## **Coupling Single Molecule Magnets to Ferromagnetic Substrates**

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We investigate the interaction of  $\text{TbPc}_2$  single molecule magnets (SMMs) with ferromagnetic Ni substrates. Using element-resolved x-ray magnetic circular dichroism, we show that  $\text{TbPc}_2$  couples antiferromagnetically to Ni films through ligand-mediated superexchange. This coupling is strongly anisotropic and can be manipulated by doping the interface with electron acceptor or donor atoms. We observe that the relative orientation of the substrate and molecule anisotropy axes critically affects the SMM magnetic behavior. TbPc<sub>2</sub> complexes deposited on perpendicularly magnetized Ni films exhibit enhanced magnetic support layer, we find that TbPc<sub>2</sub> can be magnetized parallel or antiparallel to the substrate, opening the possibility to exploit SMMs in spin valve devices.

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In future years the miniaturization of spintronic devices may require including molecular-scale elements in hybrid metal-organic architectures [1–4]. Single molecule magnets (SMMs) represent the smallest known bi-stable magnetic systems [5], thus making them ideal candidates for both classical and quantum computing applications [1,6]. Unfortunately, because of the competition between thermal spin fluctuations and magnetic anisotropy, SMMs display remanent magnetization only at low temperature. This occurs as magnetic relaxation becomes slow compared to the time scale of observations  $(\tau)$ , typically below 6 K in the archetypal  $Mn_{12}$  compound [5,7] and 40 K in mononuclear Tb double-decker complexes (TbPc<sub>2</sub>) [8,9]. Measurements of TbPc<sub>2</sub>, however, show that magnetic hysteresis is absent down to T = 7 K if  $\tau$  is greater than about 100 s [10-13]. Increasing the magnetic stability of SMMs independently of temperature is thus one of the greatest challenges faced by molecular spintronics.

Efforts to slow down magnetic relaxation in SMMs have so far relied on the synthesis of polynuclear molecules with a large number of metal ions [14] or on modifying the ligand field strength in order to raise the magnetic anisotropy energy [15]. These approaches have been moderately successful. For example, ligand oxidation has been shown to increase the blocking temperature of TbPc<sub>2</sub> by about 10 K [16]. Recently, an alternative strategy has been proposed to stabilize the magnetic moment of paramagnetic molecules against thermal fluctuations, based on the deposition of metal-porphyrins and phthalocyanines on ferromagnetic (FM) films [17–23]. Because of the planar structure of such molecules and close proximity of the metal ions to the substrate, the magnetic moment of the metal centers can efficiently couple to the surface magnetization via superexchange and direct exchange paths [19–22]. Although individual molecules cannot be magnetized independently, this approach enables the fabrication of metal-organic layers with stable magnetization up to room temperature [18,20,23]. Ultrathin molecular layers may thus be used to fabricate FM heterostructures or magnetochemical sensors [23].

In this Letter, we investigate the coupling between SMMs and FM substrates. We focus on TbPc<sub>2</sub> owing to its compact structure, which constitutes an advantage to establish an exchange path between the magnetic core of the molecule and the ferromagnet. We choose Ni layers for the substrate, as the direction of the easy axis can be controlled through epitaxial strain without changing the chemical composition of the SMM/FM interface. Using xray magnetic circular dichroism (XMCD), we show that TbPc<sub>2</sub> SMMs couple antiferromagnetically (AFM) to a FM metal. We determine the magnitude of the exchange coupling constants and show how these can be enhanced (reduced) by increasing (decreasing) the amount of charge transferred from the surface to the molecules. Our results evidence the competition between the SMM and substrate magnetic anisotropy, and show that the magnetic moment of TbPc<sub>2</sub> can be effectively stabilized against thermal fluctuations while preserving typical SMM features.

