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## Surface confinement of TbPc<sub>2</sub>-SMMs: structural, electronic and magnetic properties

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Since 2003, terbium(III) bis-phthalocyaninato complexes have been recognised as acting as single molecule magnets (SMMs), propitiating multiple studies with the aim of better understanding the single metal ion based magnetism with unusually high blocking temperatures. In the quest for novel applications, it became clear that if spintronic devices were made from SMM molecules, their confinement in the proximity of surfaces or electrodes would become difficult to circumvent. In this perspective article, we highlight the influence of the presence of different substrates on the magnetic performance of TbPc<sub>2</sub>-SMMs, in principle caused by, among other effects, electronic hybridization, dipole–dipole coupling and changing quantum tunnelling (QT) rates on the surface. We show that the improved comprehension of how SMMs interact and communicate with the environment finally leads to magnetic remanence and lower tunnelling rates, paving the way to novel classes of spintronic devices.

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### Introduction

Molecular spintronics have set a new scenario for the technology industry, where current materials are approaching the molecular level. Molecules offer the advantage of being prepared *via* a wide range of combinations, with the products having the exact characteristics. Many molecular systems have been proposed as candidates for molecular spintronics; however, amongst them, single molecule magnets (SMMs) show promising properties for acting as elementary units, given that these molecules exhibit magnetic hysteresis purely at the molecular level.<sup>1</sup>

Broadly speaking, the SMM family can be classified into transition metal- and lanthanide-containing systems, the latter being more attractive for technological applications, due to blocking of the magnetisation at the single ion level.<sup>2</sup> The first observation of such behaviour in lanthanide-based molecules

was achieved in double decker lanthanide phthalocyanine complexes in seminal work reported by Ishikawa and co-workers in 2003.<sup>2</sup> Since then, many other lanthanide-based SMMs have been reported,<sup>3</sup> with wider hysteretic loops and energy barriers up to two orders of magnitude higher than those observed in the 3d-counterparts.<sup>3,4</sup> Obviously, the subsequent unavoidable step towards the implementation of SMMs in molecular-based magneto-electronic devices is directly associated with their confinement on surfaces (Fig. 1).<sup>5</sup>

In contrast, just few of the many SMM candidates have been successfully deposited on surfaces, mainly due to their chemical instability<sup>6</sup> and their lack of physical integrity once deposited on surfaces. Interestingly, the lanthanide phthalocyanine complexes continue to play a key role in molecular spintronics research, due to their extraordinary robustness. More precisely, the uncharged TbPc<sub>2</sub> complex has been extensively studied for its neutral characteristics that allow its sublimation on a wide range of surfaces (*vide infra*).

For the successful implementation of these molecular units in devices, a thorough understanding must be achieved. In this regard, the bulk magnetic properties of lanthanide SMMs have been probed by an extensive range of spectroscopic<sup>7</sup> and magnetic techniques,<sup>8</sup> affording reasonable understanding of the bulk magnetic properties. Conversely, deposition of SMMs on surfaces represents a totally new challenge, given that although reducing intermolecular interactions and crystal packing effects, on-surface–SMM behaviour can cause distortion of the crystal field around the metal centre(s), leading to different magnetic behaviours, up to total quenching of the magnetic properties. Moreover, surface–molecule contact can

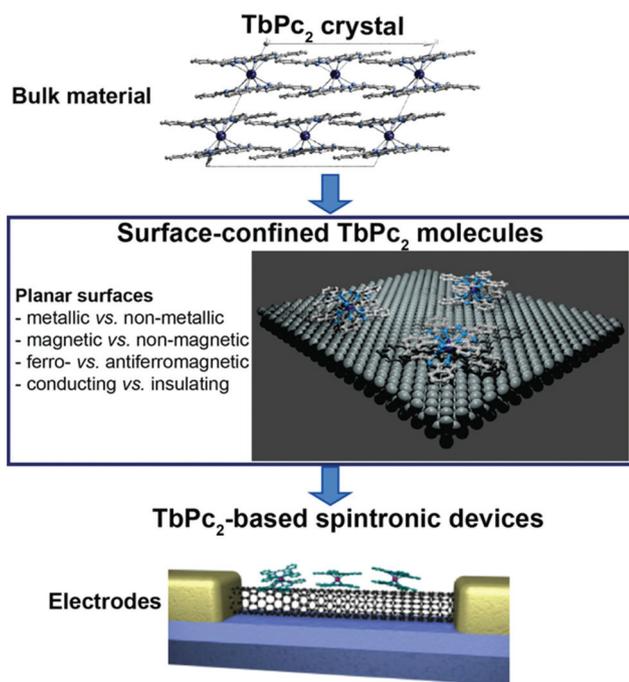
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**Fig. 1** From the bulk to the spintronic devices: the pivotal role of surface confinement in the exploitation of the magnetic properties of terbium(III) bis-phthalocyaninato (TbPc<sub>2</sub>) single molecule magnets.

introduce further interactions that need to be understood for successful application in hybrid molecular devices, *e.g.*, factors affecting the quantum tunnelling of the magnetisation and hysteresis loops at the surface level.

It is the scope of this perspective article to present the reader with an overview of the physical and magnetic properties of the very well-known TbPc<sub>2</sub> on different substrates, showing more precisely how surface-TbPc<sub>2</sub> interactions can affect the magnetic hysteresis, as well as providing some insight into the understanding of TbPc<sub>2</sub>-surface behaviour gained hitherto.

## Structure and bulk magnetism of [TbPc<sub>2</sub>]<sup>±,0</sup>

Before proceeding with our account, a brief description of the magnetic and structural characteristics of [TbPc<sub>2</sub>]<sup>±,0</sup> will be given. Along with the well-known {Mn<sub>12</sub>}<sup>9</sup> and {Fe<sub>4</sub>}<sup>6a,b</sup> complexes, [TbPc<sub>2</sub>]<sup>±,0</sup> stands as one of the most studied SMM. The discovery of the energy barrier to the relaxation of the magnetisation ( $U_{\text{eff}}$ ), at the single ion level in the TBA[LnPc<sub>2</sub>] complex (TBA = tetrabutylammonium and Ln = Tb<sup>3+</sup> and Dy<sup>3+</sup>) was realised by Ishikawa *et al.* in 2003.<sup>2a</sup> Interestingly, the terbium analogue showed the most astonishing properties.

Structurally, [TbPc<sub>2</sub>]<sup>-</sup> features a central Tb<sup>3+</sup> octa-coordinated ion sandwiched between two phthalocyanines aligned in parallel, with a skew angle between the Pc-ligands close to 45°, leading to a square-antiprismatic ( $D_{4d}$ ) coordination geometry (Fig. 2a and b). NMR and SQUID studies conducted by Ishikawa and co-workers showed a large energy separation of *ca.* 600 K between the ground state and the first excited state for the Tb<sup>3+</sup> analogue (Fig. 2c).<sup>2b</sup> The low-lying electronic structure of the TBA[TbPc<sub>2</sub>] indicates a highly axial ground state with  $m_J = \pm 6$ , the maximum possible for the Tb<sup>3+</sup>



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ion ( ${}^7F_6$ ). Subsequently, alternating-current (AC) magnetic susceptibility measurements revealed a frequency dependence of the magnetic behaviour, characteristic of SMMs. The magnetic features of TBA[TbPc<sub>2</sub>] showed an out-of-phase maximum in the  $\chi''(T)$  at 40 K (1 kHz), later corroborated by studies of the magnetically diluted material (Fig. 2d), where intermolecular effects are reduced, revealing solely the molecular magnetic properties.<sup>2a</sup> Moreover, the authors reported the observation of magnetic hysteresis in diluted samples at 1.7 K,<sup>2d</sup> later confirmed by  $\mu$ -SQUID studies. Interestingly,  $\mu$ -SQUID data showed not just the butterfly-shaped hysteretic curves, but also quantum tunnelling steps triggered by the hyperfine interaction between the  $m_J$  states ( $\pm 6$ ) of the Tb<sup>3+</sup> ion with the nuclear spin ( $I = 3/2$ ) (Fig. 2e–g).<sup>2c</sup>

Furthermore, it has been shown that it is also possible to modify the crystal field of the negative complex by either oxidation, which leads to the neutral TbPc<sub>2</sub>, with an improved  $U_{\text{eff}}$  associated with a  $\pi$ -radical ( $S = 1/2$ ) delocalised over the Pc ligands and the  $J = 6$  ground state of the Tb<sup>3+</sup> ion, or enhancement by peripheral substitution of Pc groups or oxidation.<sup>10</sup>

The neutral TbPc<sub>2</sub> analogue is the subject of this perspective article, given that it can be deposited on surfaces employing a variety of deposition techniques, allowing extensive studies by the research community.

## Deposition of TbPc<sub>2</sub> on non-magnetic metallic substrates

Deposition of TbPc<sub>2</sub> on a number of substrates has been achieved, since it withstands vacuums and temperature conditions needed for the sublimation of clean, uniform monolayers, without affecting its structural nature. In the following sections, the structural and magnetic properties of TbPc<sub>2</sub> deposited on metallic and non-magnetic surfaces will be surveyed, with the goal of identifying the boundary conditions favourable for the constitution of molecular spintronic devices.

The structural integrity of the neutral TbPc<sub>2</sub> was firstly described in 2008 by Vitali *et al.* after depositing the molecule onto the Cu(111) surface under ultrahigh vacuum (UHV), employing a dry-imprinting technique.<sup>11</sup> Discrete molecules and aggregates were obtained. The sample was characterised *via* Scanning Tunnelling Microscopy (STM) at 10 K. Analysis of the STM topographic images and conductance maps of an isolated TbPc<sub>2</sub> molecule onto the Cu(111) surface showed that the molecule lays flat on the Cu(111) surface, being totally independent of the hexagonal lattice of the substrate. Two phthalocyanines were distinguished with a skew angle  $\theta$  of  $\sim 45^\circ$ ,



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**Masahiro Yamashita**

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leading to an 8-fold symmetry pattern, in agreement with the crystal structure of the TbPc<sub>2</sub>.<sup>2</sup> The height of the TbPc<sub>2</sub> on the surface was shown to be close to 3 Å, as observed for the Pc...Pc height in the bulk (Fig. 3).

