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Magnetism of $TbPc_2$ SMMs on ferromagnetic electrodes used in organic spintronics†

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L. Malavolti,[a] L. Poggini,[a] L. Margheriti,[a] D. Chiappe,[b] P. Graziosi,[c] B. Cortigiani,[a] V. Lanzilotto,[a] F. Buatier de Mongeot,[b] P. Ohresser,[d] E. Otero,[d] F. Choueikani,[d] Ph. Sainctavit,[de] I. Bergenti,[c] V. A. Dediu,[c] M. Mannini[a] and R. Sessoli*[a]

Structural features and magnetic behaviour of $TbPc_2$ thin films sublimated on LSMO and on cobalt surfaces have been investigated by synchrotron-based XNLD and XMCD techniques. Different orientation of the molecules is observed for the two substrates. No significant magnetic interaction with the ferromagnetic substrates is detected.

Single-molecule magnets (SMMs) are a class of chemical compounds that shows at cryogenic temperatures the intriguing properties of magnetic bistability at the molecular level.[1] After having represented model systems for the study of quantum effects in magnetism[1] SMMs have attracted growing interest as active elements in organic spintronic devices (OSPDs).[2] These generally consist of a semiconductor organic film located between two ferromagnetic electrodes, acting as a spin injector and a spin analyser, while the organic film can act as tunnelling barrier or as spin carrier.[2] Recent studies have shown how OSPDs can be designed to behave as spin valves or "memristors".[3]

The intrinsic chemical fragility of most SMMs, as well as the labile character of the SMM behaviour, has restricted the field of research to a few classes of molecules able to keep their magnetic bistability once in contact with conducting substrates.[4,5] Widely investigated is the family of mononuclear double-decker terbium(III) complexes with phthalocyanine ligands in different oxidation states $[TbPc_2]^{-1/0/+1}$ (see Fig. 1); the pronounced uniaxial magnetic anisotropy of the $J = L + S = 6$ ground multiplet of Tb^{III} leads to an anisotropy barrier as high as several hundred K.[6] Moreover the high chemical stability of the neutral $TbPc_2$ complex allows its sublimation under vacuum, while the flat shape of the molecule makes it an ideal candidate for STM investigations.[7] Recently a supramolecular spin valve based on $TbPc_2$ molecules on a carbon nanotube has been realized[8] but the use of $TbPc_2$ films in standard vertical OSPD remains unexplored.

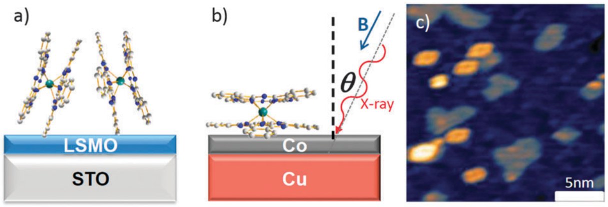

Fig. 1 Scheme of the two samples obtained by the sublimation of $TbPc_2$ on LSMO/STO (a) and Co/Cu(100) (b) with a scheme of the geometry of the synchrotron experiments. STM image (c) of the $TbPc_2$ on Co/Cu(100).

The investigation of hybrid structures based on magnetic molecules deposited on ferromagnetic electrodes requires the element selectivity and surface sensitivity of X-ray absorption spectroscopy (XAS) and related techniques, like X-ray Magnetic Circular Dichroism (XMCD). The latter allows to distinguish the magnetic signal of the deposited SMMs from the overwhelming one coming from the substrate. XMCD has been successfully used on $TbPc_2$ SMMs deposited on different surfaces. While thick evaporated films were shown to retain the typical butterfly hysteresis loop with magnetic bistability above 10 K, hysteretic effects were almost absent in thin films.[9,10] This behaviour is not necessarily due to molecule–surface interactions as it was also observed in amorphous bulk phases.[11] Sublimation of $TbPc_2$ on ferromagnetic Ni films[12] revealed a significant antiferromagnetic coupling of the Tb^{III} magnetic moment with the substrate.

