# Exchange bias of TbPc<sub>2</sub> molecular magnets on antiferromagnetic FeMn and ferromagnetic Fe films

Corneliu Nistor,<sup>1</sup> Cornelius Krull,<sup>2</sup> Aitor Mugarza,<sup>2,3</sup> Sebastian Stepanow,<sup>1</sup> Christian Stamm,<sup>1</sup> Marcio Soares,<sup>4</sup>

Svetlana Klyatskaya,<sup>5</sup> Mario Ruben,<sup>5,6</sup> and Pietro Gambardella<sup>1</sup>

<sup>1</sup>Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland

<sup>2</sup>Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB,

Bellaterra, 08193 Barcelona, Spain

<sup>3</sup>ICREA—Institució Catalana de Recerca i Estudis Avançats, Lluis Companys 23, 08010 Barcelona, Spain

<sup>4</sup>European Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France

<sup>5</sup>Institut of Nanotechnology, Karlsruhe Institut of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

<sup>6</sup>Institute de Physique et Chimie de Materiaux de Strasbourg (IPCMS), UMR 7504, CNRS-Universite de Strasbourg,

F-67034 Strasbourg, France

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Improving the magnetic stability of single-molecule magnets is a key challenge facing molecular spintronics. We use x-ray magnetic circular dichroism to explore the possibility of magnetically stabilizing  $TbPc_2$  molecules by attaching them to ultrathin Fe and FeMn films. We show that  $TbPc_2$  deposited on antiferromagnetic FeMn films exhibits magnetic hysteresis and exchange bias as a consequence of coupling to the uncompensated interfacial Fe spins. The FeMn-thickness dependence of the coercive field and exchange bias of  $TbPc_2$  is similar to that of inorganic ferromagnetic/antiferromagnetic systems. The magnetic moments are antiferromagnetically coupled to the Fe thin films as well as to the uncompensated Fe spins at the FeMn interface. The sign of the coupling changes from antiferromagnetic to ferromagnetic after doping the interface with electron-donor Li atoms.

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# I. INTRODUCTION

Single-molecule magnets (SMMs) have promising potential for nanotechnology owing to their small size, welldefined atomic structure, and unique magnetic properties [1]. Their versatility, which spans properties suitable for spin filters, hybrid-molecular electronic devices, and giantmagnetoresistive devices, has driven the growing field of molecular spintronics [2]. A major obstacle towards broader applications is the adverse effect of thermal spin fluctuations, which prevent intrinsic magnetic stability of SMMs at all but the very low temperatures. Improved magnetic stability would allow retention of spin information over large periods of time, with potential applications in high-density data storage and quantum computing. One way to increase the stability of SMMs against thermal fluctuations is to attach them to magnetically ordered substrates. It has been shown that metal-organic molecules couple magnetically to a substrate via ligand-mediated superexchange or direct exchange mechanisms [3-11]. Exchange bias is associated with the presence of magnetic hysteresis and a shift of the molecular magnetization curve along the field axis [12].