The results clearly indicated that the TbPc<sub>2</sub> molecule was very robust, withstanding ultrahigh vacuums; however, a major question emerged after the confirmation of the structural integrity of TbPc<sub>2</sub> on Cu(111), and it was whether surface–molecule interactions could hinder, preclude, or even improve its magnetic properties. Vitali and co-workers addressed this question through Scanning Tunnelling Spectroscopy (STS) studies, along with Density Functional Theory (DFT). Qualitative insight into the electronic and magnetic properties of the system was gained after comparison of (i) the dI/dV spectrum of the on-surface TbPc<sub>2</sub>, where two major peaks were present, (ii) the calculated dI/dV spectrum of an isolated neutral TbPc<sub>2</sub>, (iii) an isolated negatively charged [TbPc<sub>2</sub>]<sup>−</sup> and (iv) a fictitious TbPc<sub>2</sub> deposited on Cu(111). Analysis of the experimentally determined electronic states of the deposited neutral compound showed that the anionic system ([TbPc<sub>2</sub>]<sup>−</sup>) was formed on Cu(111). Moreover, the spin-resolved electronic states of a model TbPc<sub>2</sub> deposited on a Cu(111) surface, assuming very strong surface–molecule interactions, were computed. The strong interaction showed hybridization of the delocalised unpaired electrons of the ligands and the surface, suppressing the radical character of the ligands, but showing no net effect on the large magnetic

moment of the Tb<sup>3+</sup>. Comparison of the experimental energy resolved conductance maps of the TbPc<sub>2</sub> on Cu(111) with the computed maps of [TbPc<sub>2</sub>]<sup>−</sup> supported this picture (Fig. 3b and c). Remarkably, despite the strong hybridization, no effect on the magnetism of the 4f states of the Tb<sup>3+</sup> ion was observed.

Further proofs of the magnetic properties of the on-surface TbPc<sub>2</sub> were later provided by Stepanow and co-workers, through the element sensitive X-ray Magnetic Circular Dichroism (XMCD)<sup>12</sup> on isolated TbPc<sub>2</sub> deposited on Cu(100).<sup>13</sup> For this study, Cu(100) was chosen because of its strong molecule–substrate interactions, which prevented the formation of agglomerates commonly observed in Cu(111).<sup>14</sup> XMCD measurements allowed the determination of the orbital and spin magnetic moments separately, therefore yielding direct access to the anisotropic behaviour of TbPc<sub>2</sub>. The data acquisition of the X-ray absorption spectra (XAS) at the terbium edge (M<sub>4,5</sub>) comprised the temperature range between 300 and 8 K, in magnetic fields up to 5 T, using right (I<sup>+</sup>) and left (I<sup>−</sup>) circularly polarised light. Excellent agreement between the XAS line shape of the theoretical Tb<sup>3+</sup> 4f<sup>8</sup> configuration (with J = 6 ground state, L = 3; S = 3) and the experimental data was found. Moreover, the XMCD (I<sup>−</sup> − I<sup>+</sup>) intensity at 8 K and 5 T, along with the M<sub>4,5</sub> XMCD branching ratio suggested the presence of a large orbital moment, as expected for Tb<sup>3+</sup>. These experiments revealed the strong Ising-like properties of the surface-confined TbPc<sub>2</sub>, suggesting the full spin magnetic moment expected for a J = 6 ground state along the easy axis, and vanishing magnetisation in the hard Pc plane (Fig. 3d). X-ray natural linear dichroism (XNLD) measurements also confirmed the flat orientation of the molecules on the surface, pinpointing that the molecules were highly oriented and the 4f shell was subjected to strong crystal field effects (Fig. 3d). In this study, despite the strong anisotropic character of the on-surface molecule, no magnetic hysteresis was detected down to 8 K.<sup>13</sup> This fact was attributed to the measurement timescale being up to 7 orders of magnitude larger than measurements based on AC susceptibility.

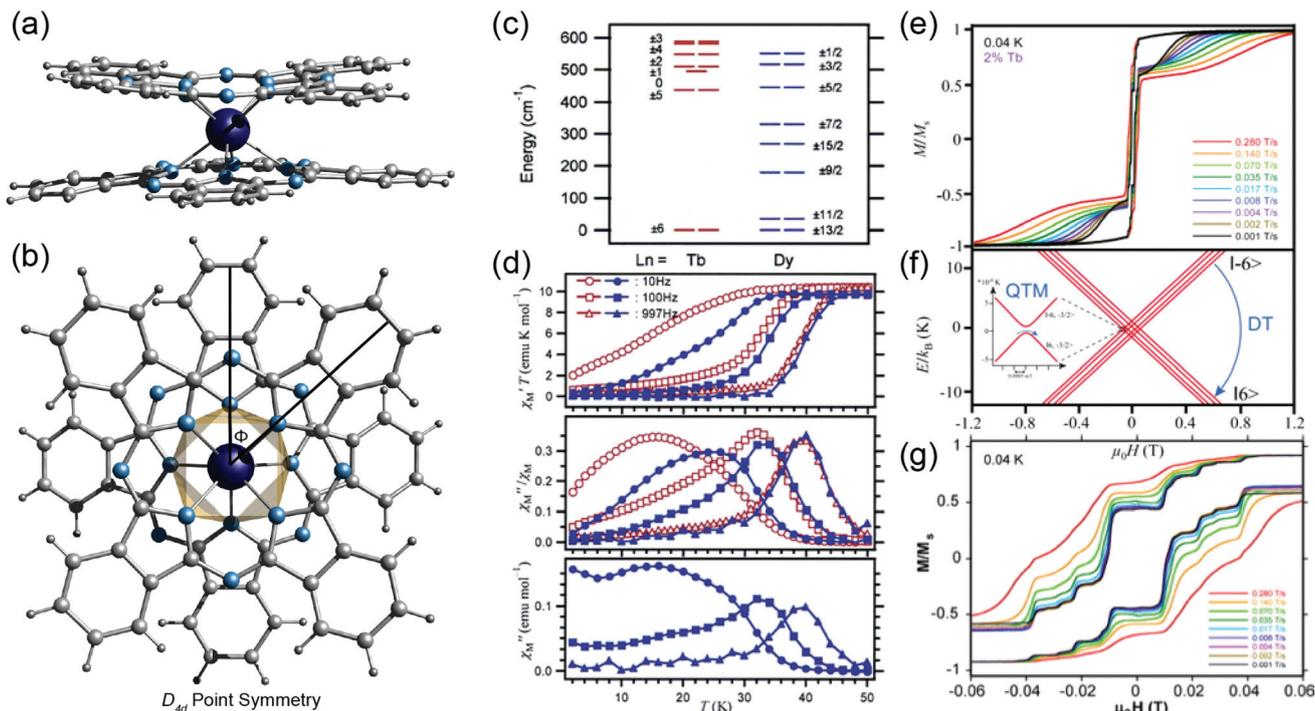
As earlier described, TbPc<sub>2</sub> can be successfully deposited onto Cu(100), preserving both the structural integrity and the magnetic properties associated with the Tb<sup>3+</sup> ion; despite this, no hysteresis was observed, which is an important requirement for data storage applications, and quantum computing.<sup>15</sup> In the quest for such properties Margheriti *et al.* explored the magnetic behaviour of the TbPc<sub>2</sub>, employing the XMCD technique.<sup>16</sup> The studies were conducted on a thick film of TbPc<sub>2</sub> deposited on aluminium foil, under UHV conditions. Thin films were also prepared, depositing TbPc<sub>2</sub> onto a Au(111) substrate. The on-surface samples were characterised using time-of-flight secondary ion mass spectrometry (ToF-SIMS), corroborating that TbPc<sub>2</sub> was intact on the surface. A strong dichroic signal was found in the TbPc<sub>2</sub>(200 nm)/Al sample in the XNLD measurements, highlighting a preferential orientation of the TbPc<sub>2</sub> on the films. The authors determined that TbPc<sub>2</sub> was arranged in a flat configuration when deposited onto Au(111) (as thin film) (Fig. 4b and inset Fig. 4a), while



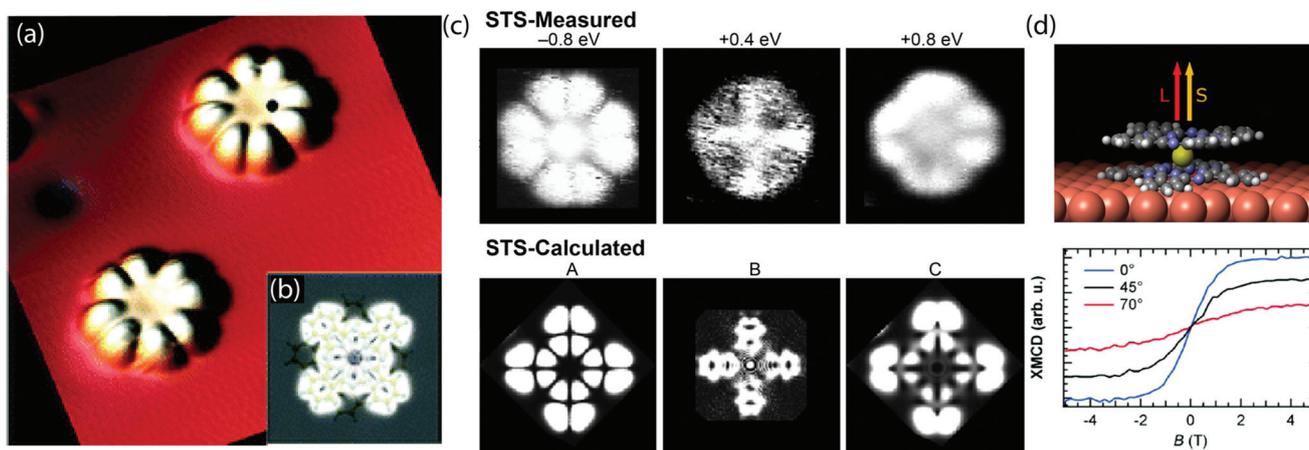
**Mario Ruben**

*Mario Ruben obtained his PhD in CO<sub>2</sub> chemistry in 1998 from the University of Jena, Germany, under the supervision of Prof. D. Walther. During a DAAD post-doctoral fellowship, he worked in Prof. J.-M. Lehn's research group at the ISIS-ULP in Strasbourg, France. 2001 he moved to the Institute of Nanotechnology in Karlsruhe, Germany. In addition, he accepted in 2010 a position as Professor Conventionné at the*