The experiments were performed at beam line ID08 of the European Synchrotron Radiation Facility (ESRF). The samples were prepared in situ by molecular beam evaporation of TbPc<sub>2</sub> on Ni films in ultrahigh vacuum. The TbPc<sub>2</sub> coverage was  $0.05 \pm 0.02$  monolayers (ML). FM films with out-of-plane (OP) and in-plane (IP) magnetic anisotropy were obtained by deposition of 13 ML of Ni on Cu(100) and 6 ML of Ni on Ag(100) sputter-annealed single crystals, respectively [24,25]. Oxidized and reduced Ni surfaces with OP magnetization were prepared by the surfactant growth of a  $c(2 \times 2)$  O phase on Ni/Cu(100) [26] and by evaporating Li on  $\text{TbPc}_2/\text{Ni}/\text{Cu}(100)$ .  $\text{TbPc}_2$ adsorbs flat on metal surfaces [10,27] as well as on oxygencovered Ni [28]. The XMCD measurements were carried out using total electron yield detection at the  $L_{2,3}$  absorption edges of Ni and  $M_{4,5}$  absorption edges of Tb, selectively probing the substrate  $(M_{Ni})$  and molecule  $(M_{Tb})$ magnetic moments. A magnetic field **B** was applied parallel to the x-ray direction at normal ( $\theta = 0^{\circ}$ ) and grazing  $(\theta = 70^{\circ})$  incidence to measure the OP and IP magnetization. The time required to record a set of Tb XMCD spectra or a hysteresis loop was about  $10^3$  s, which defines the lower limit of  $\tau$  probed in this experiment. For more details about the beam line setup, sample preparation, and XMCD measurements we refer to Refs. [10,30].

We begin by investigating the coupling of  $TbPc_2$  to OP Ni films, in which case the molecule and substrate easy axes are collinear. Figure 1(a) shows the Ni and Tb x-ray absorption (XAS) and XMCD spectra recorded at T = 8 K after saturating the magnetization at 5 T and subsequently setting the field to zero. We observe that both Ni and Tb have a strong remanent XMCD intensity, which remains stable over the time scale of the measurements. The sign of the Tb XMCD, however, is opposite to Ni, indicating that  $M_{Tb}$  and  $M_{Ni}$  are AFM coupled. Measurements of TbPc<sub>2</sub> on IP Ni films, reported in Fig. 1(b), illustrate the case where the molecule and substrate easy axes are orthogonal. Although the coupling between TbPc<sub>2</sub> and Ni remains antiferromagnetic, as expected, the remanent Tb XMCD intensity along the substrate easy axis is now strongly reduced compared to the Ni XMCD. This result shows the importance of matching the substrate and SMM magnetic anisotropy properties to effectively stabilize the SMM magnetization in the absence of external magnetic fields. Notably, this is in contrast with recent theoretical calculations of Mn<sub>12</sub> on Ni, which postulate that the magnetic easy axis of the SMM-substrate system is dictated by that of the Ni layer [31].

Element-resolved hysteresis loops provide further insight into the nature of SMM-substrate coupling. Figure 2(a) shows the out-of-plane ( $\theta = 0^{\circ}$ ) and in-plane ( $\theta = 70^{\circ}$ ) magnetization loops of the OP TbPc<sub>2</sub>/Ni/ Cu(100) sample measured by recording the XMCD intensity at the Ni  $L_3$  and Tb  $M_5$  edge as a function of applied field [28]. In the low field region,  $\mathbf{M}_{Tb}$  is aligned



FIG. 1 (color online). XMCD measurements of TbPc<sub>2</sub> on (a) OP Ni/Cu(100) and (b) IP Ni/Ag(100) films recorded at remanence, T = 8 K. Top: schematic view of the TbPc<sub>2</sub> and Ni magnetization. Middle: XAS spectra measured at the  $L_{2,3}$  edges of Ni with positive ( $I^+$ ) and negative ( $I^-$ ) circular polarization, and XMCD intensity ( $I^- - I^+$ ). Bottom: Tb spectra at the  $M_{4,5}$  edges. Because of the low TbPc<sub>2</sub> coverage, the Tb XAS is superimposed to a substrate-dependent background.

