Supplementary Information

Exchange biasing single molecule magnets: coupling of TbPc_2 to antiferromagnetic layers

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Figure S1. STM images of (a) 3 ML CoO/Ag(100). Image size: $150 \times 150 \text{ nm}^2$. (b) TbPc₂ deposited on 3 ML CoO/Ag(100). Image size: $30 \times 30 \text{ nm}^2$. (c) TbPc₂ deposited on 3 ML Mn/Ag(100). Image size: $50 \times 50 \text{ nm}^2$. Molecules on terraces and at steps are indicated by T and S, respectively.



Figure S2. (a) Schematics of the experimental setup and (b) sample geometry for recording linearly polarized x-ray absorption spectra.

A. X-ray magnetic dichroism measurements

The x-ray absorption measurements were performed at beamline ID08 of the European Synchrotron Radiation Facility using circularly and linearly polarized light. The degree of polarization was 99 ± 1 % in both cases. X-ray absorption spectra were recorded by measuring the total electron yield during photon energy scans at the $L_{2,3}$ edges of Co and Mn, and the $M_{4,5}$ edges of Tb. The photoelectron current of the sample was normalized by the incoming photon flux measured by the electron yield of a thin Au mesh placed upstream from the cryostat.

The samples were prepared and characterized in-situ (Figure S1) and transferred from the preparation chamber into the cryostat dedicated to the x-ray measurements. UHV conditions were maintained throughout the process. A magnetic field **B** of up to ± 5 T was applied parallel to the x-ray incidence direction at an angle θ with respect to the sample normal (Figure S2a) and used for field cooling of the samples as well as for x-ray magnetic circular dichroism (XMCD) measurements. XMCD spectra were obtained by subtracting consecutive absorption spectra recorded for parallel (I^+) and antiparallel (I^-) alignment of the photon helicity and sample magnetization. Element resolved magnetization curves were measured by averaging up to 16 XMCD spectra per point and reporting the XMCD intensity at the M_5 (L_3) edge of Tb (Mn) as a function of applied magnetic field, normalized by the average intensity $(I^+ + I^-)/2$ at each point. This method is extremely time consuming, but was nonetheless preferred over averaging several hysteresis loops recorded at fixed photon energy because of its accuracy, self-consistency, and because it does not require to subtract consecutive loops taken with opposite photon polarization. This also implies the possibility to detect training effects. Throughout this work, the XMCD signal is presented in units of the average XAS intensity, $(I^+ + I^-)/2$, which minimizes geometry- and field-induced effects on the electron yield and makes it proportional to the atomic magnetic moment of the element under investigation.

B. Linearly polarized absorption spectra of CoO

X-ray absorption spectra with linearly polarized light were used in addition to STM to characterize the growth and AFM properties of the CoO layers. The x-ray absorption spectra of the transition-metal oxides are dominated by multiplet effects, which constitute a tell-tale signature of their electronic structure, including their oxidation state as well as the symmetry and strength of the ligand field. Our CoO spectra, reported in Figure S3, show the characteristic features of CoO¹ and agree well with those reported in other studies of stoichiometric AFM CoO films,^{2,3} thus confirming the good quality of the substrates. Owing to the distortion of the 3*d* Co orbitals induced by the ligand field as well as to the orientation of the Co spins relative to the electric field vector (**E**) of the incoming light, the spectral lineshape depends on the x-ray polarization. As shown by Csiszar et al.,² we find that the intensity of the first peak of the L_3 absorption edge is always higher when **E** is parallel to the

sample plane for CoO films grown on Ag(100) (Figure S3a and b), indicating that the CoO layers deposited directly on Ag are compressively strained and present preferential in-plane spin orientation. On the other hand, for CoO films grown on MnO/Ag(100), the intensity of the same peak is larger when **E** is directed out-of-plane (Figure S3c), indicating that CoO deposited on MnO is under tensile strain and has perpendicular spin alignment.²



Figure S3. Linearly polarized x-ray absorption spectra of (a) CoO(10 ML)/Ag(100), (b) CoO(3 ML)/Ag(100), and (c) CoO(5 ML)/MnO(45 ML)/Ag(100) recorded at the $L_{2,3}$ edges of Co with the x-ray electric field vector making an angle $\psi = 20^{\circ}$ and 90° with respect to the surface normal. The x-ray incidence angle is $\theta = 70^{\circ}$ in both cases.