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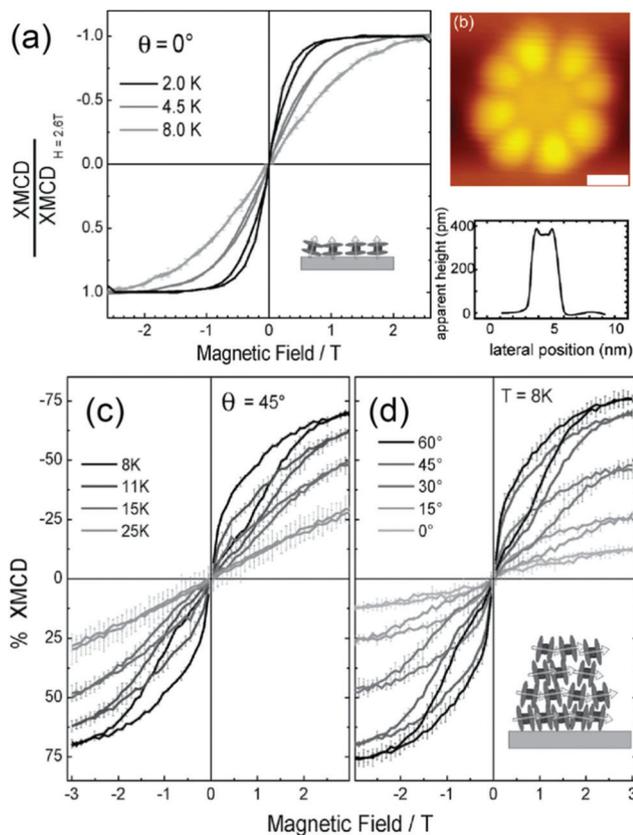
**Fig. 2** Crystal structure of  $[\text{TbPc}_2]^{\pm/0}$  (a) side and (b) top view. Panel b shows the polyhedral representation of the  $\text{TbN}_8$  coordination environment with  $D_{4d}$ -square-antiprismatic coordination geometry. Colour code: H, dark grey; C, grey; N, cyan; Tb, dark blue. The TBA counter ion was omitted for clarity. (c) Energy diagram for  $\text{TBA}[\text{LnPc}_2]$  ( $\text{Ln} = \text{Tb}^{3+}$  and  $\text{Dy}^{3+}$ ) determined by Ishikawa (note the large separation between the ground and first excited state for  $\text{Tb}^{3+}$ ). (d) Dynamic magnetic behaviour of the  $\text{TBA}[\text{TbPc}_2]$  neat sample (open symbols) and sample diluted in  $\text{TBA}[\text{YPc}_2]$  (filled symbols), at zero DC field and an oscillating field of 3.5 G at varied frequencies. (e) Reported hysteresis loops for a single crystal of diluted  $\text{TBA}[\text{Tb}_{0.02}\text{Y}_{0.98}\text{Pc}_2]$  at different scan rates collected at  $T = 40$  mK, with the field applied along the easy axes of the magnetisation. (f) Schematic representation of the magnetic ground state  $J = 6$ , split into four states with hyperfine interactions with the nuclear spin  $I = 3/2$ , with quantum tunnelling of magnetisation (QTM) at low fields and direct tunnelling (DT) at higher fields, as the two dominating tunnelling mechanisms. (g) Enlargement of the region around zero field, exhibiting steps due to the QTM. Adapted with permission from ref. 2.



**Fig. 3** (a) Topographic image at constant current of two isolated  $\text{TbPc}_2$  molecules on  $\text{Cu}(111)$  surface. (b) STM simulation image of an isolated  $\text{TbPc}_2$  molecule. (c) Experimental (top) and calculated (bottom) energy-resolved charge densities. (d) Schematic representation of  $\text{TbPc}_2$  on  $\text{Cu}(111)$  with the spin ( $S$ ) and angular momentum ( $L$ ) (top); magnetisation curves obtained from the  $\text{Tb} M_5$  XMCD intensity for  $\text{TbPc}_2$  on  $\text{Cu}(100)$  at  $T = 8$  K (bottom). Adapted with permission from ref. 11 and 13.

when deposited on Al foil (as thick film), the magnetic axes of the  $\text{TbPc}_2$  were arranged in perpendicular fashion (standing configuration) (inset Fig. 4d).

The intensity of the XMCD spectra of the thick film confirmed the XNLD results; the molecules on the Al surface were organised in standing configuration. Conversely, the XMCD of



**Fig. 4** (a) XMCD data for a TbPc<sub>2</sub> monolayer on Au(111) (thin film). (b) STM topographic image (top) and cross-sectional view of TbPc<sub>2</sub> deposited on Au(111) (bottom). (c) XMCD hysteresis loops of TbPc<sub>2</sub> deposited on Al foil (thick film). Insets in panels a and d represent the orientation of TbPc<sub>2</sub> molecules and their easy axes of magnetisation in the films; from ref. 16 and 17.

the thin film confirmed that TbPc<sub>2</sub> lays flat on the surface. Comparing the normalised XMCD intensity of thick and thin films at  $\theta = 45^\circ$ , it could be seen that in the thick film, a number of TbPc<sub>2</sub> maintained the hard axes parallel to the magnetic field.

Element sensitive hysteresis loops were collected for thin and thick samples. TbPc<sub>2</sub> deposited on Al showed the most interesting magnetic behaviour and as such, the temperature dependence was further studied, revealing butterfly-like hysteresis loops, featuring strong quantum tunnelling near zero field (Fig. 4c and d), with blocking temperature higher than observed in the bulk sample. In contrast, the thin film showed no measurable hysteresis loops under similar conditions. Experiments realised using lower temperatures revealed just a very small opening of the loops on the thin film (Fig. 4a).

The authors hypothesised that the differences in the hysteresis loops could be attributed to surface–molecule interactions. It can certainly be seen that stronger surface–TbPc<sub>2</sub> interactions could be expected when the molecule lays flat on the surface, compared to the standing configuration observed when deposited on Al foil. Contrary to the Cu(100) case (8 K), a small opening of the hysteresis loop is observed when TbPc<sub>2</sub> is

deposited on Au(111) at 2 K. Despite this, a comparison of the surface–molecule interaction strength of Cu(100) and Au(111) cannot be established, due to the different temperatures employed during the XMCD data collection.

Additionally, LnPc<sub>2</sub> analogues (Ln = Y<sup>3+</sup>, Dy<sup>3+</sup> and Tb<sup>3+</sup>) have been successfully deposited on Au(111) by Katoh *et al.*, where they studied their physical properties and their possible applicability as Field Effect Transistors (FET).<sup>17</sup> In the study, the deposition of LnPc<sub>2</sub> on Au(111) was achieved by sublimation of the pure material, heated at 600 K on the Au(111) substrate. Contrary to the results obtained on the Cu(111) surface,<sup>11</sup> STM topographic images revealed two types of molecules with four- and eight-lobed motifs, in a MPc<sub>2</sub>/MPc ratio of 4 : 1. The Pc ligands were found to be parallel to the normal of the Au(111) surface. The eight lobe pattern was consistent with that observed for TbPc<sub>2</sub> on copper surfaces, while the four-lobe structures were assigned to LnPc bricks that lost one Pc ligand. This result shows that during the deposition *via* sublimation, careful temperature conditions for both the TbPc<sub>2</sub> sample and substrate are of utmost importance to guarantee the integrity of the TbPc<sub>2</sub> molecules.<sup>18</sup> Nevertheless, alternative deposition techniques, such as electro spray deposition or brush stamping, have proven that decomposition of TbPc<sub>2</sub> SMMs can be completely avoided on metallic surfaces, leading to even larger extended monolayer assemblies.<sup>11,14</sup>

Remarkably, further studies of TbPc<sub>2</sub> on Au(111) by Komeda *et al.* showed the controlled manipulation of the Kondo peak, associated with  $S = 1/2$ , delocalised over the Pc ligands, through systematic rotation of the Pc groups.<sup>19</sup> In a similar approach, Fu *et al.* demonstrated that upon STM manipulation of TbPc<sub>2</sub> deposited on an Ir(111) sample, the chirality of the molecule can be directly addressed,<sup>20</sup> both schemes highlighting the possibility for the implementation of TbPc<sub>2</sub> in information coding at the molecular level.

## Deposition of TbPc<sub>2</sub> on magnetic metallic substrates

XMCD analysis of TbPc<sub>2</sub> deposited on Cu(100) showed no hysteresis, while hysteresis loops up to  $T = 15$  K were observed in a multilayer TbPc<sub>2</sub> deposited on Al substrate, where the TbPc<sub>2</sub> was organised in an on-edge, standing fashion. Studies of a monolayer of TbPc<sub>2</sub> however, exhibited a very shallow opening at  $T = 2$  K, demonstrating that the magnetic moment was highly perturbed upon on-surface absorption.<sup>13</sup>

In this context, it has been proposed that deposition of TbPc<sub>2</sub> on magnetic metallic surfaces could help to stabilise the TbPc<sub>2</sub> magnetic moment, diminishing undesired thermal fluctuations.<sup>21</sup> Moreover, the understanding of the electronic/magnetic properties of the molecule when interacting with magnetic interfaces is of utmost importance for the development of the molecular electronic field. In the following sections, we will show how the electronic and magnetic properties of TbPc<sub>2</sub> are modified upon absorption on a variety of ferro- and anti-ferromagnetic substrates.

## Coupling to ferromagnetic substrates

It has been shown that the stabilisation against spin fluctuation of paramagnetic molecules can be achieved through the deposition of phthalocyanine/porphyrin-based molecules onto ferromagnetic substrates, taking advantage of the planar arrangement of these molecules on the surface, and the inherent close proximity between the metal ions and the ferromagnetic substrate.<sup>21</sup> The interaction in such systems has been found to be through the superexchange and direct exchange mechanisms.<sup>21</sup> Besides reducing the spin fluctuation and the study of the underlying physical properties of the hybrid system, the deposition of molecular species onto ferromagnetic thin films also opens the possibility for heterostructures that could be employed at higher temperatures. Interestingly, it was shown recently that molecule–substrate interactions are highly mutual, *i.e.* the deposition of the Mn-phthalocyanine molecules also changes the magnetic properties of the underlying ferromagnetic substrate considerably, through an exchange bias mechanism.<sup>22</sup>

The unpaired electron delocalised on the Pc ligands ( $S = 1/2$ ) in the TbPc<sub>2</sub> plays an important role in the on/off states achieved upon STM manipulation of the Pc ligands, as realised by Komeda *et al.* on Au(111).<sup>19</sup> However, absorption of TbPc<sub>2</sub> on ferromagnetic substrates might lead to total suppression of the spin character of the radical, due to the non-innocent surface–SMM interactions. Schwöbel *et al.* suggested the possible observation of the spin of the Pc through spin-polarised STM (SP-STM), given that the single occupied molecular orbital (SOMO) of the TbPc<sub>2</sub> unit is also the lowest unoccupied molecular orbital (LUMO), allowing its observation below and above the Fermi level, having opposite spin character.<sup>23</sup> Individual, well separated TbPc<sub>2</sub> molecules were deposited under UHV conditions onto cobalt islands on Ir(111). Molecule–substrate interactions appear to be similar in Cu(100) and the ferromagnetic Co substrate, where the formation of aggregates is not prompted.<sup>13,14</sup> Point spectroscopy allowed the investigation of the spin-averaged structure of the TbPc<sub>2</sub>, resulting in two main peaks in the spin-averaged differential tunnelling conductance ( $dI/dU$ )/( $I/U$ ) at  $U = -0.9$  V and  $+1.3$  V, attributed to the HOMO and LUMO, respectively. The topographs showed the common eight-lobe structure, characteristic of the  $\pi$ -orbital of the upper phthalocyanines groups (Fig. 5).