antiparallel to  $\mathbf{M}_{\text{Ni}}$ , switching direction together with it [dashed lines in Fig. 2(a)]. Note that  $\mathbf{M}_{\text{Tb}}$  does not present a butterfly hysteresis loop with near-zero remanence typical of TbPc<sub>2</sub> in bulk crystals and nonmagnetic substrates [11,13,32], but closely follows the square  $\mathbf{M}_{\text{Ni}}$  loop as long as B < 0.1 T. At higher field, however, the Zeeman interaction overcomes antiferromagnetic exchange, inducing a gradual rotation of  $\mathbf{M}_{\text{Tb}}$  parallel to **B**.  $\mathbf{M}_{\text{Tb}}$  first changes sign at  $B = B_{\text{exc}}$ , as the external field compensates the exchange coupling to the substrate, and finally ends up parallel to  $\mathbf{M}_{\text{Ni}}$ . A similar behavior is observed for the outof-plane (left panel) and in-plane  $\mathbf{M}_{\text{Tb}}$  (right panel), albeit the Tb remanence,  $B_{\text{exc}}$ , and the magnetization at high-field depend on the orientation of **B** with respect to the SMM easy axis.

The coupling between  $\mathbf{M}_{\text{Tb}}$  and  $\mathbf{M}_{\text{Ni}}$  is necessarily mediated by the bottom Pc ligand of TbPc<sub>2</sub>, which separates the Tb ion from the surface. This likely occurs through electrons residing or transferred into a Pc  $\pi$  orbital. Therefore, we tested the possibility of tuning the exchange interaction by modifying the amount of charge transfer between surface and molecule. This can be realized in practice by (i) preparing a (2 × 2) O buffer layer



FIG. 2 (color online). Element-resolved hysteresis loops of Ni (top) and Tb (bottom) for (a) TbPc<sub>2</sub>/Ni/Cu(100), (b) TbPc<sub>2</sub>/O/Ni/Cu(100), (c) TbPc<sub>2</sub>/Li/Ni/Cu(100), and (d) TbPc<sub>2</sub>/Ni/Ag(100) measured at normal (left) and grazing (right) incidence at T = 8 K. The units of  $\mathbf{M}_{\text{Ni}}$  and  $\mathbf{M}_{\text{Tb}}$  correspond to the XMCD/XAS ratio at the  $L_3$  and  $M_5$  absorption edges, respectively [28]. The dashed lines in (a) show the Tb magnetization at low field normalized to  $\mathbf{M}_{\text{Ni}}$ . The solid lines superposed to  $\mathbf{M}_{\text{Tb}}$  are fits according to Eq. (1).

[26] between TbPc<sub>2</sub> and Ni, and (ii) "doping" the Ni surface with a strong electron donor such as Li. Although we do not control the extent of charge transfer in either case, it is safe to assume that (i) leads to oxidation and (ii) to a reduction of the Pc ligand. The reproducibility of the XMCD spectral features proves that the electronic configuration of Tb remains predominantly  $4f^8$  in either case [28,29]. However, we observe a reduction of the XMCD/

XAS ratio for TbPc<sub>2</sub>/Li/Ni/Cu(100) [28], which is consistent with moderate charge transfer into the 4*f* states, as would be expected due to increased occupancy of the Pc orbitals [12]. The effects of charge transfer on the Ni magnetization, reported in Figs. 2(b) and 2(c), are limited to changes of the coercivity, which we ascribe to modifications of the surface magnetocrystalline anisotropy energy. The magnetic behavior of TbPc<sub>2</sub>, on the other hand, changes significantly. The remanent  $\mathbf{M}_{Tb}$  decreases strongly in TbPc<sub>2</sub>/O/Ni layers compared to TbPc<sub>2</sub>/Ni, as shown in Fig. 2(b). Moreover,  $B_{exc}$  varies from 0.6 T in TbPc<sub>2</sub>/O/Ni to 2.5 T in TbPc<sub>2</sub>/Li/Ni [Fig. 3(a)], indicating that the exchange coupling energy increases significantly with the amount of charge donated to the Pc ligand.