C. Linearly polarized absorption spectra of Mn and AFM structure of Mn layers

Figure S4 shows the linearly polarized x-ray absorption spectra of a 3 ML thick Mn film deposited on Ag(100), corresponding to the sample reported in Fig. 3 and 4 of the main text. The spectra are typical of pure metallic Mn films, which present broad and featureless L_3 and L_2 peaks^{4,7} owing to the delocalization of the 3*d*-states in elemental Mn.⁵ In contrast, intermetallic Mn alloys such as MnNi,⁶ MnPt,⁷ and MnIr (Ref. 8) as well as monolayer-thick Mn films deposited on Ag(100) (Ref. 4) and Fe(100) (Ref. 9) present shoulders in the highenergy tail of the L_3 edge and a characteristic double-peak structure of the L_2 edge, which are not observed here.

The spectra also carry evidence of strong x-ray linear dichroism (XLD). The XLD asym-



Figure S4. Linearly polarized x-ray absorption spectra of 3 ML Mn/Ag(100) recorded at room temperature at the $L_{2,3}$ edges of Mn with the x-ray electric field vector making an angle $\psi = 20^{\circ}$ and 90° with respect to the surface normal. The x-ray incidence angle is $\theta = 70^{\circ}$ in both cases. The green line shows the difference (x-ray linear dichroism) between the two spectra.

metry (Fig. 4), given by the difference between the spectra measured at $\psi = 90^{\circ}$ and 20° , is larger than the XMCD measured at 5 T (Fig. 3 of the main text). Although this is typical of AFM layers, we cannot conclude on the preferred spin direction of Mn based on these data. First, because disentangling natural and magnetic XLD effects in the case of thin films is not obvious if the films do not have perfect cubic symmetry. Second, because the XLD lineshape and the relative intensity of the L_3 and L_2 features varies greatly with the Mn valence, film structure, and spin direction.^{7,9–12} Despite the large number of studies carried out on Mn/Ag(100) (Refs. 4, 13–18) the AFM termination of surface layers thicker than 1 ML remains unknown. The $c(2 \times 2)$ AFM structure has been predicted to have the lowest energy for the (100) surface of tetragonal Mn films with atomic volume and axial ratio representative of Mn/Ag(100), irrespective of the Mn thickness and type of AFM order inside the film.^{17,18} It shall be noted, however, that body centered tetragonal (bct) Mn films grown on Fe(100) present out-of-plane $c(2 \times 2)$ AFM order in the monolayer limit⁹ and layered antiferromagnetism in thicker films.¹⁹ The easy axis direction of AFM Mn films is also a matter of debate as bct Mn films with either in-plane¹⁹ or out-of-plane²⁰ spin alignment have been fabricated. Finally, surface roughness can induce frustration and deviations from ideal AFM order at the surface steps.¹⁹ Figure S1c shows that TbPc₂ molecules adsorb on terraces as well as next to the step edges. Given that our XMCD measurements integrate the signal from a macroscopic region of the surface $(0.1 \times 1 \text{ mm}^2)$, we have no means to establish if molecules adsorbed on step and terrace sites behave differently or if the presence of steps is beneficial to enhance the density of pinning sites on the surface. We hope that the present work will stimulate further research in this direction, possibly using spin-polarized scanning probe techniques with molecular-scale resolution and magnetic contrast.

D. Estimate of the density of uncompensated spins in the Mn layer

The XMCD spectra of Mn recorded at 5 T reveal that a small fraction of the Mn spins is uncompensated. This fraction can be estimated by calculating the ratio between the magnetic moment derived from the sum rule analysis of the Mn spectra, that is, the average residual magnetic moment per atom of the antiferromagnetic layer, and the local magnetic moment expected for fully polarized Mn atoms. This procedure is similar to that employed by Ohldag *et al.* to estimate the fraction of uncompensated spins in conventional FM/AFM bilayers.²¹ Figure S5 shows the integrated XAS and XMCD intensity of 3 ML Mn/Ag(100) from which the spin and orbital moments can be calculated as follows:^{22–24}

