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## Tuning of a vertical spin valve with a monolayer of single molecule magnets

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**Abstract.** The synthesis and the chemisorption from solution of a Terbium bis-phthalocyaninato complex suitable for the functionalization of Lanthanum Strontium Manganite (LSMO) are reported. Two phosphonate groups have been introduced in the double decker structure in order to allow the grafting to the ferromagnetic substrate actively used as injection electrode in organic spin valve devices. The covalent bonding of

functionalized Terbium bis-phthalocyaninato system on LSMO surface preserved its molecular properties at the nanoscale. X-ray Photoelectron Spectroscopy (XPS) confirmed the integrity of the molecules on the LSMO surface and a small magnetic hysteresis reminiscent of the typical single molecule magnet behaviour of this system was detected on surface by X-ray Magnetic Circular Dichroism (XMCD) experiments. The effect of the hybrid magnetic electrode on spin polarized injection was investigated in vertical organic spin valve devices and compared to the behaviour of similar spin valves embedding a single diamagnetic layer of alkyl phosphonate molecules analogously chemisorbed on LSMO. Magnetoresistance experiments have evidenced significant alterations of the magneto-transport by the Terbium bis-phthalocyaninato complex characterized by two distinct temperature regimes, below and above 50 K, respectively.

## 1. Introduction

In the last years the electronic and magnetic structure of interfaces formed between an organic  $\pi$ -conjugated semiconductor and a ferromagnetic layer have been investigated for a large variety of systems.<sup>[1]</sup> The formation of hybrid states with magnetic properties, or specific exchange interactions, has been shown to have a clear impact on spin injection across the interface.<sup>[2]</sup> This topic has a huge interest for both fundamental and applicative research related to organic-inorganic devices like magnetic tunnel junctions, spin valves, memristors and others, whose performances are strongly affected by the boundary region between the organic and inorganic phases.<sup>[3-9]</sup> Most important achievements have been hitherto obtained by interfacing organic materials with complex ferromagnetic metal oxides, in particular with the Lanthanum Strontium Manganite Oxide (LSMO), whose large spin polarisation of the surface (nominally 100% at 0 K) and good stability under different conditions may represent a significant advantage with respect to the use of *3d* ferromagnetic (FM) thin films.<sup>[8]</sup> On the other hand the use of molecules as building blocks allows to introduce in electronic devices

