnPc molecular layer. The challenge to obtain magnetic remanence for molecular systems stable up to room temperature has been accomplished thanks to a super-exchange path, mediated by the  $\pi$  orbital of the organic ligands of the molecule and of the graphene sheet, favoring an antiferromagnetic (AFM) alignment for the MnPc molecules with the FeCo film. This spin interface with a strong AFM coupling mediated by a graphene spacer is optimized against thermal fluctuations, presenting a well defined remanence even at room temperature, as demonstrated by the persistent dichroic signal in temperature-dependent circularly polarized x-ray absorption spectra.

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Magnetic remanence at room temperature for spin molecular interfaces can open the route to engineering highly spin-polarized, nanoscale current sources. To realize usable molecular-based spintronic applications, the first prerequisite is to fully control the organic spin interface magnetization, for example, via ferromagnetic (FM) or anti-ferromagnetic (AFM) coupling of the molecular spin state to a magnetic-metal substrate.<sup>1-3</sup> However, magnetic properties of molecular magnets on metal surfaces can be heavily influenced by the spin orbital intermixing with the metallic states,<sup>4</sup> which can lead to a strong reduction in their magnetic response, hindering the top-down design of spin molecular interface properties.<sup>5,6</sup> To enable a deterministic design route of the molecular-spin interface properties, the basic requirement is to preserve the molecular magnetic state ensuring at the same time a robust coupling to a magnetic electrode, ideally stable even at room temperature.<sup>1,7</sup> Thanks to the electronic decoupling of a graphene spacer between the magnetic molecules and the metal substrate,<sup>1,7,8</sup> the spin molecular orbitals can be selected to optimize and stabilize the magnetic configuration, as demonstrated for phthalocyanines [MPcs, (M-C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>)] with a magnetic center, adsorbed on a rippled graphene membrane, grown on a ferromagnetic substrate.<sup>1,7</sup>

The super-exchange interaction, mediated by the organic ligands and the graphene membrane, can preserve the magnetic state of the MPcs molecules, favoring a tunable FM or AFM coupling with 3d metal layer(s), unveiling the extreme sensitivity of the exchange interaction to the symmetry of the molecular orbitals responsible for the magnetic state.<sup>1,7</sup> Optimization of these spin interfaces against thermal fluctuations can be accomplished combining the high magnetic activity of FeCo layers<sup>9,10</sup> and the high versatility of MPcs, with a wide range of possible spin ground state configurations. In particular, manganese phthalocyanine can have an interesting perspective in spintronics, thanks to the high magnetic moment and high magnetic anisotropy energy. However, the low Curie temperature (8 K)<sup>11</sup> of MnPc molecular films hinders the device operation. We propose the exploitation of a stable coupling with a magnetic substrate, to open a new strategy to stabilize its magnetic response even at room temperature.

Intercalation beneath graphene (Gr)<sup>12</sup> of FeCo alloys, with high magnetic moment and anisotropy, has been proposed as a viable route<sup>9</sup> to avoid clustering and granularity and to realize homogeneous layer-by-layer growth. Intercalation of metals below Gr has proved to efficiently lead to the formation of atomically smooth

metallic layer(s),<sup>13–16</sup> where the graphene membrane can protect the confined epitaxial metallic layer(s)<sup>17,18</sup> and increase magnetic anisotropy.<sup>19–21</sup>

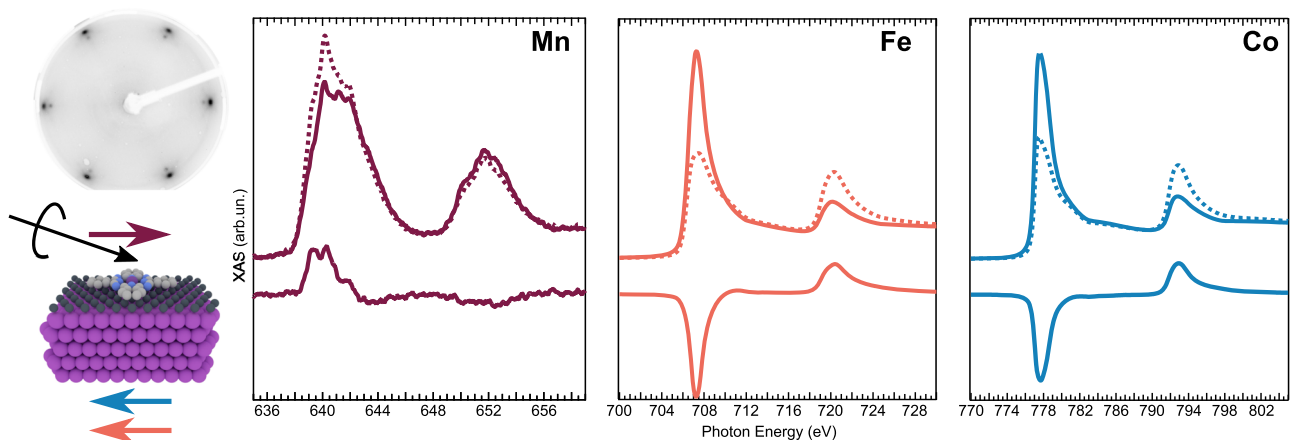
We herewith propose the assembly of MnPc molecules on equiatomic FeCo epitaxial and homogeneous layers intercalated under a graphene membrane. The magnetic coupling is sustained by a super-exchange path between the Mn ions and the FeCo layers mediated by the graphene membrane and the molecular organic ligands, as deduced by an X-ray Magnetic Circular Dichroic (XMCD) experiment. The MnPc spin orbitals, preserved by the graphene spacer, are anti-ferromagnetically aligned with the FeCo states, with a robust coupling stable against thermal fluctuations, even at room temperature (RT).