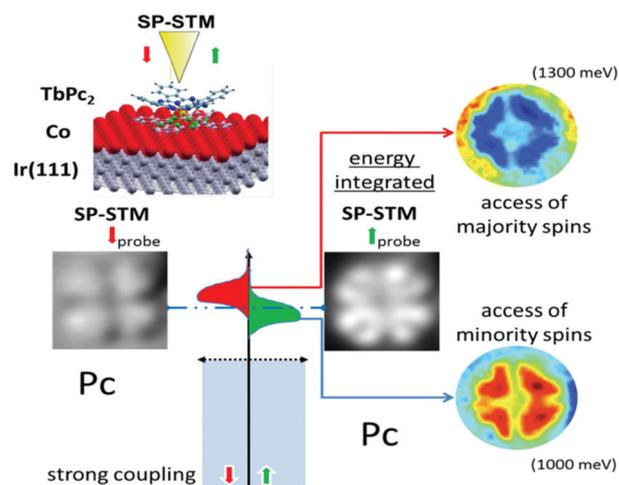
Spin-resolved measurements, where the tungsten tip of the STM was coated with a ferromagnetic material, thus increasing the spin sensitivity, showed that two distinct spin channels can be probed within the TbPc<sub>2</sub>. The two channels were addressed *via* parallel and antiparallel alignment of the STM tip and the ferromagnetic cobalt substrate, upon manipulation of the direction of the external magnetic field of  $\pm 1$  T (Fig. 5).

Two distinct behaviours were observed, where the difference is a measure of the spin polarization of the electron density residing on the Pcs (Fig. 5). This observation could be attributed to “spinterface” effect, in which the interaction of the lower Pc ligand with the ferromagnetic Co-substrate leads

to a spin-dependent shift of the molecular energy levels, dominating the spin polarisation of the resulting tunnel current.<sup>24</sup>

Fig. 5 shows the spin polarised STM images with noticeable distinct contrast for parallel and antiparallel alignment of the STM tip and the Co island, highlighting a spin-dependence of the TbPc<sub>2</sub> molecule, due to the spinterface effect. Constant height-mode measurements support the results, concluding that the ( $S = 1/2$ ) of the Pcs on the Co substrate is quenched, leading to a [TbPc<sub>2</sub>]<sup>-</sup>-like configuration of the complex on the substrate.

Besides the electronic character of the TbPc<sub>2</sub> deposited on the Co substrate, insight into its magnetic properties was pursued through XMCD measurements. The studies were carried out on a TbPc<sub>2</sub> sample deposited on a 10 ML thick Co film, at  $T \approx 10$  K with an external field of  $\pm 6$  T, investigating the magnetisation at the Co edge ( $L_3$ ) and the Tb edge ( $M_5$ ).<sup>25</sup> Unfortunately, Klar *et al.* showed that the data were dominated by a strong paramagnetic signal. Despite the latter issue, an antiferromagnetic interaction of the TbPc<sub>2</sub>/Co interface was visible close to zero field. No hysteresis loop was likewise observed on these measurements. Interestingly, the XMCD study of TbPc<sub>2</sub> on the Co surface conducted by Malavolti *et al.*, down to 2 K and magnetic field of 3.5 T, showed no sizeable magnetic coupling between the TbPc<sub>2</sub> and the Co substrate.<sup>26</sup> This divergence of results may be attributed to differences in the surface preparation (*e.g.* the importance of substrate oxi-



**Fig. 5** Schematic diagram of SP-STM experiments on TbPc<sub>2</sub> on Co/Ir(111) islands (top). To obtain spin sensitivity, the magnetisation direction of the tip is aligned either parallel (green) or antiparallel (red) by applying an external magnetic field of  $B = \pm 1$  T. The Co island nanostructure (red layer) is a hard magnet with a magnetisation that does not rotate with the field applied. Because of the tunnel magnetoresistance effect, the tunnelling current depends on the relative alignment of the tip and sample magnetisation directions. Examples of a spin-resolved measurement: SP-STM topographs (grey, parallel and antiparallel). Differences in maps of spin-resolved differential tunnelling conductance for right (green)  $U = +1.0$  V and left (red)  $U = +1.3$  V, providing maps of the spin polarization of the molecular orbitals. Both orbitals show the same spatial distribution, but have opposite spin polarization. Adapted with permission from ref. 23.

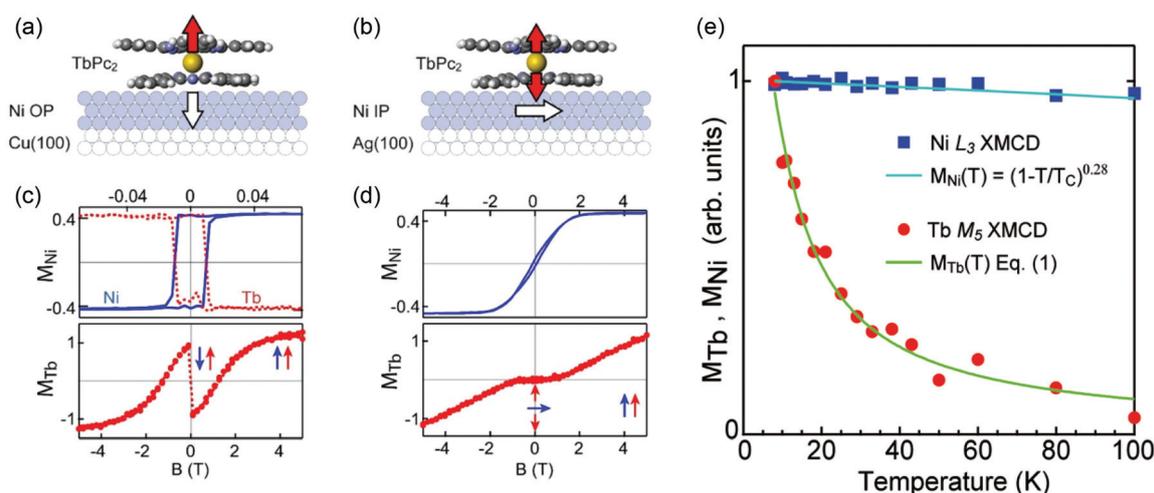
dation, *vide infra*) or molecular deposition<sup>27</sup> and needs further understanding through additional experiments.

Rizzini and co-workers further explored the magnetic coupling between the TbPc<sub>2</sub> deposited on a ferromagnetic nickel substrate, making use of XMCD studies.<sup>28</sup> The easy axis direction of the nickel substrate and the possibility of its controlled directionality through epitaxial strain made nickel an ideal candidate for the investigation. Deposition of the TbPc<sub>2</sub> was achieved *in situ* at ultrahigh vacuum conditions using molecular beam evaporation, producing coverage of  $0.05 \pm 0.02$  ML of TbPc<sub>2</sub>. To study the magnetic properties of the TbPc<sub>2</sub>/Ni interface, two magnetically different Ni films were used: (i) an out-of-plane magnetic anisotropy Ni film (OP) and (ii) an in-plane magnetic anisotropy Ni film (IP). The OP Ni film was prepared by depositing Ni onto Cu(100), whereas the IP Ni film was obtained by deposition of Ni on Ag(100) (Fig. 6a and b).

Firstly, Rizzini and co-workers investigated the interaction between the TbPc<sub>2</sub> SMM and the OP Ni film, where the easy axes of both substrate and sample were parallel, by probing the Ni (L<sub>2,3</sub>) and Tb (M<sub>4,5</sub>) edges using XAS and XMCD techniques at 8 K. A strong remanent magnetisation was obtained for both substrate and sample. Interestingly, the XMCD of the Tb/Ni/Cu(100) (OP), revealed that the magnetic moments of the terbium ( $M_{\text{Tb}}$ ) and the nickel ( $M_{\text{Ni}}$ ) substrates were weakly antiferromagnetically coupled. Characterization of the TbPc<sub>2</sub>/Ag(100) (IP) with the field applied with  $\theta = 70^\circ$  to the X-ray direction exhibited a much smaller remanence of the XMCD intensity, but still highlighting the presence of antiferromagnetic interactions. Comparison of the XMCD results of the TbPc<sub>2</sub> on OP and IP nickel films provided evidence that stabilisation of the magnetic moment can be achieved through correct matching of the easy axis of the magnetisation between the SMM and the substrate.

In order to probe the effect of the magnetic coupling into the hysteretic behaviour of the TbPc<sub>2</sub> systems, XMCD hysteresis loops were collected for TbPc<sub>2</sub>/Ni/Cu(100) (OP) and TbPc<sub>2</sub>/Ni/Ag(100) (IP) substrates at  $T = 8$  K. The data were collected at the Ni (L<sub>2,3</sub>) and Tb (M<sub>4,5</sub>) edges, as a function of applied magnetic field. The results are depicted in Fig. 6c and d, where atypical square-like hysteresis loops were obtained. The distinctive butterfly-like hysteresis loop commonly observed in bulk measurements of the TbPc<sub>2</sub> was clearly suppressed.<sup>2c</sup> The shape of the hysteresis was ascribed to the antiparallel alignment of the  $M_{\text{Tb}}$  and  $M_{\text{Ni}}$ , which were very similar to the  $M_{\text{Ni}}$  square loops for  $B < 0.1$  T. Fields larger than 0.1 T rotate the  $M_{\text{Tb}}$ , leading to the parallel alignment of  $M_{\text{Tb}}$  with  $B$ , due to the continued increase in the Zeeman energy until it becomes stronger than the antiferromagnetic interaction. In an independent control experiment, the presence of remanent magnetisation (up to a temperature of 8 K) could be confirmed; equally attributed to the weak antiferromagnetic coupling to the Ni substrate.<sup>25</sup>

It was found that the exchange coupling was indeed mediated by the Pc group in contact with the substrate, likely occurring *via* electron conduction through the  $\pi$ -orbital of the Pc. Rizzini and co-workers demonstrated that the strength of the interactions can indeed be modified through surface modification, leading to different charge transfer properties. This was achieved by the addition of an electron withdrawing oxygen buffer or an electron donor such as lithium into the surface, thus leading to oxidation or reduction of the Pc ligand in contact with the Ni film. The results showed a reduction of the XMCD/XAS ratio for the TbPc<sub>2</sub>/Li/Ni/Cu(100) interface, in good agreement with modest charge transfer to the 4f orbitals, due to the increased occupancy in the Pc orbitals. The magnetic behaviour was also well affected, with a



**Fig. 6** Schematic view of the TbPc<sub>2</sub> and Ni magnetisation (a) anisotropy axes of TbPc<sub>2</sub> deposited on Ni OP, and (b) anisotropy axes of TbPc<sub>2</sub> deposited on Ni IP. The IP case shows spin frustration. (c) Element-resolved hysteresis loops of Ni-surface-confined TbPc<sub>2</sub> exhibiting weak antiferromagnetic coupling of the collinear molecular spin in the OP (out-of-plane) case for Ni/Cu(100) and (d) the in-plane (IP) Ni/Ag(100) films recorded at remanence,  $T = 8$  K  $\theta = 0^\circ$ . (e) Temperature dependence of the remanent Ni(OP) and Tb XMCD intensities, normalised to the values at  $T = 8$  K, with remaining Tb-remnance at 100 K. Adapted with permission from ref. 28.

noticeable decrease in the remanent  $M_{Tb}$  of the  $TbPc_2/O/Ni/Cu(100)$  layer and a variation of the exchange field  $B_{exc}$  from 0.6 T in the  $TbPc_2/O/Ni/Cu(100)$  structure, to 2.5 T in the  $TbPc_2/Li/Ni/Cu(100)$  layer, clearly denoting that the exchange interaction is greatly increased by electron doping of the Pc orbitals. In contrast, the oxide layer decreases the exchange molecule-metallic surface interaction, a fact showing the importance of clean deposition while working with sensitive metal surfaces.