Among the most studied SMMs are lanthanide complexes such as bis-phthalocyaninato-terbium (TbPc<sub>2</sub>) which, owing to a large unquenched orbital moment and a strong spinorbit coupling, displays single-ion anisotropies and magnetic stability at considerably larger temperatures compared to polynuclear 3*d*-metal-ion complexes [13,14]. TbPc<sub>2</sub> consists of a single Tb (III) ion sandwiched between two planar phthalocyanine (Pc) ligands and has a large magnetic moment in the ground state (J = 6), a large molecular spin-inversion barrier, and slow magnetization relaxation. When adsorbed on a surface, its planar geometry favors uniform spacing between the Tb ions and the surface spins [9,15-17]. Furthermore, the Pc ligands host an organic spin radical that mediates exchange coupling between Tb and the substrate spins [8,18,19]. The magnetic moment of TbPc2 has been shown to stabilize when the molecule is attached to antiferromagnetic Mn and ferromagnetic Ni and Co films [8,9,12,20], whereas no significant magnetic coupling has been reported for oxide antiferromagnets, such as CoO [9,12]. Based on these observations, metallic thin films appear to be the most promising substrates to establish magnetic coupling with SMMs. In this study, we explore the magnetic coupling between  $TbPc_2$  and magnetically ordered FeMn and Fe ultrathin films, analyzing the differences and similarities between the two systems. To probe this coupling, we employ x-ray magnetic circular dichroism (XMCD), which is element selective and has a sensitivity adequate down to submonolayer coverages. This study focuses on the bielemental antiferromagnet FeMn, which is widely used in inorganic spin valve devices and presents more robust antiferromagnetic properties compared to single-element thin films or oxide antiferromagnets. From a fundamental point of view, given that the molecular footprint covers several lattice sites, it is not obvious that TbPc<sub>2</sub> should be exchange biased by FeMn. Here, we provide evidence that the FeMn-thickness dependence of the coercive and exchange-bias fields of TbPc2/FeMn is similar to that of previously studied inorganic ferromagnetic/antiferromagnetic (FM/AFM) systems. This shows that it is possible to partly extrapolate the exchange-bias behavior of molecules on antiferromagnetic surfaces from the extensive knowledge accumulated on inorganic systems. Additionally, we find that the sign of the coupling and exchange bias field of TbPc<sub>2</sub> on FeMn is opposite with respect to that previously reported for Mn [9]. Finally, we observe a sign change (from AFM to FM) in the exchange coupling of TbPc<sub>2</sub> on FeMn/Cu(100) and Fe/Cu(100) after doping with electron-donor Li.

### **II. EXPERIMENT**

TbPc<sub>2</sub>/FeMn/Cu(100) and TbPc<sub>2</sub>/Fe/Cu(100) samples were prepared at room temperature in ultrahigh vacuum (UHV) by electron-beam evaporation of Fe and Mn on a sputter-annealed Cu(100) substrate. TbPc<sub>2</sub> molecules were subsequently deposited by sublimation of TbPc2 powder at 490 °C from a molecular beam epitaxy (MBE) cell at a flux rate of 0.8 ML/min. The TbPc<sub>2</sub> coverage was estimated at 0.6  $\pm$ 0.1 ML. The FeMn and Fe films were calibrated for thickness and checked for uniformity using a quartz balance and by scanning tunneling microscopy (STM).

Following preparation, the samples were transferred without breaking vacuum into the measurement chamber of the ID08 beam line at the European Synchrotron Radiation Facility (ESRF), which provides x-ray photons with  $99 \pm 1\%$ circular polarization. A superconducting magnet allowed the application of magnetic fields of up to 5 T along the direction of the x-ray beam. The samples were mounted on a variabletemperature (8-300 K) rotary stage holder which permitted rotation of the substrate around a vertical axis.

Measurements of XMCD spectra were performed in order to characterize the magnetic coupling between TbPc2 and the FeMn and Fe films. XMCD is the difference between the absorption spectra of right- and left-handed circularly polarized x-ray photons near a core absorption edge. For Fe (Tb), these spectra are taken by sweeping the photon energy across the  $L_3$  ( $M_5$ ) and  $L_2$  ( $M_4$ ) absorption edges, which are the  $2p \rightarrow 3d \ (3d \rightarrow 4f)$  core-to-valence excitations. A magnetic field was applied along the x-ray direction at normal  $(\theta = 0^{\circ})$  and oblique  $(\theta > 0^{\circ})$  incidence. The spectra were acquired in total electron yield mode by recording the sample photocurrent as a function of x-ray photon energy. To correct for intensity fluctuations in the incident x-ray beam, the sample photocurrent was normalized by the photocurrent of a gold reference grid.