The Gr sheet was prepared by thermal decomposition of ethylene ( $C_2H_4$ ) on the Ir(111) surface, previously cleaned by cycles of sputtering and annealing at 1300 K. The Gr sheet was prepared by exposing the clean surface to  $5 \times 10^{-8}$ – $2 \times 10^{-7}$  mbar of  $C_2H_4$  and annealing at about 1300 K. Metallic Fe and Co were simultaneously deposited, at the same evaporation rates as determined by a quartz crystal monitor and ion flux measurements and confirmed by the atomic absorption at  $L_3$  edge. The substrate was kept at 500 K to facilitate intercalation under graphene, avoiding C solubility in the FeCo layer, as observed for substrate temperatures above 600 K.<sup>22,23</sup> Details on the homogeneity and quality on FeCo intercalated layers, as deduced by core level photoemission and x-ray absorption spectroscopy (XAS), are discussed in detail elsewhere.<sup>9</sup>

The XAS and XMCD measurements were performed at the BOREAS beamline<sup>24</sup> of the ALBA Synchrotron Radiation Facility (Barcelona, Spain). The spectra, acquired in total electron yield mode, are normalized with respect to the incident flux measured from a freshly prepared gold mesh. The XMCD measurements were performed at an angle of  $70^\circ$  with respect to the surface normal (grazing incidence, GI), to probe the magnetic dichroism along the easy magnetization plane of the substrate, with the magnetic field collinear with the impinging photon beam.

The magnetic response of the spin heterostructure constituted by 0.6 ML of MnPc molecules deposited on the flat commensurate Gr/7 ML FeCo/Ir(111) has been investigated by XMCD, as an efficient element-selective probe of the magnetization. At the early growth stage, the FeCo first layer is pseudomorphically commensurate with the Ir(111) surface, with an enhanced corrugation of the Gr moiré superstructure. When a thicker FeCo film is intercalated, it becomes almost commensurate to the Gr lattice, as revealed by the LEED pattern for Gr/7 ML FeCo/Ir(111), reported in Fig. 1 (left panel). However, after the released strain of the Ir(111) substrate, the FeCo film presents a lattice parameter smaller than Ir(111). The FeCo intercalated layers present a homogeneous and smooth texture under Gr,<sup>9</sup> with an energy landscape similar to that obtained for intercalation of pure Fe, with a novel hexagonal structural configuration that cannot be assigned to a bcc FeCo(111) film, as detailed in recent papers.<sup>9,25,26</sup> The superstructure of Gr grown on FeCo drives the assembly of MnPc in preferential adsorption sites in the moiré cell, as also observed for Co intercalated layers.<sup>7,27,28</sup> The MnPc molecular assembly on the flat graphene carpet is governed by the delicate balance between the molecule–molecule interaction and the graphene coupling with the organic macrocycles. This balance gives rise to ordered structural configurations, as observed in MPcs adsorption on graphene in analogous systems.<sup>8,29,30</sup>