With the perspective of realizing spintronic devices comprising this interesting SMM, we investigated the magnetic behaviour of neutral $TbPc_2$ deposited on two of the most commonly used ferromagnetic substrates for organic spintronics, *i.e.* thin films of metallic cobalt and of perovskite manganite with formula $La_{0.3}Sr_{0.7}MnO_3$ (LSMO). The latter is one of the few ferromagnetic electrodes that can be prepared *ex situ* with excellent magnetic polarization already at room temperature.[13] To the best of our knowledge only a brief report on $TbPc_2$ deposited on cobalt is available in the literature[14] while the deposition on LSMO is unexplored.

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[a] *Department of Chemistry "U. Schiff", Università di Firenze & INSTM RU, 50019 Sesto Fiorentino (FI), Italy. E-mail: roberta.sessoli@unifi.it*
[b] *Department of Physics, University of Genova, 16146 Genova, Italy*
[c] *ISMN-CNR, 40129 Bologna, Italy*
[d] *Synchrotron SOLEIL, 4891192 Gif-sur-Yvette, France*
[e] *IMPMC-CNRS, Université Pierre et Marie Curie, 75252 Paris, France*

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In our investigation we employed a 12 nm thick film of LSMO grown by channel spark ablation[15] on a strontium titanium oxide (STO) substrate. LSMO was cleaned by sonication in isopropanol before being used. Scanning Tunnelling Microscopy (STM) revealed a granular surface with an average height of *ca.* 1 nm (RMS roughness 0.29 nm) (see ESI†). $TbPc_2$, prepared as described elsewhere,[11] was sublimated *in situ* on LSMO using the preparation chamber of the SIM-X11MA beamline at the Swiss Light Source (SLS) synchrotron facility. Our evaporation procedure of intact molecules was validated by growing thick films showing the typical SMM behaviour.[11]

The hybrid $TbPc_2$–LSMO surface was characterized by X-ray absorption spectroscopy at the Mn $L_{2,3}$ and Tb $M_{4,5}$ edges by employing both circularly and linearly polarized light. All spectra reported were recorded in total electron yield mode with the magnetic field applied along the photon propagation vector (Fig. 1b) at a temperature of 2 K, unless otherwise indicated. In Fig. 2a the XAS spectra acquired in the presence of a 3 T field at the Mn $L_{2,3}$ edges, using the two circular polarization (σ^+; σ^-), and the resulting ($\sigma^- - \sigma^+$) XMCD spectrum are shown, both presenting features similar to those reported in the literature for LSMO films.[16] In order to fully characterize the magnetic behaviour of this system the field dependence of the XMCD signal at the L_3 edge of Mn was recorded at two angles, θ, between the magnetic field and the surface normal (see Fig. 1b): namely $\theta = 0°$ and 45°. The hysteresis loops (Fig. 3a) show the expected angular dependence for a film with an in-plane magnetic anisotropy.

The same investigation was repeated at the Tb $M_{4,5}$ edges to address the magnetic properties of the molecular film; in Fig. 2b the XAS and XMCD spectra showing the expected strong dichroic signal of $TbPc_2$ are shown.[9] Linearly polarized light was also used in order to get information about the orientation of the molecules with respect to the surface. The XNLD spectrum, defined as the difference between the absorption of vertically (σ^V) and horizontally (σ^H) polarized light (see ESI†), was measured at $\theta = 45°$. The spectrum (see Fig. 2c) reveals a dichroic contribution indicative of a partial molecular orientation on the surface. By comparison with literature reports[9] standing-up geometry with respect to the LSMO surface seems to be preferred. This finding, that cannot be confirmed by STM due to the roughness of the substrate, is in line with the growing mode of simple metal-phthalocyanines on oxides.[17] The hysteresis loops at the Tb M_5 edge (Fig. 3b) show just a small butterfly-shaped opening, narrower than that observed for this SMM in the bulk phase (see ESI†) or thick films.[9,11] The XMCD signal recorded at $\theta = 45°$ is slightly larger than at $\theta = 0°$, in agreement with the XNLD results and the roughness of the substrate. In contrast to what is found in the case of other ferromagnetic substrates,[12,14,18] no sizable antiferromagnetic coupling between $TbPc_2$ molecules and the LSMO was detected; moreover $TbPc_2$ hysteresis loops showed no correlation with those of the substrate (Fig. 3a and b).

