Electronic Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information

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

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1 - Magnetic characterization of the pristine $TbPc_2$ powder

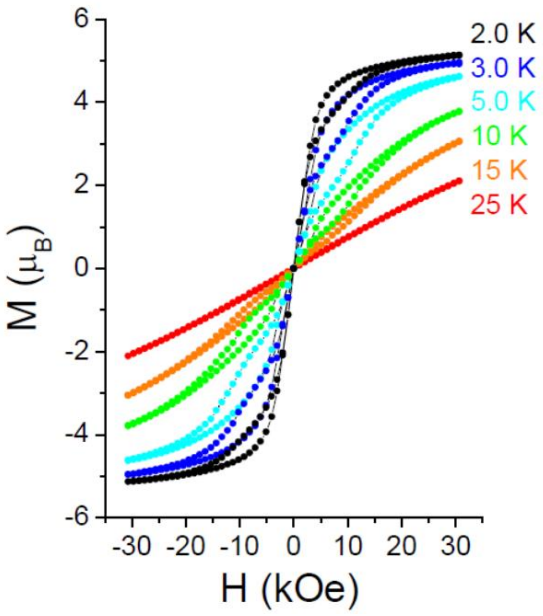

Fig. S1: Temperature dependence of the hysteresis loops recorded on a pure microcrystalline powder sample. The field sweeping rate is 50 Oe/s.

2 - Morphological characterization of the LSMO surface

2.1- STM characterization

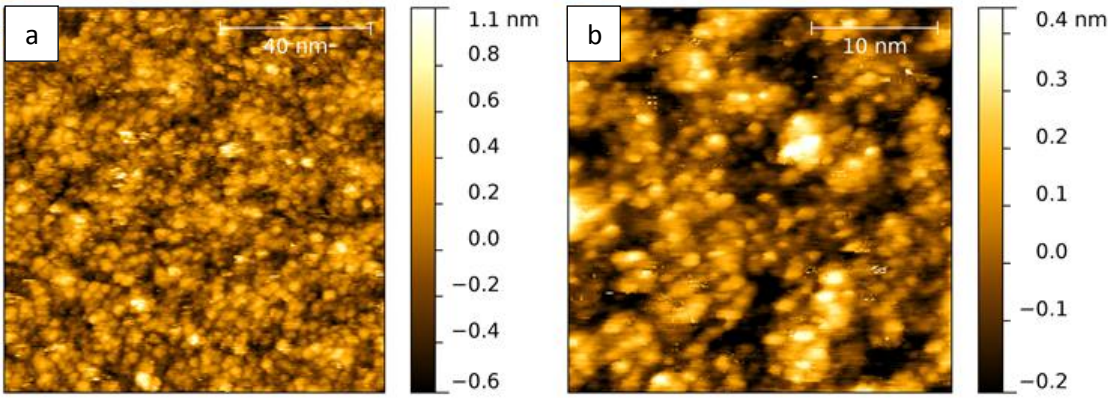

Fig. S2: STM images of 12 nm LSMO on STO, the surface was annealed 30 minutes at 250°C in UHV before being investigated. 100 x 100 nm^2 (a) and 30x30 nm^2 (b) both acquired with 50mV bias and 50pA of current.

3 - XAS measurements with linearly polarized light

3.1- $TbPc_2$/LSMO

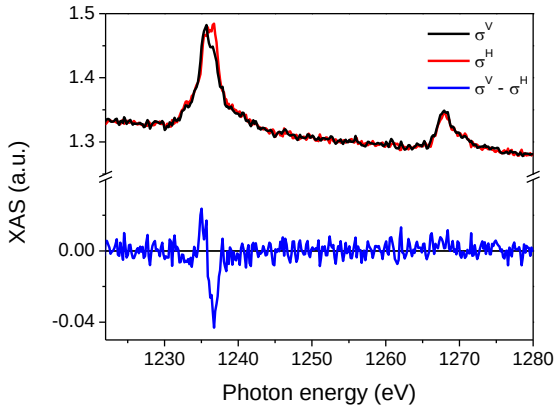

Fig. S3: XAS measurements acquired at the Tb $M_{4,5}$ edges with the two linear polarizations (σ^V, σ^H) and the resulting XNLD spectrum (σ^V - σ^H) of the $TbPc_2$/LSMO/STO sample (θ=45°).