The competition between the intrinsic SMM properties, namely, the magnetic anisotropy, Zeeman interaction of  $TbPc_2$ , and antiferromagnetic exchange to the substrate, can be described using the following Hamiltonian:

$$H = \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} - \lambda \mathbf{L} \cdot \mathbf{S} + V_{\rm CF} + \hat{\mathbf{M}}_{\rm Ni} \cdot \mathbf{K} \cdot \hat{\mathbf{S}}$$
(1)

where  $\mu_B$  is the Bohr magneton, **S** and **L** the spin and orbital moments of Tb,  $\lambda = 212$  meV the spin-orbit energy, and  $V_{\rm CF} = -B_2 O_2^0 - B_4 O_4^0 - B_6 O_6^0$  the Tb crystal field potential as a function of the Stevens operators  $O_k^m$ . Since  $V_{CF}$  is not affected by deposition on metals [10], we use the same coefficients  $B_2 = 414$ ,  $B_4 = -228$ , and  $B_6 =$  $33 \text{ cm}^{-1}$  as for the free molecule, which give a magnetic anisotropy barrier of about 590 cm<sup>-1</sup> (73 meV) [9,33]. **K** represents the superexchange tensor between Ni and Tb, of which we consider only the diagonal out-of-plane  $K^{\perp}$  and in-plane  $K^{\parallel}$  components. The dipolar magnetic field produced by the substrate can be neglected [28]. We use Eq. (1) to calculate the expectation value of  $M_{Tb} =$  $-\mu_B(\langle \mathbf{L} \rangle + 2 \langle \mathbf{S} \rangle)$  as a function of applied field and temperature and fit the curves reported in Fig. 2. The fit is restricted to the bottom J = L + S = 6 multiplet of TbPc<sub>2</sub> [33]. For simplicity, we take  $\hat{M}_{Ni} = \pm 1$  for  $B \ge 0$ . The fit has three free parameters:  $K^{\perp}$ ,  $K^{\parallel}$ , and a multiplicative



FIG. 3 (color online). (a) Exchange field  $(B_{\text{exc}})$  and coupling constants  $(K^{\perp}, K^{\parallel})$  derived from Fig. 2 and Eq. (1), respectively. (b) Temperature dependence of the remanent Ni and Tb XMCD intensity, normalized to the values at T = 8 K. Solid lines represent the calculated  $\mathbf{M}_{\text{Tb}}$  and  $\mathbf{M}_{\text{Ni}}$  (see text).

factor that scales  $M_{Tb}$  to the XMCD intensity. Such parameters reduce to two when  $\theta = 0^{\circ}$  for the curves shown in Figs. 2(a)–2(c), where  $K^{\parallel}$  plays no role. The results, shown as solid lines, reproduce remarkably well the easy and hard axis behavior of TbPc<sub>2</sub>, demonstrating that our model captures the main features of the interaction between SMM and OP substrates. The situation appears to be more complicated for the IP substrate [Fig. 2(d)], where  $M_{Tb}$  saturates at a slower rate compared to the OP case. Presently, we cannot explain such a difference using Eq. (1). However, we can qualitatively interpret the shape of the out-of-plane loop [left panel in Fig. 2(d)], where  $M_{Tb}$  is approximately zero up to  $B = \pm 0.7$  T. This peculiar behavior is consistent with the fact that, due to the strong perpendicular anisotropy, only the out-of-plane component of  $\mathbf{M}_{Ni}$  can polarize  $\mathbf{M}_{Tb}$ , whereas the in-plane exchange field mixes in equal amount up and down magnetic states. As long as  $M_{\rm Ni}$  is linear with B, the outof-plane antiferromagnetic exchange term  $K^{\perp}\hat{M}_{\rm Ni}$  compensates the Zeeman energy  $\mu_B(\mathbf{L} + 2\mathbf{S})B$ , leading to  $M_{\rm Tb} \approx 0.$ 