To complete our study we performed a similar characterisation for a $TbPc_2$ submonolayer sublimated on a cobalt surface epitaxially grown on a Cu(100) single crystal. In house cobalt evaporation tests were carried out in a multi-instrument UHV system to establish the optimal conditions for the deposition of an epitaxial layer of Co. Surface quality was checked by several techniques (see ESI†) including STM, which, beyond showing typical Co islands, allowed us to detect also tetra-lobed features characteristic of this molecule (Fig. 1c).

The *in situ* preparation of this hybrid surface for an XMCD-based investigation required specific UHV facilities as those available in the preparation chamber of the DEIMOS beamline at SOLEIL

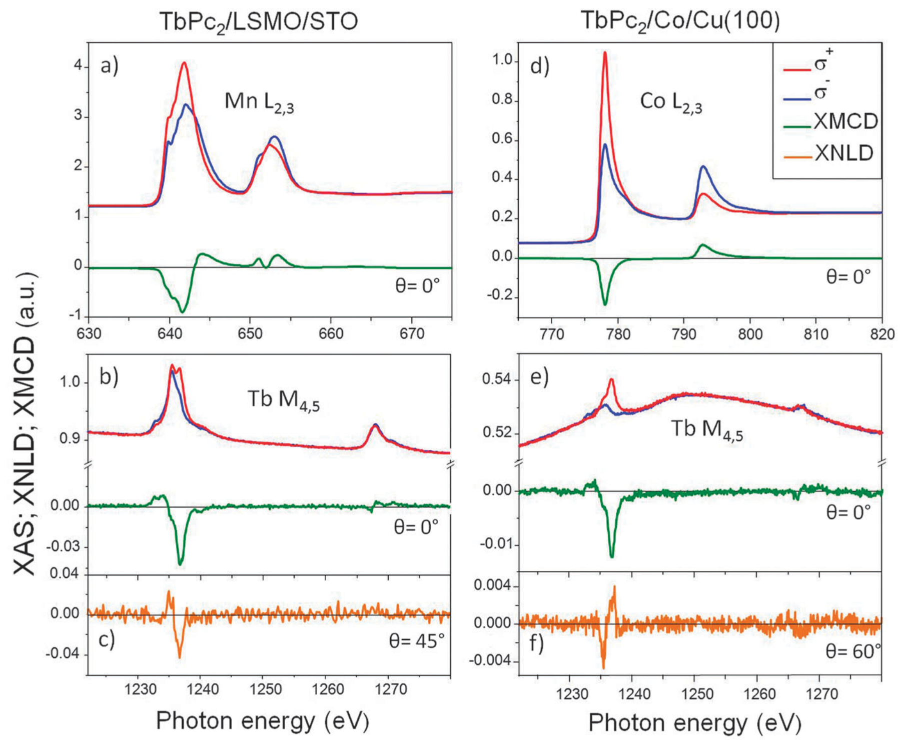

Fig. 2 XAS, XMCD and XNLD spectra of $TbPc_2$/LSMO/STO (a–c) and $TbPc_2$/Co/Cu(100) (d–f) at the indicated edges measured, respectively, at T = 2 K, B = 3 T (a–c) and T = 2 K, B = 5 T (d–f).