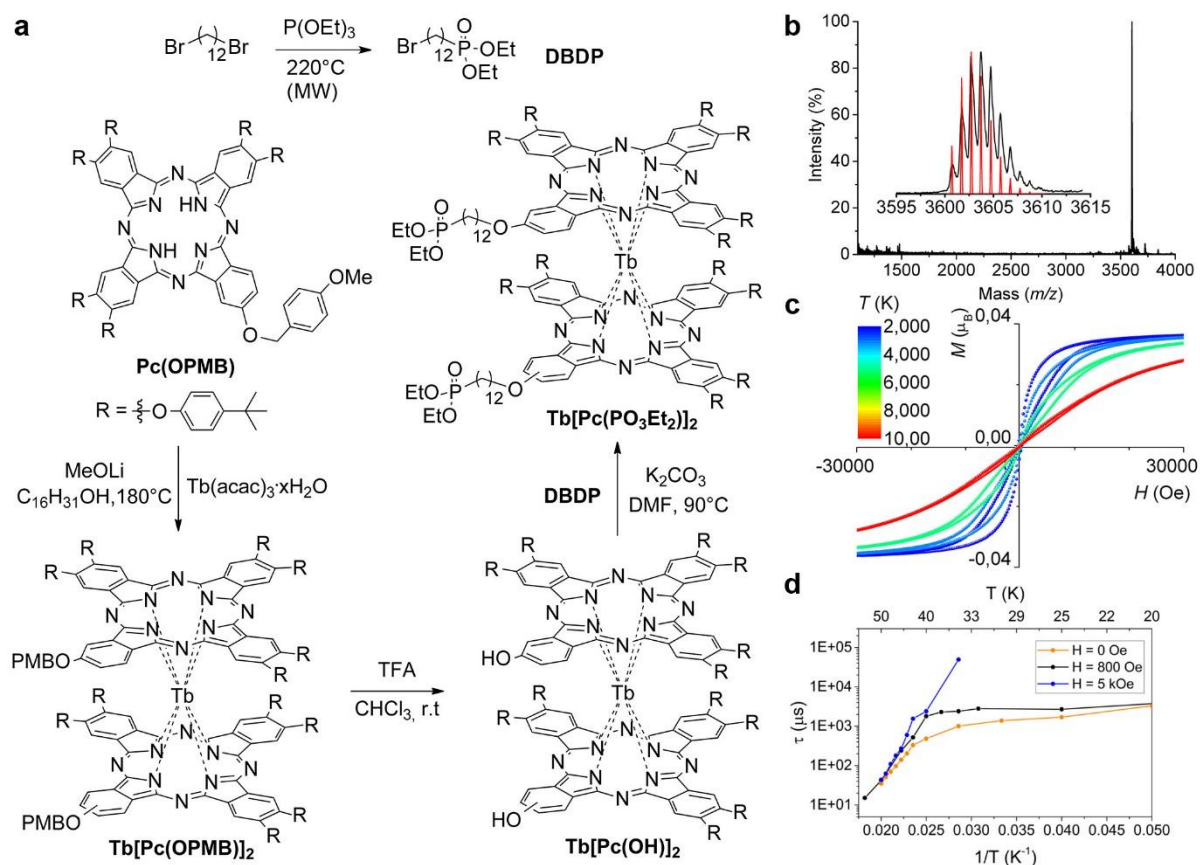
new functionalities due to the almost infinite combination offered by synthesis of complex and tunable molecular objects.<sup>[10]</sup> In particular the introduction of monolayers of magnetic molecules is attracting broad interest thanks to their potential technological applications in molecular spintronics<sup>[11]</sup> and quantum computation.<sup>[12]</sup> Self-assembled monolayer (SAM)-based protocols<sup>[13]</sup> are among the most used techniques to achieve a bidimensional organization of molecules adsorbed on surface. In this context the wet chemistry-based deposition of monolayer of magnetically bistable molecules, known as Single Molecule Magnets (SMM),<sup>[14]</sup> has been widely explored,<sup>[15–21]</sup> evidencing suitable strategies for the stabilization<sup>[19]</sup> or even the enhancement<sup>[21]</sup> of the SMM behaviour when these fragile complexes are chemisorbed on surface. We recently adopted a SAM-based strategy to tune the LSMO interface by introducing a monolayer of chemisorbed organic radicals<sup>[22]</sup> that alters the spin injection performances at low temperature through a spin-filtering effect. Here we aim to combine these concepts by developing a specific functionalization strategy to promote chemisorption of a modified Terbium (III) double decker system, an archetypal SMM, on the LSMO surface. A diethyl phosphonate group has been selected as linker agent compatible with the chemistry of the core structure of TbPc<sub>2</sub>. This modified hybrid spin injecting electrode has been then used to realize a vertical organic spin valve comprising Gaq<sub>3</sub> as organic semiconductor and Cobalt as the second magnetic electrode. The performances of this type of devices have been compared with those of a similar one obtained by replacing the double decker layer with diamagnetic molecules, the diethyl(11-iodoundecyl)phosphonate, bearing the same linking group promoting the chemisorption. This strategy has been developed in order to disentangle the effect of the chemical functionalization of the manganite, which has been addressed also in earlier reports,<sup>[23,24]</sup> from more specific effects, due to the presence of a layer of magnetic molecules forming an *additional spinterface* for the spin injection into the organic semiconductor.

## 2. Results

### 2.1. Synthesis and bulk characterization of the LSMO-graftable Tb double decker

We synthesized a homoleptic Terbium(III) bis-phthalocyaninato ( $\text{TbPc}_2$ ) complex bearing two peripheral diethyl phosphonate groups ( $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$ , Fig. 1a) for covalent grafting on LSMO surface. Phosphonic esters ensure the formation of robust monolayers *via* strong P-O-metal linkages.<sup>[25,26]</sup> Since these anchoring functionalities were found to be unstable under the harsh conditions required for both phthalocyanine (Pc)<sup>[27]</sup> and  $\text{TbPc}_2$  formations, the post-functionalization of already formed  $\text{TbPc}_2$  complexes was implemented. The preparation of the dihydroxy-functionalized double decker  $\text{Tb}[\text{Pc}(\text{OH})]_2$  was achieved in two steps starting from the asymmetric  $\text{A}_3\text{B}$ -type phthalocyanine  $\text{Pc}(\text{OPMB})$ , modifying a protocol reported by Pushkarev *et al.*<sup>[28]</sup> *p*-methoxybenzyl (PMB) group was used as protection of the hydroxyl functionality during the statistical macrocyclisation and the subsequent ligand exchange reaction. Instead, the choice of *p*-*tert*-butylphenoxy substituents on Pc's residual positions was required to increase their solubility, hampering the formation of aggregates by steric repulsion. Complex formation was performed reacting the phthalocyaninato ligand  $\text{Pc}(\text{OPMB})$  with terbium (III) acetyl-acetonate hydrate in 1-hexadecanol at 453 K in presence of lithium methoxide.  $\text{Tb}[\text{Pc}(\text{OPMB})]_2$  was obtained as a mixture of constitutional isomers in 35% yield and characterized by UV-Vis spectroscopy and high-resolution matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF). The deprotection of the two hydroxyl functionalities with trifluoroacetic acid (TFA) in DCM at room temperature afforded  $\text{Tb}[\text{Pc}(\text{OH})]_2$  in quantitative yield. Finally, the introduction of the phosphonate groups was realized *via* nucleophilic substitution of diethyl 12-bromododecylphosphonate (BDP), obtained by microwave assisted Arbuzov reaction between 1,12-dibromododecane and a substoichiometric amount of triethyl phosphite. As demonstrated in our recent works,<sup>[21,29,30]</sup> long aliphatic spacers are required to preserve the reactivity of the peripheral functionalities in the following steps.  $\text{Tb}[\text{Pc}(\text{OH})]_2$  was reacted