#### **III. RESULTS**

#### A. Coupling of TbPc<sub>2</sub> to FeMn films

We first investigate the coupling between TbPc<sub>2</sub> and FeMn on a set of three samples with different FeMn thicknesses (3, 6, and 8 ML). Cu(100) was chosen as the substrate due to the low lattice mismatch with FeMn, which promotes the growth of virtually unstrained FeMn films [21]. STM micrographs of the TbPc<sub>2</sub>/FeMn/Cu(100) samples before and after the TbPc<sub>2</sub> deposition are shown in Fig. 1. For coverages larger than 3 ML, we find that the FeMn films grow in a layerby-layer fashion, in agreement with previous studies [21,22]. The elemental composition of the FeMn films, estimated from the jumps at the Fe and Mn  $L_3$  edges in the x-ray absorption spectroscopy (XAS) spectra are Fe<sub>36</sub>Mn<sub>64</sub> (3 ML), Fe<sub>63</sub>Mn<sub>37</sub> (6 ML), and Fe<sub>56</sub>Mn<sub>44</sub> (8 ML). Variations in the relative elemental composition between different thicknesses are not expected to affect the spin structure of the films, since all three compositions belong to the same bulk magnetic



TbPc, /FeMn(8 ML)/Cu(100)

FIG. 1. (Color online) STM micrographs of TbPc2/FeMn/ Cu(100) for different thicknesses of the FeMn layer, taken at room temperature before and after TbPc2 deposition on different sample regions.

phase (the 3Q noncollinear spin structure) of the Fe-Mn alloy system [23,24]. Following the deposition of TbPc<sub>2</sub>, we observe from the Tb linear dichroism spectra taken at  $60^{\circ}$  incidence that the molecules adopt a planar adsorption geometry favored by bonding to the metallic substrate, without forming ordered two-dimensional structures. We attribute the lack of lateral order to the reduced mobility of TbPc<sub>2</sub> on transition-metal substrates, similar to what has been reported for Ni and contrary to the self-assembly behavior observed on Au(111) and on weakly interacting oxide and graphite surfaces [9,25,26].

Figure 2 displays the XAS and XMCD spectra of Fe, Mn, and Tb measured on the TbPc2/FeMn(6 ML)/Cu(100) sample at T = 8 K in a field B = 4.5 T applied perpendicular to the substrate. All data were taken after cooling the samples from room temperature down to T = 8 K in a field of 4.5 T applied perpendicular to the substrate. The expectation value of the Fe and Mn (Tb) magnetic moment (projected on the incidence direction of the x-ray beam) is proportional to the ratio between the peak XMCD value and the jump in the average XAS intensity at the  $L_3$  ( $M_5$ ) edge, namely to  $2(I^- - I^+)/(I^- + I^+)$ . This ratio is about 0.05 for Fe and 0.02 for Mn, much smaller than the typical asymmetry measured for ferromagnetic Fe films ( $\approx 0.6$ ) and saturated paramagnetic Mn atoms ( $\approx$ 1) [27], indicating that the magnetization of FeMn, even at 4.5 T, is mostly compensated. The XMCD spectra



FIG. 2. (Color online) XAS and XMCD spectra of TbPc<sub>2</sub>/ FeMn(6ML)/Cu(100) at (a) the  $L_{2,3}$  Fe edge, (b) the  $M_{4,5}$  Tb edge, and (c) the  $L_{2,3}$  Mn edge. The data were taken at T = 8 K in a field B = 4.5 T applied perpendicular to the sample. The XAS signal was rescaled to have an  $L_3$  edge jump equal to 1.

further show that the Fe and Mn magnetic moments tend to align parallel to the external field at 4.5 T, as expected for both compensated and uncompensated spins. The Tb magnetic moment is practically saturated at this temperature and field, in agreement with previous studies of  $TbPc_2$  on magnetic substrates [8,9,12,20].

In order to understand the coupling between TbPc<sub>2</sub> and FeMn, we need to first review the expected surface spin structure of FeMn/Cu(100). Below the Néel temperature, bulk FeMn with 35–80% Fe has a three-dimensional noncollinear antiferromagnetic spin structure in which the spins of the corner atom of the fcc unit cell and the three adjacent face-centered atoms point towards the center of the common tertrahedron (the 3Q spin structure) [24,28]. In the (100) atomic planes, the spins are out-of-plane tilted at  $\pm 35.3^{\circ}$  and point along the [110] and [ $\bar{1}10$ ] in-plane crystallographic axes [24]. Aside from step edges (which can retain uncompensated moments), the net in-plane spin component in the (100) planes is zero (fully in-plane compensated surface); however, the out-of-plane spin component is nonzero and alternates direction between adjacent (100) planes. Using photoelectron emission microscopy,