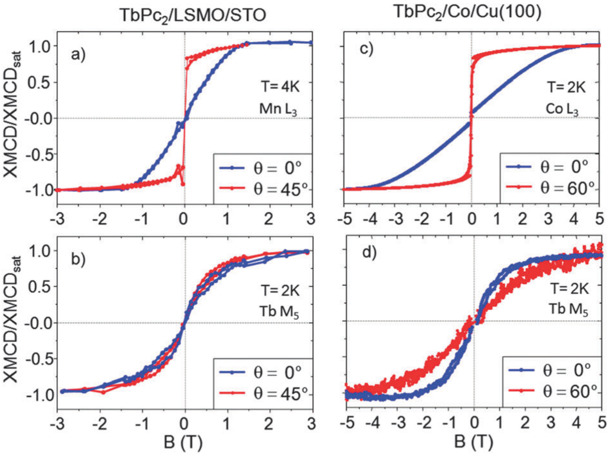

Fig. 3 Field dependence of the XMCD signal measured at the maximum of the dichroic signal at the indicated edge for TbPc$_2$/LSMO/STO (a and b) and TbPc$_2$/Co/Cu(100) (c and d).

synchrotron (France). Epitaxial growth of Co, confirmed by an *in situ* STM characterization (see ESI†), was extended to *ca.* 5 MLs to achieve a strong in-plane magnetization anisotropy of the film.[19] The thickness was verified using the Co $L_{2,3}$ edge jump ratio. On top of the cobalt substrate a sub-monolayer of TbPc$_2$ molecules was sublimated to obtain the hybrid surface. By applying the XMCD sum rules[20,21] to the spectra recorded at the Co $L_{2,3}$ edges (Fig. 2d), the ratio between the orbital (M_{orb}) and the spin (M_{spin}) moments was estimated (see ESI†) and the resulting $M_{\text{orb}}/M_{\text{spin}}$ = 0.125 was found to agree with reported data.[22] Field and angular dependence of the XMCD signal at the Co L_3 edge (Fig. 3c) confirms the strong magnetic anisotropy, and the anisotropy field of ~3.7 T matches the expected one for this thickness.[19] XAS and XMCD spectra, recorded at the $M_{4,5}$ Tb edges, are shown in Fig. 2e. The features are similar to those observed on LSMO. More interesting is the XNLD spectrum measured at $\theta = 60°$, which reveals a reversed dichroic signal compared to the one of TbPc$_2$ on LSMO. This confirms that on cobalt the molecules lie on the surface in agreement with the STM characterization (Fig. 1c). By recording the field dependence of the signal at the Tb M_5 edge (Fig. 3d), a paramagnetic behaviour is observed with no detectable hysteresis loop at the investigated temperature of 2 K, as well as a pronounced angular dependence, reflecting the preferred orientation of the molecules on the surface. The observed behaviour is similar to that found on noble metal surfaces,[9,10] and differs from the antiferromagnetic coupling observed by other authors for TbPc$_2$ on Co thin films.[14] The origin of this discrepancy remains unclear but the presence in our sample of multilayers decoupled from the substrate can be reasonably excluded. The measured XAS intensity at the Tb edge, compared to the EXAFS oscillations of the Cu substrate, suggests that we deposited a sub-monolayer of TbPc$_2$ molecules, in agreement with similar reports.[12,14,18]

In conclusion, the TbPc$_2$ sublimation on the two surfaces commonly used as electrodes in OSPDs evidences that two different orientations are obtained depending on the starting surface. Moreover the TbPc$_2$ molecules at the interface are characterised by the disappearance of the wide butterfly shaped hysteresis loop observed in the crystalline phase. Changes in the hysteretic behaviour are however observed using diamagnetic glassy matrices[23] or amorphous samples[11] and are therefore not uniquely associated with the interaction with the substrate. The development of vertical devices based on TbPc$_2$ is currently in progress and relevant effects in the magneto transport can be envisaged but, on the basis of the results presented here, additional interface engineering seems to be necessary if TbPc$_2$ molecules have to retain their magnetic bistability at the surface.

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