Finally, the temperature dependent behaviour of the XMCD was studied, leading to the observation of finite remanence of the  $M_{Tb}$ , as high as 100 K (Fig. 6e). The results undoubtedly demonstrated that the interaction of the  $TbPc_2$  with the nickel substrate significantly enhanced the magnetic properties of  $TbPc_2$  at zero field, where 100% remanence is eluded, a result that certainly deserves to be further investigated, in view of the desired higher working temperatures of spintronic devices.

The authors also compared the results for  $TbPc_2$  on the ferromagnetic material and mononuclear porphyrin and phthalocyanine paramagnets on ferromagnetic substrates, revealing that in mononuclear cases, the exchange is ferromagnetic in nature, due to the close proximity of the porphyrin/phthalocyanine metal ion and the ferromagnetic substrates, while in the  $TbPc_2$ , a larger separation favours the antiferromagnetic coupling.

Nistor and co-workers later investigated the magnetic properties of a  $TbPc_2/Fe$  heterostructure by depositing  $TbPc_2$  onto a 4.6 ML Fe film placed on  $Cu(100)$ .<sup>29</sup> In similar fashion to the  $TbPc_2/Ni$  systems, an antiferromagnetic alignment between the  $M_{Tb}$  and  $M_{Fe}$  systems was observed in XMCD loops collected at  $T = 8$  K (Fig. 7a). At  $B = 1.8$  T, it was observed that the  $M_{Tb}$  moments changed signs, overcoming the antiferromagnetic  $TbPc_2/Fe$  interaction, leading to the alignment of the  $M_{Tb}$  with the magnetic field.

The charge transfer effect was also probed by the addition of Li to the  $TbPc_2/Fe/Cu(100)$  heterostructure. Remarkably, the Tb magnetisation changed sign and aligned parallel to the Fe magnetisation in the whole field range, showing a similar profile to that of the Fe substrate, in agreement with ferromagnetic exchange interactions (Fig. 7b).

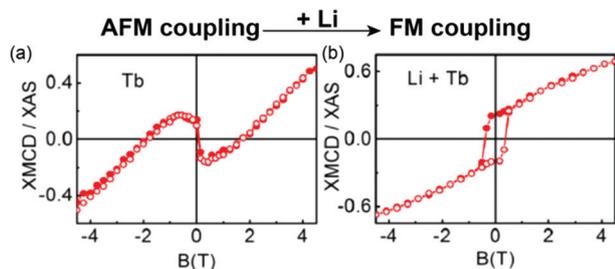


Fig. 7 XMCD Tb magnetisation curves for  $TbPc_2/Fe/Cu(100)$  (a) before and (b) after deposition of Li. The data were taken at  $T = 8$  K at oblique incidence [ $\theta = 73^\circ$  for (a) and  $\theta = 60^\circ$  for (b)], following field cooling in the zero field. Adapted with permission from ref. 29.

## Coupling to antiferromagnetic substrates

The studies previously described highlight that the deposition of  $TbPc_2$  on ferromagnetic substrates leads to a strong enhancement of its magnetic properties, leading to finite remanence of the  $M_{Tb}$ , even at 100 K, undoubtedly representing a great advantage for certain applications where large coercivity fields are required. However, some problems are foreseen: if the magnetisation of the substrates were an order of magnitude higher than the molecular species, and the magnetic moment was tightly connected to the substrate magnetisation, it would become impossible for the independent manipulation of the magnetic moment of the molecule from the substrate. A different alternative for the stabilisation and enhancement of the magnetic behaviour is through the deposition of the SMM onto antiferromagnetic substrates. Several issues with this proposal have been discussed by Rizzini *et al.*;<sup>6d,30</sup> however, the investigation of the  $TbPc_2$  AFM substrate led to some degree of understanding of the magnetic properties of the heterostructures. In the following sections, we will briefly discuss the magnetic properties of  $TbPc_2$  deposited on antiferromagnetic substrates such as CoO, Mn and FeMn.

In the quest for exchange bias effects on  $TbPc_2$  deposited on antiferromagnetic (AFM) substrates, Rizzini and co-workers studied  $TbPc_2$  deposited on a 10 ML thick CoO layer chosen as the substrate, due to its magnetocrystallinity, and the facile tuning of magnetic anisotropy.<sup>30</sup> The surface was prepared *via* molecular beam epitaxy in ultrahigh vacuum, followed by *in situ* deposition of  $TbPc_2$  at UHV conditions. The sample was cooled down to 8 K in an applied field of 5 T, normal to the surface. XAS measurements were then conducted on the Co and Tb edges respectively, with a magnetic field of  $\pm 5$  T applied parallel to the X-ray incidence radiation. As expected, due to the AFM nature of the substrate and very few uncompensated polarised Co spins, a very weak XMCD response was recorded. Conversely, the  $TbPc_2$  XMCD data showed a strong XMCD response after saturation at +5 T. No hysteresis was found in the XMCD loop of the  $Tb^{3+}$  ion, showing no sizeable exchange bias of the heterostructure. Some inflections at  $B = \pm 0.5$  T were observed, consistent with the butterfly-like hysteresis observed on the bulk; notably, they vanish upon charge doping. In light of the results, the authors proceeded to study the thickness dependence of the CoO film, resulting in an unclear indication of exchange bias. These results suggest that the CoO AFM substrate is not suitable for exchange bias molecule-substrate structures, in good agreement with the behaviour observed for the  $TbPc_2/O/Ni/Cu(100)$  heterostructure, where a weaker exchange interaction was found.

The previous results showed that oxygen covered substrates prompted weak molecule-substrate interactions, compared to neat metallic surfaces (*vide supra*). To test whether the same reasoning held for oxygen free AFM structures, the XMCD properties of  $TbPc_2$  deposited on bare Mn were investigated. The sample studied was comprised of 3 ML of Mn film deposited on  $Ag(100)$ . The XMCD of the Mn edge showed an extremely

weak signal (compared to the paramagnetic Mn sample), highlighting the AFM nature of the Mn substrate. Field dependent behaviour of the XMCD intensity was additionally observed, implying uncompensated Mn spins, some of them able to rotate, while others remained pinned to the structure ( $\sim 7\%$ ); the total of uncompensated spins was *ca.* 3%.

Finite hystereses were detected through XMCD experiments of the TbPc<sub>2</sub>/Mn/Ag(100) sample, with a coercivity of  $H_C = 44 \pm 4$  mT, while shifting of  $H_E = -22 \pm 4$  mT was observed for  $M_{Tb}$ , which are signatures of exchange bias. The observations, *e.g.*, sign and shift, are in good agreement with the low field XMCD data shown in Fig. 8.

The authors hypothesised that due to the skewed shaped loop and the small remanence of the  $M_{Tb}$ , only a small fraction of the on-surface TbPc<sub>2</sub> was exchange-coupled to the unpinned spins of the Mn substrate. This is consistent with the small fraction of unpinned spins of the Mn substrate and in contrast to the TbPc<sub>2</sub>/Ni/Cu(100) case, where the square-shaped hysteresis loops indicate that most TbPc<sub>2</sub> molecules were interacting with the Ni substrate. Due to the average detection mode of XMCD over all molecules interacting and not interacting, it could in principle be possible to obtain much larger  $H_E$  and  $H_C$  if the measurements could be conducted solely on interacting TbPc<sub>2</sub>.

A comparative study of TbPc<sub>2</sub> on ferromagnetic and anti-ferromagnetic substrates was conducted by Gambardella's group.<sup>29</sup> The study was performed by employing ferromagnetic Fe and anti-ferromagnetic FeMn substrates. While the description of the former has been previously addressed (*vide supra*), we focus our attention in this section on the anti-ferromagnetic FeMn substrate and its interaction with the TbPc<sub>2</sub>.

Three TbPc<sub>2</sub>/FeMn/Cu(100) samples with different FeMn thicknesses (3, 6 and 8 ML) were prepared by electron beam evaporation of Fe and Mn on Cu(100) substrate at room temperature, while TbPc<sub>2</sub> was sublimed on the surface using a

molecular beam epitaxy cell with a flux rate of  $0.8 \text{ ML min}^{-1}$ . The final TbPc<sub>2</sub> coverage was  $0.6 \pm 0.1 \text{ ML}$ . XAS and XMCD measurements indicated that on the surface, most of the FeMn spins were compensated by parallel alignment of the  $M_{Fe}$  and  $M_{Mn}$  with the external magnetic field. The magnetic moment on the Tb<sup>3+</sup> ions was almost saturated at the experimental temperature and field. All samples showed some hysteretic behaviour, with the more pronounced hysteresis observed in the sample with thickest FeMn coverage *i.e.* TbPc<sub>2</sub>/FeMn(8 ML)/Cu(100), which along with the shift in field, indicated that the anti-ferromagnetic regime was reached.

A coercivity of  $H_C = -10 \pm 1$  mT and a field displacement of  $H_E = 21 \pm 1$  mT were obtained from magnetisation curves of Tb, the effect arising from exchange interactions with the pinned Fe ions on the surface. The results showed that the TbPc<sub>2</sub>/FeMn/Cu(100) exhibited anti-ferromagnetic interactions. Relatively strong TbPc<sub>2</sub>/FeMn substrate interaction can be inferred from the absence of the butterfly-like hysteresis loop and the plateaus in the Tb magnetisation curve.