$$m_{spin} + m_{dip} = -n_h \frac{6p - 4q}{2r} \tag{S1}$$

$$m_{orb} = -n_h \frac{4q}{6r},\tag{S2}$$

where m_{spin} , m_{dip} , m_{orb} represent the spin, spin dipole, and orbital magnetic moments in μ_B/atom , n_h the number of holes in the Mn 3d shell, and p, q, and r the integrated spectral intensities defined in Fig. S4. The spin dipole moment m_{dip} can be safely neglected for Mn due to the near spherical symmetry of the half-filled d-shell. By applying Eqs. 1 and 2 to the spectra reported in Figure S5 and taking $n_h \approx 5^{25}$ we obtain $m_{spin} = 0.075 \pm 0.005 \ \mu_B$ and $m_{orb} = 0.022 \pm 0.005 \ \mu_B$. In the case of Mn, however, the overlap of the spectral intensity due to $2p_{3/2} \rightarrow 3d \ (L_3 \text{ edge})$ and $2p_{1/2} \rightarrow 3d \ (L_2 \text{ edge})$ transitions results in severe underestimation of m_{spin} calculated using Eq. 1, which must be multiplied by a factor of the order of 1.8 in order to obtain the correct m_{spin} .^{25,26} We thus have $m_{spin} = 0.13 \pm 0.01 \ \mu_B$. This value represents the average spin magnetic moment per Mn atom of the 3 ML film. In order to estimate the fraction of uncompensated spins in the whole film, we divide m_{spin} by the local spin magnetic moment of Mn obtained using ab-initio electronic structure calculations of Mn thin films^{17,27} $m_{Mn} = 3.5 - 4 \ \mu_B$. According to the ratio m_{spin}/m_{Mn} ,



Figure S5. Circularly polarized x-ray absorption spectra and XMCD of $\text{TbPc}_2/\text{Mn}(3 \text{ ML})/\text{Ag}$ recorded at the $L_{2,3}$ edge of Mn after field cooling from room temperature to 8 K at B = 5 T and $\theta = 0^{\circ}$. The right-hand scale refers to the integrated XAS and XMCD intensity used in the sum rules analysis described in the text.

about $3\pm1\%$ of the Mn spins in the 3 ML film are uncompensated. The uncertainty is given by the sum of the relative errors on m_{spin} , m_{Mn} , and n_h . The fraction of uncompensated spins corresponds to a nominal thickness of 0.09 ML, which is considerably smaller with respect to the 0.52 ML found for Co/IrMn films.²¹ We speculate that this difference is due to the weaker coupling of TbPc₂ to the substrate and the small density of magnetic centers compared to all-metal FM/AFM bilayers. The vertical shift of the Mn magnetization loop observed in Fig. 3 (a) of the main text indicates that about 7% of the total uncompensated moments are pinned. This corresponds to a coverage of pinned spins of less than 0.01 ML, consistently with our conclusion that only a small fraction of the TbPc₂ molecules is exchange biased.

E. Magnetization of TbPc₂/Mn/Ag(100) field cooled at $\theta = 90^{\circ}$

In order to verify the influence of the field cooling direction on the onset of exchange bias for TbPc₂ deposited on Mn/Ag(100), a TbPc₂/Mn(3 ML)/Ag sample was prepared anew and field cooled it from 300 to 8 K in a field of +5 T at $\theta = 90^{\circ}$. In this geometry,



Figure S6. Magnetization loops of Mn (a) and Tb (b) measured on TbPc₂/Mn(3ML)/Ag(100), after FC at $\theta = 90^{\circ}$ and B = 5 T, recorded at $\theta = 70^{\circ}$ and T = 8 K. Inset: Detail of the low field region. Units refer to the intensity ratio $2(I^+ - I^-)/(I^+ + I^-)$ measured at the L_3 Mn edge (a) and M_5 Tb edge (b).

the field direction is perpendicular to the easy axis of TbPc₂, which, owing to the strong magnetic anisotropy of Tb, leads to a much weaker field-induced polarization of the molecule magnetic moment compared to $\theta = 0^{\circ}$.²⁸ Figure S6 shows the Mn and Tb magnetization curves measured at $\theta = 70^{\circ}$ after field cooling. The Mn layer presents a slight S-shaped magnetization compared to Mn field cooled and measured at $\theta = 0^{\circ}$ (Fig. 4a of the main text). This suggests that in-plane spin alignment of the uncompensated Mn spins is favored over out-of-plane alignment. The Mn curve is also shifted vertically by about $4 \pm 3\%$, indicating pinning of uncompensated Mn spins parallel to the field cooling direction, likely induced by the field itself. The Tb magnetization loop, however, presents a much reduced coercivity $H_C = 20 \pm 20$ mT and horizontal shift $H_E = -9 \pm 9$ mT compared to the sample field cooled parallel to the TbPc₂ easy axis (Fig. 4b of the main text). These values represent an upper estimate of both H_C and H_E as the forward (+5 T \rightarrow -5 T) and backward (-5 T \rightarrow +5 T) legs of the magnetization do not close on each other, for reasons that we could not identify during the measurements. We conclude that the Mn substrate can support pinned uncompensated spins in both the out-of-plane and in-plane directions, whereas the exchange bias of TbPc_2 is most effective for field cooling parallel to the Tb easy axis.

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