3.2- $TbPc_2$/Co

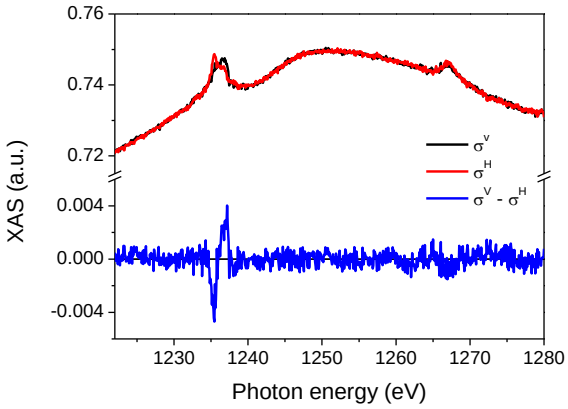

Fig. S4: XAS measurements acquired at the Tb $M_{4,5}$ edges with the two linear polarizations (σ^V, σ^H) and the resulting XNLD spectrum (σ^V - σ^H) of the $TbPc_2$/Co/Cu(100) sample (θ=60°).

4- In house preparation and characterization of Co/Cu(100) surface

4.1- STM

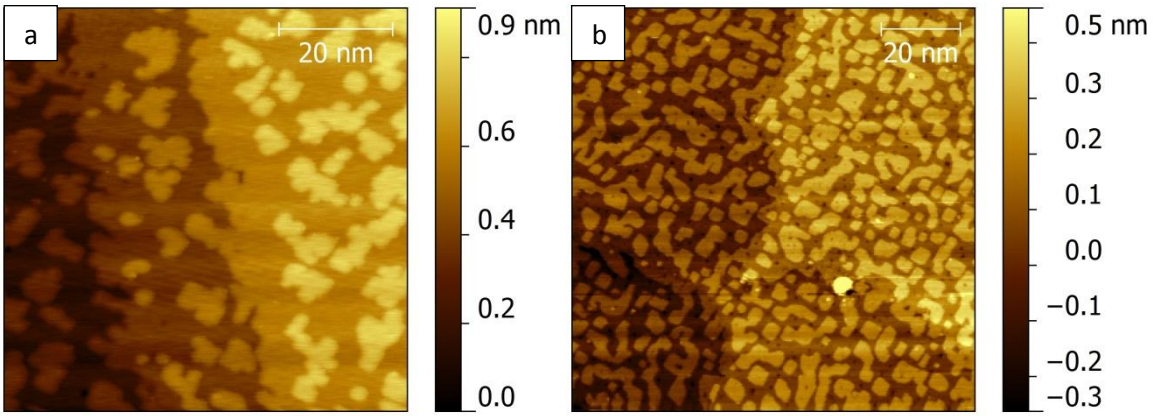

Fig. S5: STM image of 2.1ML (70x70nm^2, 400pA, -0.4V) (a) and 4ML of Co on Cu(100) (100x100nm^2, 900pA, 1.4V) (b). They show the typical cobalt rounded edge islands preferentially orientated along the Cu [±110] directions.

4.2- XPS

The XPS technique was employed to estimate the cobalt film thickness in the in-house experiments. We assumed the system as constituted by an uniform deposit of Co on the Cu(100) surface and we considered the escape length of the Co *2p* photoelectrons equal to the escape length of the Cu *2p* photoelectrons, obtaining the following simplified formula:

$$\frac{I'_A}{I'_B} = \frac{N_A\left\{1-exp\left[-d/\lambda_{A,A}cos\theta\right]\right\}}{N_B\left\{exp\left[-d/\lambda_{B,A}cos\theta\right]\right\}} \quad (1)$$

where $\lambda_{A,A}$ and $\lambda_{B,A}$ are the inelastic mean free paths of the electrons in A (second index letter) emitted by the element A or B (first index letter), and N_A and N_B are the number of atoms constituting the analyzed surface portion. The emission angle θ of the electrons is given with respect to the surface normal (polar angle).