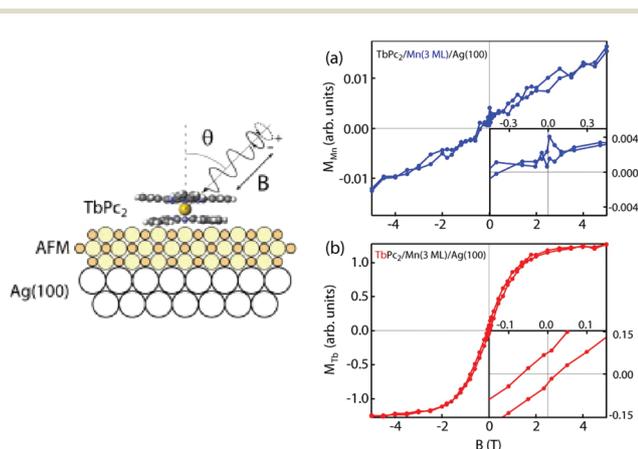
## Grafting TbPc<sub>2</sub> to non-metallic substrates

As shown up to this point, the electronic and magnetic properties of the TbPc<sub>2</sub> SMM are highly affected by the substrate with deposits, due to hybridization with the Pc orbitals, leading to improved magnetic behaviours, as observed in the TbPc<sub>2</sub> on Ni films, or preclusion of the hysteretic magnetic properties of the TbPc<sub>2</sub>, as observed on CoO. In order to observe the inherent magnetic properties of the TbPc<sub>2</sub> at the molecular level, less interacting substrates are envisaged. In this context, grafting of TbPc<sub>2</sub> on highly conjugated carbon containing materials, such as carbon nanotubes (CNT), graphene, highly oriented pyrolytic graphite (HOPG) or insulators, such as SiO<sub>2</sub> and MgO, seems promising. Deposition of TbPc<sub>2</sub> on these substrates would limit the number of electrons migrating between the molecule and surface, therefore allowing the observation of less perturbed magnetic properties of the SMM. Furthermore, several manipulation schemes can be envisaged for a molecule on a sp<sup>2</sup>-carbon substrate, expanding the research interest. Similarly, the exploration of the magnetic properties of TbPc<sub>2</sub> on insulators can shed some light into the type of tunnelling events occurring when the TbPc<sub>2</sub> is in contact with strongly interacting substrates.

### Grafting TbPc<sub>2</sub> to sp<sup>2</sup>-carbon-containing substrates

In this section, the magnetic and electronic properties of TbPc<sub>2</sub> on single-walled carbon nanotubes (SWCNT), graphene and highly oriented pyrolytic graphite (HOPG) are surveyed. The authors have shown that due to the weak TbPc<sub>2</sub>-substrate interactions, a more bulk-like magnetic behaviour is detected, leading to several spintronic proposals for the physical implementation of TbPc<sub>2</sub> in technological applications.

In 2009 Klyatskaya and co-workers firstly explored the magnetic properties of a chemically modified version of the



**Fig. 8** Exchange bias between TbPc<sub>2</sub> and Mn. Magnetisation loops of Mn (a) and Tb (b) measured on TbPc<sub>2</sub>/Mn(3 ML)/Ag(100), after FC at  $\theta = 0^\circ$  and  $B = 5$  T, recorded at  $\theta = 0^\circ$  and  $T = 8$  K. Inset: Details of the low field region. Units refer to the intensity ratio  $2(I^+ - I^-)/(I^+ + I^-)$  measured at the L<sub>3</sub> Mn edge (a) and M<sub>5</sub> Tb edge (b). Ref. 30.

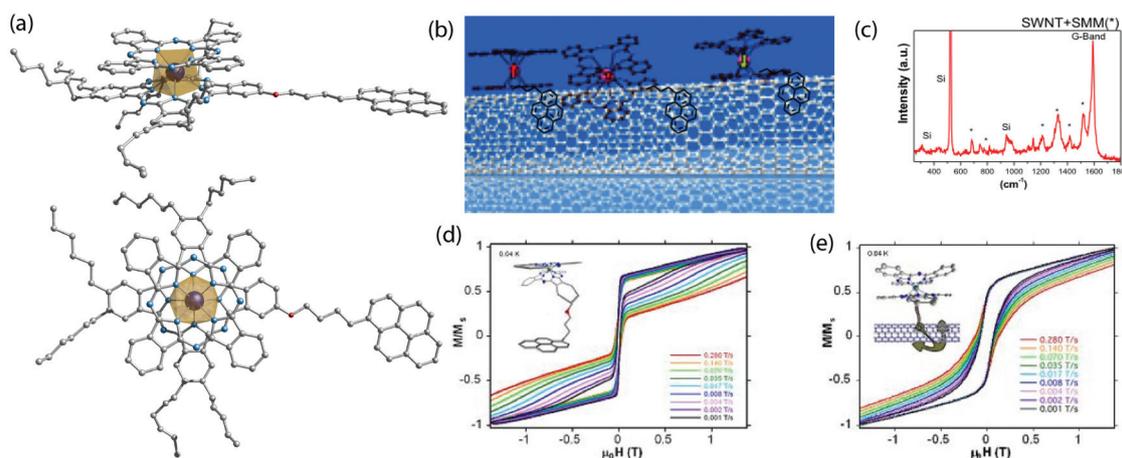
well-known TbPc<sub>2</sub> when attached to single-walled carbon nanotubes (SWCNT) through a range of physical and magnetic techniques.<sup>31</sup> SWCNTs were chosen as substrates, due to their relevance in technological applications and cross-sections analogous to that of the TbPc<sub>2</sub>. In the study, a tailored design version of the TbPc<sub>2</sub> was chemically engineered and synthesised. The molecule was a heteroleptic TbPc<sub>2</sub> molecule, where one of the phthalocyanine ligands was substituted with six hexyl groups and one 4-(4-pyren-1-ylbutoxy) group (from now on, called TbPc<sub>2</sub>\*). It was observed that the hexyl and the pyrene groups show considerable  $\pi$ - $\pi$  stacking in sp<sup>2</sup>-carbon containing materials. The TbPc<sub>2</sub>\* was attached to SWCNT and characterised through a range of surface techniques, revealing that the TbPc<sub>2</sub>\* molecules were grafted to the CNT (Fig. 9).

In order to probe whether the magnetic properties of the SWCNT-SMM hybrid were present, AC susceptibility measurements were conducted, showing a clear maximum in the  $\chi''(T)$  at 45 K (1 kHz) yielding a  $U_{\text{eff}} = 500$  K. Interestingly, the dynamic magnetic behaviour showed an enhancement of the dynamic properties, compared to the diluted TbPc<sub>2</sub> sample. Confirmation of the magnetic properties of the TbPc<sub>2</sub>\* was gained through  $\mu$ -SQUID measurements at 40 mK. As observed in Fig. 9d and e, hysteresis loops were observed at different scan rates, confirming that the magnetic properties of the TbPc<sub>2</sub>\* in the SWCNT-SMM are present. Step-like loops were not detected, due to the smearing effect of the randomly oriented TbPc<sub>2</sub>\* on the SWCNTs.

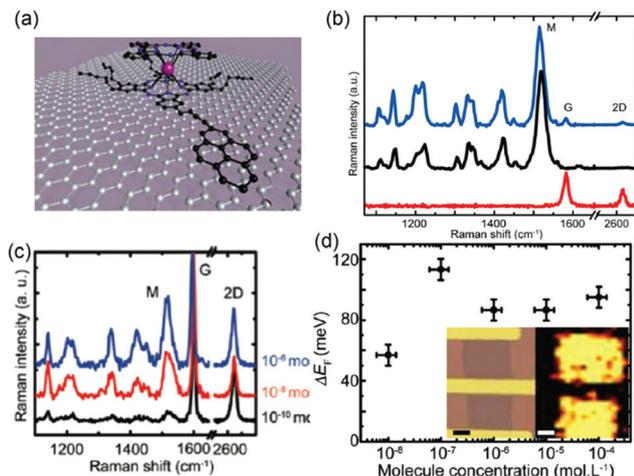
The chemically engineered TbPc<sub>2</sub>\*-SWCNT hybrid has been the subject of a number of state-of-the-art investigations as a molecular spin valve device, leading to the observation of magneto resistivity, strong spin-phonon coupling, Landau-Zener tunnelling, and suppression of quantum tunnelling of magnetisation (QTM).<sup>32</sup>

The intriguingly impressive electrical and mechanical properties of graphene make it a promising material in spintronic,<sup>33</sup> electronic<sup>34</sup> and nanomechanic applications.<sup>35</sup> In light of the behaviour observed for TbPc<sub>2</sub>\* grafted on CNT and the bewildering properties of graphene, it immediately prompted the investigation of the coupled behaviour of the SMM and graphene. For the study, molecular grafting of the TbPc<sub>2</sub>\* through  $\pi$ - $\pi$  stacking was envisioned, which beside the grafting properties of the pyrene and hexyl legs, the anchoring groups additionally mediated indirect coupling as observed on CNT.<sup>32</sup> Atomic force microscopy (AFM) and Raman studies showed that upon grafting, the TbPc<sub>2</sub>\* unit was intact, as well as the graphene substrate (Fig. 10). AFM roughness analysis indicated the formation of molecular clusters formed by less than five molecules at concentrations lower than 10<sup>-5</sup> mol L<sup>-1</sup>, whereas higher concentrations led to the formation of much larger cluster aggregates. A slight shift of the G band of graphene was also observed in Raman spectra, consistent with small interactions of the TbPc<sub>2</sub>\* with the surface.<sup>36</sup>

To obtain more insight regarding the thickness of TbPc<sub>2</sub>\* on graphene and its effect, AFM contact mode and Raman map experiments were conducted, which showed a logarithmic dependence of the Raman intensity of the deposited TbPc<sub>2</sub>\*, in good agreement with the enhancement through molecular variation of the polarizability *via* charge transfer of the substrate. This occurs only in the limit of molecules directly interacting with the graphene substrate; *i.e.*, thicker films would not dramatically enhance the Raman intensity. The authors estimated the enhancement of the SMM signal grafted on graphene to be as low as 10<sup>-10</sup> mol L<sup>-1</sup>. *Ab initio* density functional theory calculations were likewise computed, employing just the pyrene fragment of the TbPc<sub>2</sub>\*, for computational reasons. The results show that the G band of the graphene shifts slightly to lower frequencies, in excellent agreement



**Fig. 9** The TbPc<sub>2</sub>\*-confinement on SWCNTs. (a) Crystal structure of the pyrene-substituted TbPc<sub>2</sub>\*, side and top view. The lower panel shows the polyhedral representation of the TbN<sub>8</sub> coordination environment with  $D_{4d}$ -square-antiprismatic coordination geometry. Colour code: C, grey; N, cyan; Tb, dark blue. Hydrogens were omitted for clarity. (b) Schematic representation of the surface confinement; (d)  $\mu$ -Raman spectra of the SWCNT-SMM hybrid showing the fingerprint of both TbPc<sub>2</sub>\* and the SWCNT. (d)  $\mu$ -SQUID measurements of (left) the TbPc<sub>2</sub>\* bulk and (right) the SWCNT-SMM hybrid exhibiting reduced QT rates at zero field, due to reduced dipole-dipole interactions. Adapted with permission from ref. 31.