Figure 3(a) compares the values of  $K^{\perp}$ ,  $K^{\parallel}$ , and  $B_{\text{exc}}^* = \mu_B(L+2S)B_{\text{exc}}$  measured at  $\theta = 0^\circ$  and 70°. We observe that  $K^{\perp}$  and  $B_{\text{exc}}^*(\theta = 0^\circ)$  nearly match each other, as expected for an Ising-like system.  $K^{\perp}$  increases by about a factor of 4 going from TbPc<sub>2</sub>/O/Ni to TbPc<sub>2</sub>/Li/Ni. Moreover, we find that **K** is strongly anisotropic, since  $K^{\parallel}$ is generally much greater than  $K^{\perp}$ . Such a strong superexchange anisotropy is not unusual for rare earth ions with unquenched **L** since the spin-orbit interaction is significant compared to  $V_{\text{CF}}$  [34]. In such a case, a rotation of the 4*f* spin carries the orbital wave functions with it, thereby significantly varying the electronic overlap with neighboring orbitals that is at the origin of superexchange.

Finally, we address the magnetic stability of TbPc<sub>2</sub> on Ni as a function of temperature. From the data reported in Fig. 2, it is evident that the interaction with Ni greatly enhances  $\mathbf{M}_{\text{Tb}}$  at zero field compared to TbPc<sub>2</sub> in the bulk and on nonmagnetic substrates [11,13], where resonant quantum tunnelling between hyperfine levels prevents reaching 100% remanence [32]. Figure 3(b) shows that finite remanence is observed up to T = 100 K, indicating that the coupling with Ni stabilizes  $\mathbf{M}_{\text{Tb}}$  on a time scale of the order of  $10^3$  s. The solid lines represent  $M_{\text{Tb}}(T)$  calculated using Eq. (1) and  $M_{\text{Ni}}(T) = (1 - T/T_C)^{\beta}$ , with  $T_C = 575$  K and  $\beta = 0.28 \pm 0.04$  [24]. Note that  $\mathbf{M}_{\text{Tb}}$  relaxes independently of  $\mathbf{M}_{\text{Ni}}$ , as expected for a paramagnetic system described by Eq. (1) in the presence of an exchange field.

Before concluding, we provide a comparison of our results with previous measurements of paramagnetic molecules deposited on FM metal films [18–23]. Unlike the above systems, the magnetic metal ion of TbPc<sub>2</sub> is separated from the surface by a complex ligand structure and has f rather than d character. The coupling of TbPc<sub>2</sub> to Ni

is antiferromangetic, whereas metal-porphyrins and phthalocyanines always couple ferromagentically to bare metal surfaces either through direct exchange or by 90° superexchange [17–23]. Both mechanisms are unlikely to occur in SMMs because the metal centers are placed further away from the surface. Such separation also favors 180° antiferromangetic superexchange paths over 90° FM ones. Most importantly, the magnetization of metalporphyrins and phthalocyanines always mimic that of the FM substrate, whereas  $TbPc_2$  and Ni clearly behave as two different magnetic systems. This is attributed to the smaller superexchange interaction of SMMs compared to planar molecules [20] as well as to the strong magnetic anisotropy and large magnetic moment intrinsic to SMMs.

In summary, we have proven that SMMs couple to FM metal layers. The superexchange interaction mediating the coupling can be tuned by oxidizing or reducing the FM substrate. Element-resolved hysteresis curves reveal that the SMM magnetization depends critically on the alignment of the molecule and substrate easy axes as well as on the balance between interface-dependent superexchange and applied magnetic field. All together, our results show that SMMs behave as coupled but separate magnetic units from an underlying FM surface. The enhanced thermal stability of the TbPc<sub>2</sub> magnetic moment and the possibility to orient it parallel or antiparallel to a macroscopic FM layer make TbPc<sub>2</sub> very interesting for applications in hybrid devices. Future experiments may address the coupling of different SMM families to ferromagnets as well as the transport properties of SMM-FM spin valves.