With the approximation $\lambda_{A,A} \approx \lambda_{B,A} = \lambda$ we can write for the layer thickness d:

$$d = \lambda cos\theta \ln\left(\frac{I'_A N_B}{I'_B N_A} + 1\right) = \lambda cos\theta \ln\left(\frac{I'_A I_{B\infty}}{I'_B I_{A\infty}} + 1\right) \quad (2)$$

where $I_{A\infty}$ and $I_{B\infty}$ are the intensities of the signals of pure bulk elements A and B. The accuracy of d using Eq. (2) is affected by the incertitude on N_B/N_A and $I_{B\infty}/I_{A\infty}$. With a good approximation we can assume that $I_{A\infty}$ and $I_{B\infty}$ are equal to the photoionization cross section of the respective element (http://ulisse.elettra.trieste.it/services/elements/WebElements.html), while I'_A and I'_B correspond to the intensity of XPS signal. In our case the intensity of the signal for each element corresponds to the area of the peak, calculated by standard deconvolution using for each component a mixed Gaussian (G) and Lorentzian (L) line-shapes (ratio G= 70% L= 30%) and subtracting the inelastic background by means of the Shirley method. XPS experiments were carried out in a UHV chamber equipped with X-ray source (non

monochromatized Al K_α source, 1486.6 eV) and hemispherical analyser by VSW mounting a 16-channel detector. The X-ray source, mounted at 54.44° with respect to the analyser, was operated at a power of 100 W (10 kV and 10 mA). XPS spectra were measured at normal emission with a fixed pass energy of 44 eV.

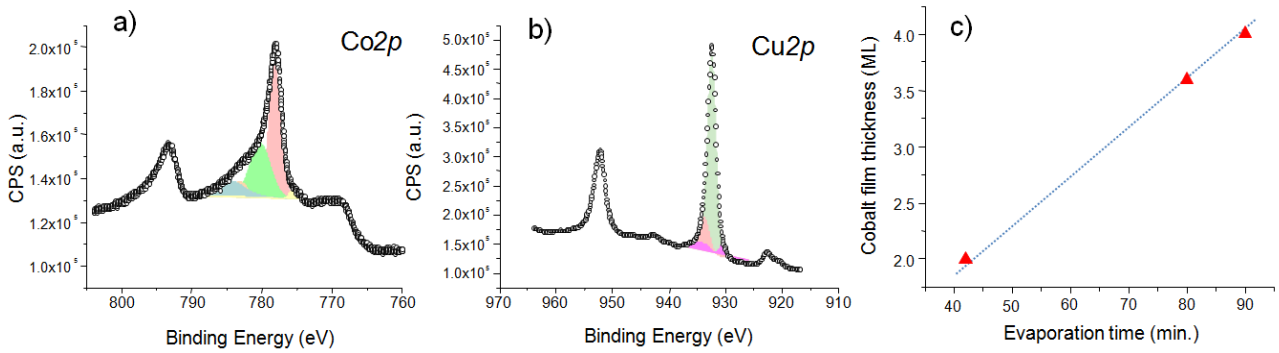

Fig. S6: XPS spectra of Cu *2p* (a) and Co *2p* regions (b) showing the fits of the 2p *3/2* peaks used to estimate the 2.1 ML cobalt thickness of the film evaporated on Cu(100). (c) Calibration of the Co deposition: cobalt film thickness vs. evaporation time as estimated by the XPS (samples are the same of the LEIS characterization).