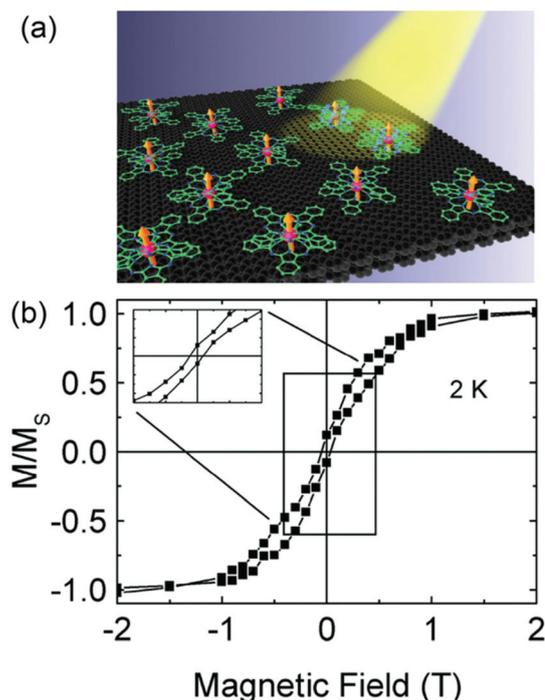


**Fig. 10** (a) Scheme of  $\text{TbPc}_2^*$  grafted to graphene. (b) Raman spectra of the neat graphene (bottom, red),  $\text{TbPc}_2$  powder (middle, black), and  $\text{TbPc}_2$  molecules on graphene (top, blue). The G and 2D modes of graphene and the bands of  $\text{TbPc}_2$  (M) are indicated. (c) Raman spectra of  $\text{TbPc}_2$  molecules deposited on graphene at three concentrations. (d) Concentration dependence of the shift of the Fermi energy relative to the pristine device. Inset: Optical image and Raman intensity map of the M doublet of the device (scale bars 1 m). Adapted with permission from ref. 36.

with the doping-induced change of the Fermi level, indicating that the behaviour comes from just the molecules directly interacting with the graphene substrate (Fig. 10a and b). A molecular spin valve like device was also constructed, based on a contacted graphene- $\text{TbPc}_2^*$  hybrid.<sup>37</sup>

Moreover, the self-assembly and magnetic behaviour of an analogue of  $\text{TbPc}_2$  on highly ordered pyrolytic graphite (HOPG) was first performed by Veciana *et al.* in 2006,<sup>38</sup> and later continued by Gonidec *et al.* in 2011.<sup>39</sup> The subject of investigation was a double decker terbium phthalocyanine complex with formula  $\text{Tb}^{\text{i}}\text{Pc}_2$ , where  $\text{iPc}$  = tetrakis-isopropylidenedioxyphthalocyanine, deposited on the HOPG substrate through the drop casting technique with a  $10^{-6}$  M solution. AFM experiments showed highly regular bar-like island motifs of  $\text{Tb}^{\text{i}}\text{Pc}_2$  on the surface, with regular orientation of *ca.*  $120^\circ$  between the bars, suggesting that the growth of these supramolecular islands occurs along one of the three principal graphite symmetry directions.

In order to probe whether any interaction of the  $\text{Tb}^{\text{i}}\text{Pc}_2$ -HOPG sample could diminish the SMM behaviour, the authors systematically studied the magnetic properties of two different  $\text{Tb}^{\text{i}}\text{Pc}_2$ -HOPG through XMCD spectroscopy: (i) a submonolayer and (ii) thick layer sample, after drop casting  $\text{Tb}^{\text{i}}\text{Pc}_2$  in HOPG. The authors expected a more pronounced and surface dependent XMCD behaviour of the thin layer sample and a more bulk-like behaviour for the multi-layered sample. The hysteresis loops for both samples were obtained at  $\theta = 0$  and  $45^\circ$  grazing angles in relation to the applied magnetic field measured at the  $\text{M}_{4,5}$  Tb edge after magnetizing the samples up to 5 T, followed by demagnetisation. The results



**Fig. 11** (a) Schematic representation of  $\text{TbPc}_2$  grafted to HOPG. (b) XMCD loop of  $\text{TbPc}_2$  on HOPG taken at the Tb  $\text{M}_5$  edge at  $T = 2$  K. Adapted with permission from ref. 40.

showed butterfly-like hysteric loops, with a small remnant magnetisation for both samples, demonstrating that in both cases the magnetic behaviours were very similar and that the  $\text{Tb}^{\text{i}}\text{Pc}_2$ -HOPG interaction had little effect on the surface deposited SMM.

More recently Klar and co-workers reported the hysteric behaviour of  $\text{TbPc}_2$  on HOPG at very low temperatures.<sup>40</sup> Deposition of  $\text{TbPc}_2$  was achieved by *in situ* thermal evaporation of pristine  $\text{TbPc}_2$  on freshly sliced HOPG crystal under UHV conditions. The XAS spectra of Tb was measured at several angles, *i.e.*,  $\theta = 0, 45$  and  $65^\circ$  X-ray angles at  $T = 2$  K and external magnetic field of 6 T, which afforded no XMCD shape change in relation to the angle variation, with only changes in the magnitude of the XMCD signal (Fig. 11).

The field dependent study at 2 K showed that the saturation of the magnetisation was achieved at 1 T, with a well-defined opening of the hysteresis loops with coercive field of *ca.* 50 mT. Remarkably, just a small narrowing, close to  $B = 0$ , was present in the hysteresis, with no closing of the loop at zero field, usually associated with fast QTM, often affording butterfly-like hysteresis. This effect was ascribed to slower quantum tunnelling at this temperature and reduced interaction of  $\text{TbPc}_2$  with the surroundings when deposited on HOPG.

#### **$\text{TbPc}_2$ on insulators**

In the previous section, it was shown that upon deposition of  $\text{TbPc}_2$  on  $\text{sp}^2$ -based substrates the magnetic properties of the SMM were less perturbed, due to the weak coupling between

the substrate and the SMM, leading to the observation of hysteresis with less QTM near zero field. In the HOPG and SWCNT cases, more precisely, through XMCD and conductivity experiments, it was found that reduction of the quantum tunnelling can be achieved, affording less QTM close to zero applied field. In the quest for wider hysteresis loops at higher temperatures, some researchers have recently turned their attention towards insulator materials, such as SiO<sub>2</sub> and MgO, where the substrate can act as a tunnelling barrier. Moreover, the study of TbPc<sub>2</sub> on insulators such as SiO<sub>2</sub>, a high quality electrical insulator and MgO acting as barrier in spin-tunnelling barriers, is of utmost relevance given their technological relevance and applicability in device production. In this section the magnetic properties of TbPc<sub>2</sub> on these two insulator substrates will be surveyed.

Silicon, besides being a well-known electrical insulator, also offers the possibility for doping, which could be employed as a tool for the manipulation of the electronic properties of the deposited sample. As observed, the on-surface Pc group is very susceptible to the electronic properties of the substrates, which in turn is reflected in the magnetic properties of the Tb<sup>3+</sup> ion, due to the coupling between the unpaired  $\pi$ -electrons delocalised over the Pc groups and the  $J = 6$  of the Tb ion, making SiO<sub>2</sub> a very promising substrate for hybrid devices. With this aim in mind and the quest for understanding the magnetic properties of TbPc<sub>2</sub> on the SiO<sub>2</sub> substrate, Mannini *et al.* studied the magnetic properties of an analogue of the TbPc<sub>2</sub> complex through XMCD measurements.<sup>41</sup> The approach consisted of the chemical deposition and grafting of a functionalised TbPc<sub>2</sub>, namely TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub>, which allowed direct Si-C bonds *via* thermal hydrosilylation. Structural characterization of the compound was achieved *via* MALDI-ToF, UV-Visible, X-ray photoelectron spectroscopy (XPS) and NMR techniques, while the bulk magnetic properties were probed through AC magnetometry, all together validating the proposed structure and the SMM character of the sample.

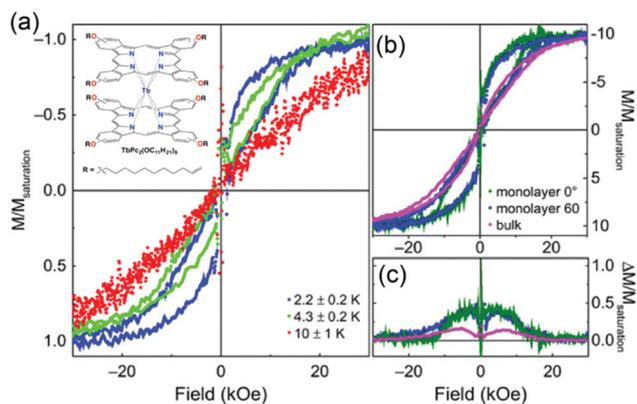
Following characterization of the bulk sample, a monolayer of TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub> was grafted to a SiO<sub>2</sub>(100) wafer through hydrosilylation, leading to direct linking of TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub> to the SiO<sub>2</sub> surface *via* Si-C bonds. The substrate was afterwards subjected to several cleaning procedures to ensure that just the chemically bound TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub> was present on the surface. XPS analysis of the TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub>/SiO<sub>2</sub>(100) system confirmed that the molecules were grafted to the surface. Interestingly, XPS spectra also revealed two peaks in the spectrum of the monolayer film, compared to a single peak observed in thicker film prepared by the drop casting procedure. The authors ascribed the appearance of the second peak to a possible oxidised form of the TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub>, which could be a surface-induced effect. The XPS results were further supported by DFT calculations.