FIG. 3. (Color online) (a)–(c) Fe (blue) and Tb (red) magnetization curves of TbPc<sub>2</sub>/FeMn(t)/Cu(100) for t = 3, 6, and 8 ML, respectively, following field cooling in B = 4.5 T applied perpendicular to the sample. Insets: low-field region of the Tb magnetization curve. (d) Fe and Tb magnetization curves of TbPc<sub>2</sub>/FeMn(8 ML)/Cu(100) after Li deposition. All data were recorded at T = 8 K. The XMCD signal was normalized by the jump in the averaged XAS signal at the corresponding edge.

it was shown that a noncollinear antiferromagnetic spin structure similar to the bulk 3Q spin structure is present also in ultrathin fcc FeMn [29,30]. A rearrangement of the 3Q spin structure towards the 1Q (out-of-plane spins pointing in opposite directions in adjacent atomic planes) or 2Q (in-plane spins pointing oppositely along face diagonals rotated by 90° between neighboring atomic planes) spin structures has also been proposed for FM/FeMn bilayers [31].

Figures 3(a)-3(c) show the perpendicular magnetization curves of TbPc<sub>2</sub>/FeMn/Cu(100) measured by recording the field dependence of the XMCD/XAS ratio at the Fe (Tb)  $L_3$ ( $M_5$ ) edge. The curves demonstrate the existence of unpinned



FIG. 4. (Color online) Fe and Tb magnetization curves of TbPc<sub>2</sub>/Fe/Cu(100) (a),(b) before and (c),(d) after deposition of Li. The data were taken at T = 8 K at oblique incidence [ $\theta = 73^{\circ}$  for (a),(b);  $\theta = 60^{\circ}$  for (c),(d)], following field cooling in the zero field. Insets: Detail of the low-field region. The XMCD signal was normalized by the jump in the averaged XAS signal at the corresponding edge.

(field-rotatable) and pinned (locked to the antiferromagnetic lattice) Fe spins, which can be identified as a finite amplitude of the magnetization curve [Figs. 3(a)-3(c)] or as a shift in the magnetization curve along the magnetization axis [Fig. 3(c)], respectively. The Fe magnetization curve of the thinnest FeMn (3 ML) film [Fig. 3(a)] has a small hysteretic component superimposed on a paramagnetic curve which does not reach saturation, suggesting that antiferromagnetic ordering is not fully established in this system. The Tb magnetization curve is nonhysteretic and vertically centered, similar to measurements of TbPc<sub>2</sub> on nonmagnetic substrates at the same temperature [15,16].

The Fe magnetization curve of the thicker FeMn (6 ML) film [Fig. 3(b)] has a more pronounced ferromagnetic shape and appears to saturate, which suggests that the FeMn film has established antiferromagnetic order with an out-of-plane anisotropy axis for the unpinned spins. From the height of the Fe magnetization curve and assuming a uniform distribution of uncompensated Fe spins within the film, we estimate that the surface coverage of uncompensated Fe spins is about 6%. The presence of AFM ordering is further confirmed by the value of the field-induced XMCD at 4.5 T, which is much smaller compared to that of ferromagnetic samples measured in the same conditions, for which an XMCD (normalized to XAS) of about 0.6 is measured, as reported below [and illustrated in Fig. 4(a)]. The Tb magnetization curve is hysteretic, with a coercive field  $H_c = -59 \pm 3$  mT. Its finite remanence is interpreted as a consequence of exchange coupling between Tb and the field-rotatable, hysteretic interfacial Fe spins. We estimate the fraction of molecules that is exchange biased in the zero field from the ratio between the remanence and the height of the Tb magnetization curve, which gives a value of approximately 3%. Taking into account the 0.5 ML TbPc<sub>2</sub> coverage for this sample gives a surface coverage of exchange-biased molecules of about 1.5%. Since Tb and Fe have remanent magnetizations of opposite sign [see inset of Fig. 3(b)], we infer that their coupling is antiferromagnetic. This result confirms that coercivity is not necessarily intrinsic to the ferromagnetic ordering of the biased system, similar to inorganic exchange-biased FM/AFM systems [32]. In our case, the molecules acquire coercivity directly from the hysteretic behavior of the biasing system (i.e., the unpinned interfacial Fe spins).