4.3- LEIS

Low Energy Ion Scattering (LEIS) experiments were carried out in order to extract information about the topmost layer deposit, thanks to the exceptional surface selectivity of the technique.
To attribute each observed LEIS peak to the different elements present on surface we used the scattering formula:[S1]

$$E_i/E_i^0 = \{\pm[(M_t^2 - M_i^2 sin^2\theta)^{1/2} + M_i cos\theta]/(M_i + M_t)\}^2 \qquad (3)$$

where θ is the scattering angle, E_i^0 is the energy of ions that are accelerated to the surface, E_i is the ion's energy after scattering, while M_i and M_t are the ion and target atoms mass, respectively.
LEIS experiments were carried out in the same ultrahigh vacuum (UHV) chamber of the XPS setup with a base pressure lower than 10-10mbar. To record LEIS spectra we used a focused (approximately 1/2mm^2) beam of He^+ ions generated by a Omicron ISE 100 Gun with an energy of 1.0 keV impinging on the surface at an angle of 45°. The scattering angle was 135° and the kinetic energy of the scattered ions was measured by using the same hemispherical analyser employed for XPS.
By setting the incident ion beam energy to E_o = 1000 *eV* we deduced that the Cobalt is expected at E_{iCo} = 783 eV while Copper at $E_{i\,Cu}$ = 797 eV.

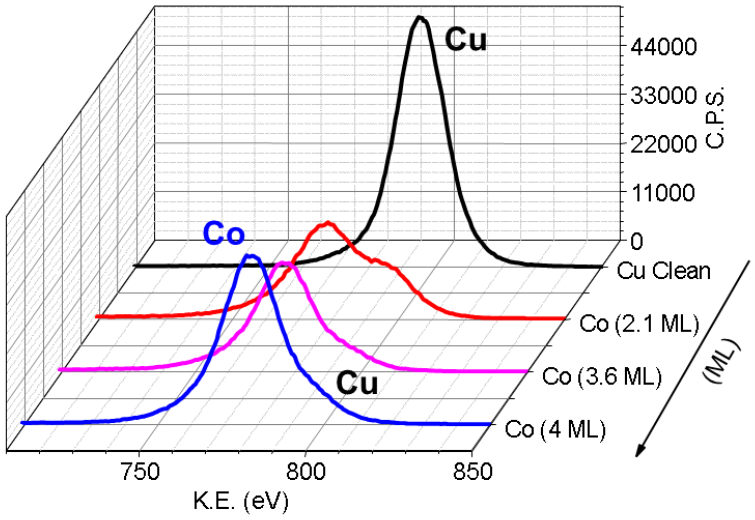

Fig. S7: LEIS spectra of clean Cu (100) surface (black curve) and after subsequent Co deposition : red curve, pink curve and blue curve are for 2.1 ML, 3.6 ML and 4 ML respectively.

5 - In house characterization of $TbPc_2$/Co/Cu(100)

5.1- STM

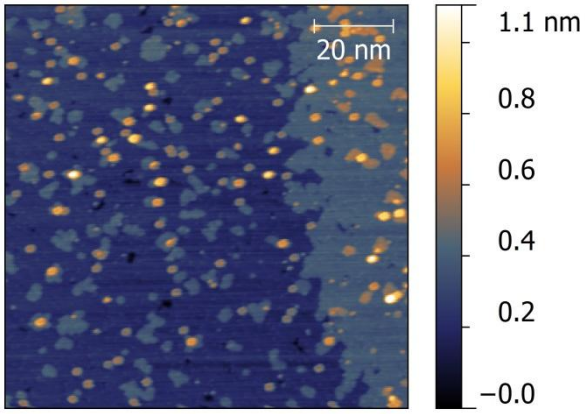

Fig. S8: STM image of $TbPc_2$/Co/Cu(100), (100x100nm^2, 200pA, 1.5V).

6- In situ STM characterization of Co/Cu(100)

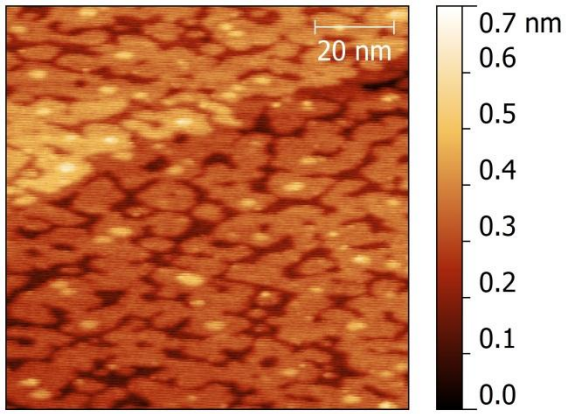

Fig. S9: *In situ* STM image of a 2.5 ML of Cobalt evaporated on Cu(100) (100x100nm^2, 100pA, 1.0V).