XNLD measurements performed on the TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub>/SiO<sub>2</sub>(100) sample at the M<sub>4,5</sub> Tb edges showed that most molecules lay with a face-on configuration on the SiO<sub>2</sub>(100) surface, as commonly observed for TbPc<sub>2</sub>. On the other hand, XMCD measurements at low temperature with a magnetic field of 5 T

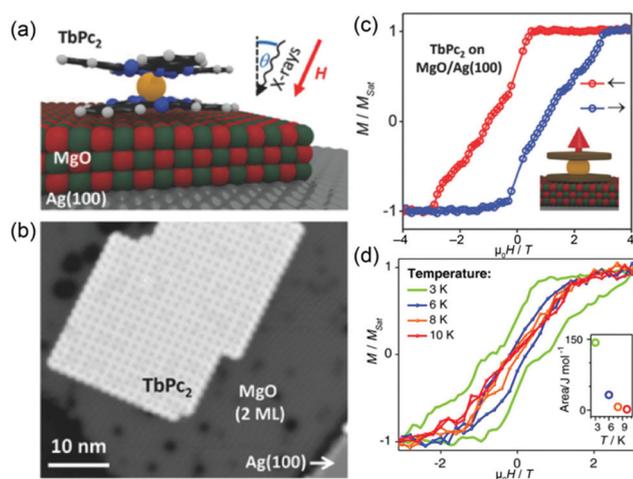
parallel to the X-ray light propagation vector measured at the M<sub>5</sub> edge of Tb affords hysteresis loops down to 4.3 K. The authors compared the loops of the monolayer sample with that of a drop casted thick film on SiO<sub>2</sub> (with bulk-like magnetic properties), revealing a smaller opening of the loop in the latter case (Fig. 12). As observed in Fig. 12b, the monolayer showed a larger hysteresis, compared to that of the bulk-like material. Moreover, the authors proposed that upon chemical binding of the TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub> to the SiO<sub>2</sub> substrate, an oxidizing-like effect could take place, therefore enhancing the magnetic properties of the TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub>, as shown for TbPc<sub>2</sub><sup>+</sup>.<sup>10b</sup> Unfortunately, despite depositing TbPc<sub>2</sub> on an insulator substrate, the quantum tunnelling at zero field was still present.

Although hysteretic magnetic behaviour was afforded upon deposition of an analogous TbPc<sub>2</sub> on SiO<sub>2</sub> after chemical grafting, the collected hystereses were narrow and with visible QTM at zero field, indicating that efficient suppression of QTM was not achieved. Recently, through a similar approach, the record hysteresis for a surface deposited SMM was realised after depositing TbPc<sub>2</sub> on a MgO insulating layer deposited onto Ag(100) with composition TbPc<sub>2</sub>(0.6 ML)/MgO(5 ML)/Ag(100).<sup>42</sup> STM analysis confirmed that the TbPc<sub>2</sub> molecules maintained a flat arrangement on the surface, leading to 2D islands on the MgO surface, showing the typical eight-lobed pattern from the staggered configuration of the Pc groups. XNLD also corroborated the face-on configuration of the TbPc<sub>2</sub> on the MgO film, supporting the STM observations (Fig. 13a).

XMCD measurements showed a strong remanence of the magnetisation, with hysteresis loops opening up to 3 T at 3 K, demonstrating that the QTM had been strongly suppressed (Fig. 13c). In order to obtain some insight into the mechanism leading to suppression of the QTM on the TbPc<sub>2</sub>/MgO/Ag(100),



**Fig. 12** (a) XMCD hysteresis curves for  $\theta = 60^\circ$  as a function of the temperature in the TbPc<sub>2</sub>(OC<sub>11</sub>H<sub>21</sub>)<sub>8</sub>@Si monolayer. (b, c) Comparison of the behaviour of the thick film and the monolayer, the latter being measured for  $\theta = 0^\circ$  and  $60^\circ$ . These magnetisation curves, measured under the same conditions for all the samples ( $2.2 \pm 0.2$  K and 500 Oe s<sup>-1</sup> scan speed) through the XMCD technique, are reported in b with their experimental error. In c, the hysteresis opening is estimated as  $\Delta M(H)$ , according to the procedure described in the text. Adapted with permission from ref. 41.



**Fig. 13** Self-assembly and exceptional magnetic remanence and hysteresis of TbPc<sub>2</sub> molecules on insulating MgO films. (a) Sketch of a TbPc<sub>2</sub> molecule on an ultrathin MgO film on Ag(100). (b) Scanning tunnelling microscopy image revealing self-assembled arrays of TbPc<sub>2</sub> on two monolayers (MLs) of MgO. (c) Hysteresis loop obtained with XMCD at 3 K for 0.6 ML TbPc<sub>2</sub> on 5 ML MgO. (d) Temperature-dependent magnetisation curves of TbPc<sub>2</sub>/MgO/Ag(100). With increasing temperature, the magnetisation loop gradually closes until the hysteresis fully vanishes at 10 K (X-ray flux  $\phi_0$ , 0.3 ML TbPc<sub>2</sub> on 4.8 ML MgO). The area of the hysteresis opening is plotted in the inset. Adapted with permission from ref. 42.

the authors studied three other samples: (i) a multi-layered TbPc<sub>2</sub> deposited on MgO film; (ii) TbPc<sub>2</sub>/Ag(100) and (iii) TbPc<sub>2</sub> deposited on a well-known insulator, such as hexagonal boron nitride (*h*-BN). The results unveiled strong quantum tunnelling when TbPc<sub>2</sub> was deposited on bare Ag(100), with the hysteresis loop nearly closing at 3 K, while when multi-layered TbPc<sub>2</sub> was deposited on a MgO film, the QT was reduced, compared to the TbPc<sub>2</sub>/Ag(100), but increased when compared to the monolayer TbPc<sub>2</sub>/MgO/Ag(100) sample; this was attributed to the magnetic interaction between neighbouring TbPc<sub>2</sub> molecules in the dense packing (see Fig. 13c and d).

Studies of TbPc<sub>2</sub> on *h*-BN likewise showed some degree of suppression of the QT; however, due to the intrinsic monolayer self-assembly properties of *h*-BN, compared to MgO, suppression of the QT is not as effective as in the case of MgO. Given that TbPc<sub>2</sub> self-organization was similar on MgO, *h*-BN and Ag(100) surfaces, with face-on arrangement, the authors were able to ascribe the wide hysteresis loops to the insulating properties of MgO. Temperature dependent hysteresis loop measurements were carried out, affording slow relaxation of the magnetisation up to 8 K, the highest blocking temperature reported for a surface-deposited SMM (Fig. 13d). The magnetic remanence and wide hysteresis loops of TbPc<sub>2</sub> on MgO were attributed to the suppression of the electron fluctuations and scattering on the surface by the MgO barrier, with an exponential dependence of the tunnelling rate on the MgO thickness.

Furthermore, the authors also propose that the magnetic behaviour could be attributed to a minimum TbPc<sub>2</sub>-MgO hybridization, which leads to practically no distortion of the

$D_{4d}$  symmetry of the TbPc<sub>2</sub> on the surface; therefore less QT is prompted. Moreover, a comparison of the XMCD of monolayer and multilayer TbPc<sub>2</sub> on MgO showed that lateral (horizontal) exchange interactions play a smaller role in the tunnelling events, while vertical interactions enhance magnetic relaxations.

## Conclusions

In the quest for molecular spintronic devices made from SMMs, it has become clear that the confinement of magnetic molecules in the proximity of surfaces and electrodes has similar impact on the magnetic performance of the SMMs to that found in molecular engineering approaches, *e.g.*, creating strongly axial ligand fields,<sup>43</sup> or introducing exchange bias.<sup>4d</sup>

The results of several studies show that upon deposition of the TbPc<sub>2</sub> SMM on different substrates, enhancement or quenching of the hysteresis loops is achieved, depending solely on the nature of the substrate. Deposition of TbPc<sub>2</sub> at monolayer coverage level on non-magnetic metallic substrates yields practically unopened hysteresis loops, despite the unperturbed nature of the Ising-type behaviour of the Tb<sup>3+</sup> ion. Only a very small opening of the magnetic hysteresis was observed at 2 K when TbPc<sub>2</sub> was deposited on Au(111). This fact can be ascribed to accelerated QT rates of the SMM *via* the spin-phonon interface, but also to metal- $\pi$ -orbital hybridization and changing of the dipole-dipole coupling paths, evidencing that strong interactions are harmful to the SMM properties when deposited on these surfaces.

Astonishingly, the deposition of TbPc<sub>2</sub> on magnetic substrates has a contrasting effect. TbPc<sub>2</sub> on ferromagnetic substrates, such as nickel, leads to antiferromagnetic coupling of the molecular  $J = 6$  spin to the out-of-plane magnetic moment of the nickel substrate, attributed to an exchange mechanism, present even after the insertion of a graphene layer between the TbPc<sub>2</sub> and Ni substrate.<sup>44</sup> Remarkably, the observation of finite remanence of the  $\mathbf{M}_{\text{Tb}}$ , as high as 100 K, demonstrates how the SMM-ferromagnetic-substrate interactions can significantly enhance the magnetic properties of TbPc<sub>2</sub> at zero field. Likewise, in the quest for the systematic manipulation of the substrate-molecule exchange interaction, it has been shown that upon addition of electron withdrawing or donor agents to the surface, some degree of control can be attained. Recently, Candini *et al.* also showed that a similar effect is achieved by changing the anisotropic lanthanide ion residing in the double decker LnPc<sub>2</sub>.<sup>45</sup> A much weaker, although sizeable, interaction is achieved after the deposition of the SMM on antiferromagnetic substrates, such as Mn, leading to the observation of the exchange bias mechanism. These are very promising results in the ongoing search for increased working temperatures for future molecular spintronic devices.

Conversely, TbPc<sub>2</sub> on less interacting substrates, like HOPG, leads to some degree of suppression of QT near zero field, due to weak interaction of the TbPc<sub>2</sub> with the HOPG surface. The results on graphene and SWCNTs undoubtedly highlight the pivotal role of the control of the spin-phonon coupling.

By suspending SWCNTs and exploiting their quantum properties (e.g. discrete phonon energies of the SWCNTs),<sup>32d</sup> it is possible to completely suppress the QT in a surface-confined TbPc<sub>2</sub> SMMs.

Finally, more efficient suppression of the QT rate is achieved on insulators such as SiO<sub>2</sub> and MgO, leading to the observation of a giant hysteresis up to 8 K in the latter case, emphasising the importance of insulating layers on the magnetic properties of the SMM. This sets a new scenario towards SMM-based tunnel devices. In addition, these results demonstrate that engineering the spin–phonon coupling at the molecule–substrate interface is a valid approach in the long-lasting search for increased blocking temperatures of SMMs.

It is evident that for the successful implementation of SMM on quantum computing or tunnelling devices, a thorough understanding of the magnetic behaviour of SMMs at the surface level is as necessary as the understanding of properties of the surface where deposited. As a final remark, although this perspective article has been entirely devoted to surface-confined TbPc<sub>2</sub>, the understanding of the magnetic characteristics of this SMM on surfaces offers the scientific community some insight into the underlying characteristics of on-surface SMMs, which must be taken into consideration for the realisation of hybrid SMM-spintronic devices.

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