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## Supplementary Online Material Coupling single molecule magnets to ferromagnetic substrates

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# I. ORIENTATION OF TBPC<sub>2</sub> MOLECULES ON NI AND $(2 \times 2)$ O/NI SURFACES

TbPc<sub>2</sub> is known to adsorb flat on metals<sup>1-3</sup> and graphite<sup>4-6</sup>. Scanning tunneling microscopy (STM) images recorded ex-situ (Fig. S1) show that TbPc<sub>2</sub> adsorb flat also on oxygen-covered metal surfaces, specifically on the  $c(2 \times 2)$  O phase grown on Ni/Cu(100). This surface was prepared by dosing a clean Cu(100) single crystal with 1345 L of O<sub>2</sub> at 500 K and subsequent evaporation of 6 monolayers of Ni at 320 K, following Ref. 7. TbPc<sub>2</sub> molecules were thermally evaporated with the substrate held at room temperature. Note that the adsorption behavior of TbPc<sub>2</sub> is similar to that of phthalocyanine and porphyrin species, which adsorb flat on bare<sup>8</sup> as well as O-covered metal substrates<sup>9,10</sup>, semiconductors<sup>11</sup>, and thin insulating films<sup>12</sup>.



FIG. 1: (a) STM image of TbPc<sub>2</sub> deposited on  $c(2 \times 2)$  O/Ni/Cu(100), image size  $50 \times 50$  Å<sup>2</sup>. The bright horizontal region represents a dislocation line, typical of Ni films grown on Cu(100)<sup>7</sup>. (b) Atomic-resolution detail of the substrate showing the  $c(2 \times 2)$  O superstructure on Ni, with 3.7 Å lateral periodicity. Image size  $34 \times 34$  Å<sup>2</sup>.

### II. MAGNETIZATION CURVES MEASURED BY XMCD

The magnetization curves are measured by recording the peak XMCD intensity at 854.5 (1242.5) eV for Ni (Tb) as a function of applied field. There are different ways to perform such a measurement. The first one is to measure pairs of  $I^+$  and  $I^-$  spectra at each field. This is extremely time-consuming for dilute samples, as a single pair of spectra does not provide enough signal-to-noise ratio. Moreover, the need to reverse the photon polarization at each field increases the measuring time considerably. The second method consists in performing two sweeps of the applied magnetic field, one for positive and the other for negative circularly polarized light. During each sweep, only the pre-edge intensity at 845 (1230) eV and the  $L_3$  ( $M_5$ ) peak intensity at 854.5 (1242.5) eV for Ni (Tb) are measured, thus optimizing the acquisition time for the energy point where the XMCD is maximum. The peak intensity values are divided by the pre-edge intensity at each field in order to eliminate the dependence of the electron yield on the sample orientation and magnetic field. Finally, the normalized intensity from the first loop is subtracted from the second in order to obtain the XMCD intensity. This is a well-established method to measure magnetization curves using XMCD<sup>13-15</sup>, which gives better results than just plotting the peak intensity as a function of field as done for relatively thick metal films<sup>16</sup>. The curves in Fig. 2 have been obtained in this way. In order to define a common intensity scale, we have scaled each curve so that the intensity at 5 T matches the XMCD/XAS ratio obtained from



FIG. 2: (Color online). (a) XAS intensity of Ni recorded for TbPc<sub>2</sub>/Ni/Cu(100) at B = 5 T, T = 8 K,  $\theta = 0^{\circ}$ .  $I^+$  (blue, dashed line),  $I^-$  (red, solid line), and  $(I^+ + I^-)/2$  (green dash-dot line). The average XAS has been normalized to 1 at the  $L_3$  edge. (b) Corresponding XMCD intensity  $(I^- - I^+)$ . (c) XMCD magnetization curve recorded at the  $L_3$  Ni edge. The intensity scale is the same as (b). (d-f) Analogous plots for Tb.

the spectra at the same field, as shown in Fig. S2. This procedure has no influence on the fits of the magnetization curves, since the saturation magnetization is a free parameter of each fit.

We recall here that the XMCD/XAS asymmetry is a self-consistent quantity that can be related to the atomic magnetic moment of the element under investigation. This ratio, defined as  $(I^- - I^+)/[(I^+ + I^-)/2]$ , can be calculated by integrating whole spectra or part of the spectra, or by taking the ratio of the peak XMCD and XAS intensity at the  $L_3$  ( $M_5$ ) peaks, where the XMCD is maximum. These two methods are equivalent as long as the XMCD lineshape does not change with applied magnetic field, which is practically always the case as the Zeeman splitting is small with respect to the atomic level spacing due to electron-electron interactions, crystal field, and charge transfer effects. The peak intensity method works better for dilute samples, since it reduces errors due to the integration of noise in the XMCD baseline and does not require the subtraction of background XAS spectra.