7- Estimation of spin and orbital moments of cobalt in Co/Cu(100)

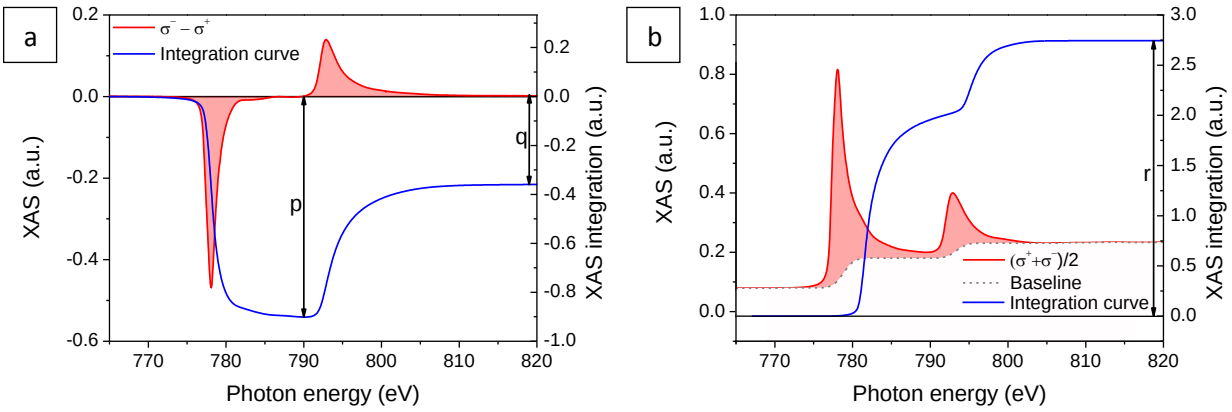

Fig. S10: a) XMCD (σ^- - σ^+) (red line) of 5ML of cobalt evaporated on Cu(100) substrate and the resulting integration (blue line) corresponding to the pale red area; b)(σ^++ σ^-)/2 spectra with a double step baseline and the resulting integrated curve corresponding to the pale red area .

The moments and the m_{orb}/m_{spin} ratio were calculated as:[S2]

$$m_{orb} = \frac{-4q \cdot n_{3d}}{6r} \; ; \; m_{spin} = \frac{-(6p-4q) \cdot n_{3d}}{2r} \; ; \; \frac{m_{orb}}{m_{spin}} = \frac{4q}{(6p-4q) \cdot 3} \qquad (4)$$

Where n_{3d} is the number of d holes, p and q are the integrated areas of the XMCD spectrum at the L_3 and L_2 edges, respectively, while r corresponds to the total area of the (σ^-+σ^+)/2 spectrum after subtraction of a double step baseline (with a step height ratio L_3:L_2 of 2:1), see Fig. S10.
From this analysis, by imposing n_{3d} = 2.43[S3] we estimated m_{orb} = 0.22 μ_B, m_{spin} = 1.75 μ_B and the resulting ratio m_{orb}/m_{spin} = 0.125.

References:

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(S2) Chen, C.; Idzerda, Y.; Lin, H.-J.; Smith, N.; Meigs, G.; Chaban, E.; Ho, G.; Pellegrin, E. and Sette, F. *Phys. Rev. Lett.* **1995**, *75*, 152–155.

(S3) Srivastava, P.; Wilhelm, F.; Ney, a.; Farle, M.; Wende, H.; Haack, N.; Ceballos, G. and Baberschke, K. *Phys. Rev. B* **1998**, *58*, 5701–5706.