The Fe magnetization curve of the thickest FeMn (8 ML) film [Fig. 3(c)] shows, aside from hysteresis, a shift along the magnetization axis, which indicates that antiferromagnetic order is established, with an uncompensated spin component perpendicular to the surface, as expected. From the height of the Fe magnetization curve and assuming a uniform distribution of uncompensated Fe spins across the film, we estimate that the surface coverage of uncompensated Fe spins is about 2% of the top monolayer. From the ratio between the vertical shift of the Fe magnetization curve and its amplitude, it can be inferred that  $35 \pm 3\%$  of the uncompensated Fe moments are pinned along the direction of the field applied during sample cooling. The Tb magnetization curve has a coercivity  $H_c = -10 \pm 1$  mT and is displaced along the field axis by an amount  $H_E = 21 \pm 1$  mT, due to exchange coupling with the pinned interfacial Fe spins. We note that TbPc<sub>2</sub> deposited on Mn/Cu(100) also displays exchange bias, but of the ferromagnetic type, with a negative exchange-bias field  $H_E = -22 \pm 4$  mT [12]. In contrast, TbPc<sub>2</sub>/FeMn (8 ML) has a positive exchange bias ( $H_E$  has the same direction as the cooling field). Positive exchange bias occurs if the cooling field is large enough to align the uncompensated AFM spins along the field direction above  $T_N$  and if the FM-AFM exchange coupling is antiferromagnetic [33]. The opposite vertical shifts of the Tb and Fe magnetization curves confirm that the exchange coupling is antiferromagnetic. From the vertical shift of the Tb magnetization loop, we infer that  $1 \pm 0.1\%$  of the TbPc<sub>2</sub> molecules are exchange biased at remanence in the TbPc2/FeMn (8 ML) sample. We recall that the XMCD data is measured on a macroscopic area of the sample. Since only about 1% of the TbPc<sub>2</sub> molecules are exchange biased and contribute to the macroscopic  $H_E$  value of  $21 \pm 1$  mT, we expect that a measurement of  $H_E$  on a single exchange-biased molecule would yield a value roughly 100 times larger than the macroscopic  $H_E$ , that is,  $\approx 2$  T. This value is in reasonable qualitative agreement with the exchange field of 1.3 T measured in TbPc2/Ni/Cu(100) [8]. We emphasize that the foregoing discussion applies to a model in which the vertical shift of the Fe magnetization curve is ascribed to Fe spins pinned parallel to the cooling field direction. However, this shift can be alternatively explained by a spin configuration in which the Fe biasing spins are not pinned, but rather tilted out of plane (similar to the 3Q bulk configuration) at an angle that changes with the applied field. In this latter configuration, the same (field-rotatable) spins would be responsible for both the exchange-bias field and the hysteresis of the molecular film. We also note that the exchange-bias field points along the surface normal, a direction favored by the perpendicular anisotropy of TbPc<sub>2</sub>.

One can draw a parallel between the AFM thickness dependence of the coercive and exchange fields of TbPc<sub>2</sub>/FeMn and FM/AFM bilayers, respectively. In an exchange-biased system such as FeNi/FeMn or Co/FeMn, the FM layer coercivity increases at first with the AFM layer thickness, peaking just at the onset of the biasing effect. This thickness dependence can be understood as follows: as the AFM layer thickness decreases, the AFM anisotropy is reduced, such that the FM spins can "drag" more AFM spins, increasing the FM coercivity. At low enough AFM thicknesses, the antiferromagnetic ordering starts to vanish, restraining less the FM rotation and lowering the FM coercivity [34-36]. The behavior of TbPc2/FeMn is similar. The thinnest TbPc2/FeMn (3 ML) has negligible coercive and exchange fields, while the thicker TbPc<sub>2</sub>/FeMn (6 ML) has finite coercivity and a negligible exchange field. In the thickest FeMn (8 ML) sample, the coercivity drops sharply compared to the FeMn (6ML) sample, whereas the exchange field increases. We also note the absence of the "butterfly" plateaus in the Tb magnetization curve, which indicates a relatively strong interaction between the TbPc<sub>2</sub> molecules and the metallic substrate [15,16].