### III. EFFECT OF O AND LI ADSORPTION ON THE MAGNETIC PROPERTIES OF TBPC2 AND NI

The XMCD lineshape is very sensitive to changes of the electronic and magnetic ground state of metal  $ions^{17-20}$ . Figure S3 (a) reports the Ni XMCD spectra recorded for TbPc<sub>2</sub>/Ni/Cu(100), TbPc<sub>2</sub>/O/Ni/Cu(100), TbPc<sub>2</sub>/Ni/Cu(100), and TbPc<sub>2</sub>/Ni/Ag(100). The intensity of the XMCD signal is given with respect to the average  $L_3$  XAS intensity,  $(I^+ + I^-)/2$ , which has been scaled to 1 for each sample. The spectra show that neither the intensity nor the lineshape of the Ni XMCD change significantly due to either Li or O adsorption. Even though XMCD is sensitive to the first 5-10 surface layers<sup>21</sup>, strong changes of the electronic and magnetic properties of the topmost layer would show up in the spectra, as the latter contributes most to the electron yield signal. Since this is not the case, we conclude that the magnetic moment per Ni atom is similar for all the substrates investigated in this study. Note that, in the case of the TbPc<sub>2</sub>/O/Ni/Cu(100), the  $c(2 \times 2)/Ni(100)$  layer obtained by O-surfactant growth of Ni on Cu(100) represents a chemisorbed superstructure, not a NiO layer<sup>7</sup>.

Figure S3 (b) reports the Tb XMCD spectra obtained on the Ni substrates shown in (a). We observe that the XMCD lineshape does not vary from sample to sample, indicating that the magnetic ground state of Tb is predominantly of  $4f^8$  character, in agreement with previous studies of Tb compounds<sup>17,18</sup> and TbPc<sub>2</sub><sup>2,3,5,6</sup>. However, the intensity of the XMCD spectra at 5 T is significantly reduced for TbPc<sub>2</sub>/Li/Ni/Cu(100) compared to the other samples. Given that the easy axis magnetization of TbPc<sub>2</sub>/Li/Ni/Cu(100) appears to saturate near 5 T [Fig. 2(c)], this effect can possibly be attributed to a reduction of the Tb atomic magnetic moment induced by charge transfer. Indeed, a previous study of the negatively charged TbPc<sub>2</sub> moiety has shown that even a very moderate charge transfer to the 4f Tb states, of the order of 0.1 electrons, can lead to significant reduction of the SMCD/XAS ratio at finite field<sup>5</sup>. XAS spectra recorded with linearly polarized light also show a reduction of the Spectral weight of the  $M_5$  features at 1242 and 1243.2 eV, which is consistent with increased occupancy of the Tb 4f states (Fig. S4). This interpretation



FIG. 3: (Color online). (a) Comparison of the Ni XMCD spectra obtained at B = 5 T, T = 8 K, and  $\theta = 0^{\circ}$  for different substrates. (b) Same for the Tb spectra. The vertical units represent the XMCD/XAS ratio at the  $L_3$  ( $M_5$ ) edge of Ni (Tb).



FIG. 4: (Color online). (a) Linearly polarized absorption spectra of  $\text{TbPc}_2/\text{Ni}/\text{Cu}(100)$  recorded at the  $M_5$  edge of Tb at T = 8K with **E** parallel to the surface plane (dashed line) and 70° out-of-plane (solid line). (b) Same after Li evaporation.

agrees with our hypothesis of charge donation from Li to TbPc<sub>2</sub>. Note that, according to Refs. 5 and 22, most of the negative charge of the TbPc<sub>2</sub> anion is localized on the Pc ligands, and only a small fraction of it is effectively transferred into the Tb 4f states.