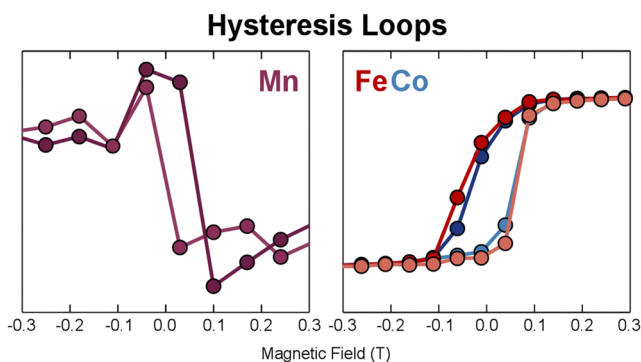
XAS and XMCD measurements at the Mn (left), Fe (center), and Co (right)  $L_{2,3}$  absorption edges for 0.6 ML MnPc deposited on Gr/7 ML FeCo/Ir, at a low sample temperature ( $T = 2$  K), are reported in Fig. 1 (right panels). XAS spectra are acquired with left- and right-circularly polarized radiation and with photons impinging grazing to the surface, in remanence conditions. The XMCD spectra, obtained as the difference between the absorption edges acquired with left- and right-circularly polarized radiation, are reported in the lower part of the panels. The Fe and Co density in the intercalated film, as well as its stoichiometry, has been evaluated via the jump-edge ratio, recording in a single spectrum the  $L_{2,3}$  absorption



**FIG. 1.** Left panel: (top) Low energy electron diffraction pattern of Gr/7 ML FeCo/Ir(111); (bottom) sketch of the MnPc/Gr/FeCo heterostructure with the circularly polarized photons impinging at grazing incidence. Right panels: X-ray absorption spectroscopy measurements and the x-ray magnetic circular dichroic (XMCD) difference for Mn (left), Fe (center), and Co (right)  $L_{2,3}$  absorption edges, for 0.6 ML MnPc adsorbed on Gr/7 ML FeCo/Ir(111); the XMCD experiment was performed in remanence with magnetic field  $B = 0$ , at substrate temperature  $T = 2$  K.

edges for both the Co and Fe elements. The Gr/7 ML FeCo/Ir heterostructure is constituted by an equiatomic FeCo intercalated layer, as detailed in Ref. 9. The dichroic response for Fe and Co  $L_{2,3}$  XMCD at grazing incidence corresponds to an in-plane easy magnetization axis of the equiatomic FeCo film.<sup>9</sup> The graphene layer electronically decouples the spin interface, as revealed by the XAS line shape at Mn  $L_{2,3}$  absorption edge, similar to that of a MnPc thick film.<sup>7</sup> The decoupling of the graphene spacer preserves the MnPc orbital configuration and the effective  $Mn^{2+}$  magnetic moment, hindering a direct interaction with the FeCo layer. The Mn XMCD, recorded along the substrate easy magnetization axes, presents an opposite sign with respect to the dichroic signal of Fe and Co XMCD data, suggesting an AFM coupling between the central Mn ions and the FeCo intercalated layer. The shape of the Mn XMCD spectrum is analogous to the dichroism observed in the MnPc/Gr/Co heterostructure, with similar magnetization response against the applied magnetic field. The symmetry of the molecular orbitals determines the sign of the MnPc–FeCo magnetic coupling, as recently observed also for MnPc–Gr–Co.<sup>7</sup> The MnPc molecule, with a  $4E_g$  ground state and the  $S = 3/2$  spin state, presents three half-filled spin molecular orbitals, exhibiting both in-plane and out-of-plane projections. Since a direct channel of magnetic coupling can be neglected because of the low magnetic polarization of the Gr sheet and the expected large MPc–Gr distance,<sup>1</sup> an indirect super-exchange Mn–N–Gr–FeCo channel between the Mn ion and the FeCo layer can be proposed. A super-exchange coupling is analogous to those observed for the MnPc and FePc heterostructures on Gr/Co,<sup>1,7</sup> whose spin orbitals perpendicular to the molecular plane prevail in the magnetic coupling. In these cases, the super-exchange path is mediated by the  $\pi$  orbital of the molecular ligands and of the graphene carpet favoring an AFM alignment for the MnPc out-of-plane spin orbitals with the FeCo film.

The element-sensitive hysteresis loops for Mn, Fe, and Co, acquired in the same experimental conditions, were obtained by normalizing the field-dependent  $L_3$  XMCD intensity at a pre-edge signal, as shown in Fig. 2. The hysteresis loops for Mn, Fe, and Co confirm the AFM coupling, as it can be appreciated by the reverse sign of the Mn loop with respect to the Fe or Co ones (Fig. 2). The magnetization loop of Mn reproduces the coercivity of the equiatomic FeCo