Figure 3(b) shows the presence of kinks in the Fe magnetization curve around B = 0 T, approximately in the range from -0.04 to +0.04 T. From the ratio between the kink magnitude and the height of the full magnetization curve, we estimate that the kinks account for the reversal of about 10% of the uncompensated Fe spins. Recalling that the surface coverage of uncompensated Fe spins is about 6% of the top monolayer, it follows that the kinks account for the reversal of approximately 0.6% of all surface spins, which is a value comparable to the percentage of exchange-biased molecules, which was estimated at about 3%. A possible reason for the Fe magnetization kinks can be the presence of inhomogeneous FeMn regions (such as Fe islands coupled antiferromagnetically to the AFM matrix), which can result in a spatial variation of the Fe coercive field. An alternative explanation for the kinks can be associated with the interaction between the interfacial Fe spins and the TbPc<sub>2</sub> molecules. It is known that at low temperatures, diluted TbPc<sub>2</sub> single crystals exhibit quantum tunneling jumps between hyperfine split energy levels of the ground state [37]. We therefore suggest the possibility that the Fe magnetization kinks are triggered by molecular quantum tunneling transitions in a fraction of the exchange-biased molecules [15,16]. Because of the small fraction of TbPc2 molecules coupled to uncompensated Fe spins, however, such kinks would not be directly visible in the Tb magnetization loops. A conclusive test of this hypothesis would be a comparison between Fe magnetization loops taken before and after deposition of molecules, which unfortunately was not possible during the limited time frame of this experiment.

## B. Coupling of TbPc<sub>2</sub> to Fe films

Next we investigate the magnetic coupling between  $\text{TbPc}_2$ and Fe. The magnetic structure of Fe films grown on Cu(100) is extremely complex, i.e., dependent on coverage, temperature, and deposition conditions [38–42]. Below a thickness of 4 ML, both perpendicular [38–41] and in-plane [40,42] magnetic anisotropy have been reported, whereas between 6–11 MLs, the top bilayer has been found to be ferromagnetic with a perpendicular easy axis and the deeper layers in a spin-spiral state [40,42]. In the course of the present study, we could not perform a systematic investigation of the Fe magnetic structure as a function of coverage and temperature. We thus focus on a single Fe film with nominal thickness of 4.6(2) ML in order to investigate the nature of the exchange coupling in this system and compare it with FeMn. We analyze the oblique incidence magnetization curves of Fe and Tb, shown in Figs. 4(a) and 4(b). The data were taken after cooling down the sample from room temperature to T = 8 K in the zero field. Figure 4(b) shows that at low applied fields, the Tb magnetization is aligned antiparallel to the Fe magnetization and reverse simultaneously, which is consistent with antiferromagnetic exchange coupling between TbPc<sub>2</sub> and the top Fe monolayer, as reported for FeMn [see inset of Fig. 4(a)]. As the in-plane field increases,  $M_{\rm Tb}$ switches sign at B = 1.8 T, above which the Zeeman energy starts to dominate the antiferromagnetic exchange coupling and the perpendicular molecular anisotropy, resulting in a gradual alignment of the Tb magnetization with the field.  $M_{\rm Tb}$ does not reach saturation up to the maximum applied field B = 4.5 T, likely due to the TbPc<sub>2</sub> perpendicular anisotropy field, similar to TbPc<sub>2</sub> coupled to in-plane magnetized Ni films [8].