#### IV. DIPOLAR FIELD FROM THE SUBSTRATE

The antiparallel ordering of the TbPc<sub>2</sub> and Ni magnetic moments is attributed to ligand-mediated superexchange coupling. In principle, however, antiferromagnetic coupling can also be attributed to the dipolar field emanating from the Ni surface atoms. Although the dipolar field produced by a continuous magnetization density with either in-plane (IP) or out-of-plane (OP) orientation is zero outside an infinite surface plane, the discrete atomic lattice structure of a real surface may give rise to sizeable fields close to the surface<sup>23</sup>, the magnitude of which depends also on the x,y position within the surface unit cell as well as on roughness<sup>24,25</sup>. In order to address this point, we have carried out a model calculation of the dipolar field produced by a (100) Ni surface layer made of 2100 by 2100 atoms. The effects of roughness are included by simulating second layer islands of 10 to 20 nm lateral size. A diagram of the simulated Ni surface is shown in Fig. S5 (a). A TbPc<sub>2</sub> molecule is shown to scale with the Ni lattice constant. The



FIG. 5: (a) Schematic of the Ni surface employed in the calculations of the dipolar field  $(B_{dip})$ . Dark blue areas indicate second layer Ni islands, blue dots the position of Ni atoms. (b)  $B_{dip}$  as a function of z calculated for a single Ni layer with OP magnetization and lattice spacing pseudomorphic to Cu(100). (c)  $B_{dip}$  as a function of x calculated along the red line shown in (a) for OP Ni. (d)  $B_{dip}$  as a function of z calculated for a single Ni layer with IP magnetization and lattice spacing pseudomorphic to Ag(100). (c)  $B_{dip}$  as a function of x calculated along the red line shown in (a) for IP Ni.

distance between the Pc ligand and the topmost Ni atoms is taken to be 2.5 Å from density functional calculations of metal-Pc adsorbed on metal surfaces<sup>26,27</sup>, whereas the distance between the bottom and top Pc ligand is taken from Ref. 6. The number of atoms in the simulation is such that the results can be considered accurate: for instance, adding an additional bottom layer would not change significantly the value of the dipolar field on the surface, due to the exponential decrease of the field with z.

The calculations were done by adding dipolar fields from individual dipoles, giving a resultant field

$$\mathbf{B}_{dip} = \frac{\mu_0}{4\pi} \sum_i \left( 3 \frac{(\mu \cdot \mathbf{r}_i) \mathbf{r}_i}{r_i^5} - \frac{\mu}{r_i^3} \right),\tag{1}$$

where  $\mathbf{r}_i$  is the position of the i-th atom, and  $\mu$  its magnetic moment. For the calculation, we take  $\mu = 1 \mu_B$  to provide a "worse case" estimate of  $B_{dip}$ , given that the magnetic moment of Ni surface atoms is about 0.7  $\mu_B$ . The calculations were performed for Ni atoms with out-of-plane (OP) magnetization and Cu(100) lattice spacing [Fig. S5 (b) and (c)] as well as for Ni atoms with in-plane (IP) magnetization and Ag(100) lattice spacing [Fig. S5 (d) and (e)]. Figures S5 (b) and (d) show that  $B_{dip}$  decreases exponentially with increasing distance from a homogenous Ni layer, reaching values well below 0.01 T for z > 2 Å . Oscillations of  $B_{dip}$  moving in the xy plane from on-top to hollow sites are already very small at this distance. Figures S5 (c) and (e) report  $B_{dip}$  calculated at z = 4.45 Å above the Ni surface plane, along the red line shown in (a). The effects of roughness are most visible at the edges of the islands, where  $B_{dip}$  attains a maximum value of about 0.07 T on both OP and IP surfaces. This is still very small compared to the exchange fields evidenced by our study. Moreover,  $B_{dip}$  changes sign for molecules on top or between islands, resulting in an average field below 0.002 T. Since our XMCD measurements are sensitive to macroscopic surface areas of the order of  $0.1 \times 1 \text{ mm}^2$ , dipolar fields can have only a very small influence on the magnetic properties of TbPc<sub>2</sub> on Ni. We therefore conclude that the antiferromagnetic coupling of TbPc<sub>2</sub> on Ni is due to exchange forces.

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