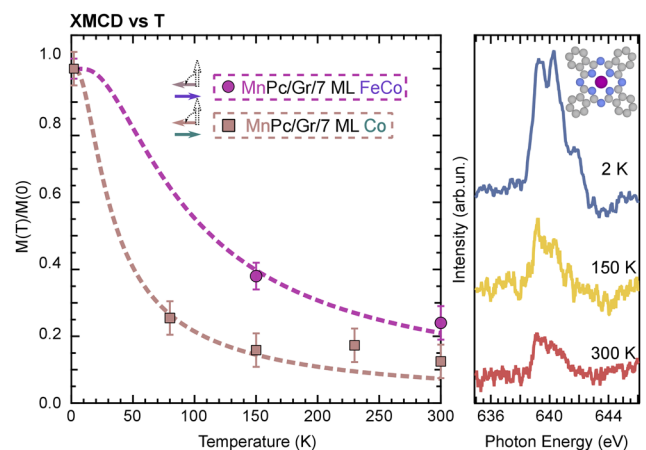
**FIG. 2.** Normalized magnetization curves deduced from the  $L_3$  XMCD signal taken along the easy magnetization direction, for Mn (pink) in the left panel, and Fe (red) and Co (blue) in the right panel for the 0.6 ML MnPc/Gr/7 ML FeCo heterostructure at  $T = 2$  K.

underlayer, and the signal at zero field indicates a robust remanent magnetic signal of the MnPc molecules. This suggests that the electronic and magnetic interactions between adsorbed MnPc molecules and intercalated magnetic metals are similar for FeCo alloys and for pure Co, driven by a super-exchange interaction mediated by the organic ligand and the graphene carpet.<sup>1,7</sup>

To evaluate the robustness of the magnetic response against thermal fluctuations of the MnPc/Gr/FeCo heterostructure, temperature-dependent XMCD measurements were performed and the results are reported in the right panel of Fig. 3. All XMCD measurements, acquired in the absence of a magnetic field for several hours, have revealed a very long relaxation time and a stable magnetic configuration. The XMCD intensity, displayed as a function of temperature, for the spin interface with MnPc adsorbed on Gr/FeCo is compared with the intensity of the Gr/Co substrate, in the left panel of Fig. 3. The super-exchange path stabilizes the AFM coupling up to room temperature ( $T = 300$  K) for MnPc/Gr/FeCo, and the XMCD still exhibits at RT a dichroic intensity of about one fourth of the maximum intensity recorded at  $T = 2$  K.

Although an analogous coupling process has been observed for the MnPc/Gr/Co interface,<sup>1</sup> we find higher coupling and thermal stability when the driving magnetic layer is the  $Fe_{50}Co_{50}$  alloy, as in the present work. This can be explained by the well known highest magnetic moment present in the  $Fe_{50}Co_{50}$  alloy with respect to the pure 3d transition metals,<sup>31,32</sup> which increases the magnetic coupling with the MnPc molecules, also reinforced by the reduced dimensionality.<sup>9,10</sup> It is also worth noting that the observed reduction as a function of temperature is lower than that observed for MnPc/Gr/Co.<sup>1</sup> The magnetic coupling between the equiatomic FeCo layers and Mn ions is stabilized against thermal fluctuations up to room temperature, though the easy magnetization axis of the MnPc molecules is perpendicular to the molecular plane and it is not aligned to that of the FeCo substrate.

A Brillouin fit over the thermal evolution of the XMCD intensity can give an evaluation of the strength of the exchange interaction, leading to a coupling energy of  $10.0 \pm 1.0$  meV for MnPc



**FIG. 3.** XMCD at Mn  $L_3$  absorption edge for MnPc/Gr/7 ML FeCo as a function of temperature (right panel). Integrated XMCD signal for MnPc/Gr/7 ML FeCo compared with MnPc/Gr/7 ML Co as a function of temperature (left panel); the Brillouin curve is superimposed as a dashed curve to fit the experimental data.

on Gr/7 ML FeCo, the highest value obtained for this class of systems, compared to  $3.4 \pm 0.4$  meV, calculated for the MnPc molecules assembled on Gr/7 ML Co. The spin orbital intermixing of the MnPc molecules assembled on the Gr/FeCo system is negligible, thanks to the insertion of the graphene spacer, and the superexchange interaction channel stabilizes the magnetic response of the adsorbed molecular units even at room temperature, preserving their original spin state and magnetic identity.

In conclusion, employing an element-selective XMCD technique, we demonstrate that the MnPc-based graphene-supported molecular spin interface coupled to a FeCo film presents a preserved molecular orbital hierarchy and robust AFM coupling to the FeCo layer. The AFM coupling, driven by a Mn–N–Gr–Co superexchange channel, is favored by the presence of out-of-plane molecular orbitals and enforced by the organic ligands and graphene. As far as we know, the stability against thermal fluctuations of this spin interface is the most robust among analogous molecular systems coupled with ferromagnets. This is the first observation of a spin interface with AFM coupling mediated by a graphene spacer optimized against thermal fluctuations, with a remanence detectable even at room temperature with an exchange energy of about 10 meV. Stabilizing the molecular magnetic state against thermal fluctuation up to the device working temperature is an indispensable step toward the application of molecular systems in spintronic devices.

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## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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