## C. Influence of electron doping on the coupling of TbPc<sub>2</sub> to FeMn and Fe films

The bottom Pc ligand, which separates the Tb ion from the surface Fe spins, is likely involved in the exchange-coupling mechanism. It has been shown that by changing the amount of charge transfer between the surface and the molecule, one can modify the exchange interaction [8]. We investigate this possibility by depositing electron-donor Li atoms onto the sample, which are known to be efficient dopants for Pc ligands [43-45]. The magnetization curves acquired after Li deposition onto the TbPc<sub>2</sub>/FeMn(8 ML)/Cu(100) sample are shown in Fig. 3(d). Following Li deposition, the exchange-bias field changes sign and increases to  $H_E = -37 \pm 2$  mT, as evidenced by the vertical shift of opposite sign in the Tb magnetization curve. Changes in the magnitude of the exchange-bias field have been previously reported [8]; however, our study reports a change in sign of the coupling following doping with electron-donor Li. The Tb coercivity changes sign but remains largely unchanged at  $H_c = 14 \pm 2$  mT. The percentage of pinned Fe spins is estimated at  $7 \pm 3\%$  of the total uncompensated Fe spins. From the ratio between the vertical shift of the Tb magnetization loop and its height, we estimate that  $1.7 \pm 0.1\%$  of the Tb ions are pinned at remanence following Li deposition. Charge transfer between the surface and the molecule therefore changes the exchange coupling from AFM to FM.

We next probed the effect of charge transfer on the exchange coupling by depositing Li onto the  $TbPc_2/Fe/Cu(100)$  sample and measuring the Fe and Tb magnetization curves, shown in Figs. 4(c) and 4(d). The Fe magnetization curve displays a change in the Fe coercivity and remanent magnetization, which can be partly attributed to a change in perpendicular magnetic anisotropy. Even more significantly, the Tb magnetization is now aligned parallel to the Fe magnetization at all fields and reverses in the same field range, consistent with ferromagnetic exchange coupling. Charge transfer therefore has the same effect as in TbPc<sub>2</sub>/FeMn/Cu(100), changing the coupling from antiferromagnetic to ferromagnetic.

#### IV. CONCLUSIONS

Magnetic exchange coupling between TbPc2 and FeMn/Cu(100) has been studied using x-ray magnetic circular dichroism. We find that TbPc2 couples antiferromagnetically to the uncompensated, unpinned interfacial Fe spins of FeMn(6 ML)/Cu(100) and FeMn(8 ML)/Cu(100). This result is confirmed in the TbPc<sub>2</sub>/Fe/Cu(100) system, which displays antiferromagnetic exchange coupling as well. Additionally, a fraction of the TbPc2 molecules deposited on FeMn(8 ML)/Cu(100) are shown to be exchange biased by the pinned surface Fe spins. The effect of this exchange-bias field is evident in the Tb as well as in the Fe magnetization curves of FeMn(8 ML)/Cu(100), which appear vertically shifted with respect to the origin. The vertical shift of the Fe curves is extremely pronounced, corresponding to about 35% of the uncompensated Fe spins pinned along the direction of the cooling field. This translates to an equivalent of roughly 0.01 ML of interfacial pinned Fe moments, that is, the pinned Fe sites make up roughly 1% of the interface. On the other hand, the percentage of TbPc<sub>2</sub> molecules exchange biased to the pinned Fe moments is about 1%, close to the statistical probability of TbPc<sub>2</sub> adsorbing on pinned Fe sites. The horizontal shift of the Tb magnetization curve is about 20 mT. When this value is rescaled to take into account the percentage of pinned molecules relative to the total TbPc<sub>2</sub> coverage, one obtains an exchange-bias field of the order of 2 T, similar to the compensation threshold between the external magnetic field and exchange interaction found on ferromagnetic substrates. We provide evidence that the TbPc<sub>2</sub> coercive and exchange-bias fields display a dependence of the FeMn thickness that is consistent with inorganic FM/AFM exchange-biased systems. The exchange coupling of TbPc<sub>2</sub> to FeMn/Cu(100) and Fe/Cu(100) changes sign following interface doping with electron-donor Li.

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