with BDP in *N,N*-dimethylformamide (DMF) at 363 K in presence of potassium carbonate.  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$  was obtained in 48% yield after column chromatography and was characterized by NMR and UV-Vis spectroscopies (see SI, Fig. S1-S3) and MALDI-TOF. In particular, the MALDI-TOF spectrum (Fig. 1b) reveals the presence of the molecular peak, with an isotopic distribution pattern in agreement with the theoretical one.



**Figure 1.** a) Synthesis of  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$ ; b) high-resolution MALDI-TOF spectrum of  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$ , with experimental (black line) versus theoretical (red line) isotopic distribution in the inset; c) magnetisation vs. field measurements of  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$  performed in the temperature range between 2 K and 10 K (colour scale in the inset) and scanning the field between 30 kOe and  $-30$  kOe at  $50 \text{ Oe s}^{-1}$ ; d) relaxations times of  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$  against inverse temperature (for the temperature range 20 – 55 K) at three different static magnetic fields: 0 Oe, 800 Oe and 5 kOe.

The characterization carried out with traditional DC and AC magnetometry allows a complete evaluation of the magnetic properties of the complex in its bulk phase. As already observed for other TbPc<sub>2</sub> complexes<sup>[31–35]</sup> the hysteresis in the magnetization curves is visible below 15 K thus indicating that the functionalization does not alter significantly the SMM behaviour of this double decker system (Fig. 1c). Zero static field AC susceptibility measurements as a function of temperature are shown in Fig. S4 and in the out-of-phase component a frequency dependent peak occurring at relatively high temperatures is visible. The extended Debye model,<sup>[14]</sup> adopted to analyse these data in the range 0.5 Hz – 10 kHz, allows to extract the relaxation time,  $\tau$ , of this system for different temperatures (Fig. 1d). In the high temperature regime,  $T > 40$  K, the characteristic magnetization dynamic parameters for the systems have been extracted on the basis of an Arrhenius model, *i.e.*  $\tau = \tau_0 \exp(\Delta E/k_B T)$ . The estimated energy barrier in the thermally activated process,  $\Delta E = 614(11)$  K, is smaller than that found for the crystalline phase of TbPc<sub>2</sub> (965 K)<sup>[35]</sup> but in line with the value observed in similar conditions for amorphous unfunctionalized TbPc<sub>2</sub> systems,<sup>[32]</sup> in agreement with the amorphous character of Tb[PC<sub>2</sub>(PO<sub>3</sub>Et<sub>2</sub>)<sub>2</sub>]<sub>2</sub> sample. The extracted pre-exponential factor is  $\tau_0 = 17(4) \cdot 10^{-11}$  s. Below 40 K the relaxation becomes temperature independent, indicating the onset of a tunnel mechanism of inversion of magnetization, with a significant increase of the width of the distribution of the relaxation times (see SI). The application of a static field of (Fig. S5 and S6) leaves unaltered the high temperature behaviour as shown in Fig. 1d, but significantly affects the magnetic relaxation below 40 K, suppressing the tunnelling mechanism with  $\tau$  exceeding the accessible timescale of the AC susceptometry. A narrower distribution of  $\tau$  is observed in static field in analogy to what previously found for other functionalized and unfunctionalized TbPc<sub>2</sub> complexes.<sup>[35,36]</sup> This can be explained with the fact that, when tunnelling is not suppressed by the external field, the distortions from idealized D<sub>4d</sub> strongly affect the tunnelling efficiency.

## 2.2. Chemisorption of the Tb double-decker on LSMO

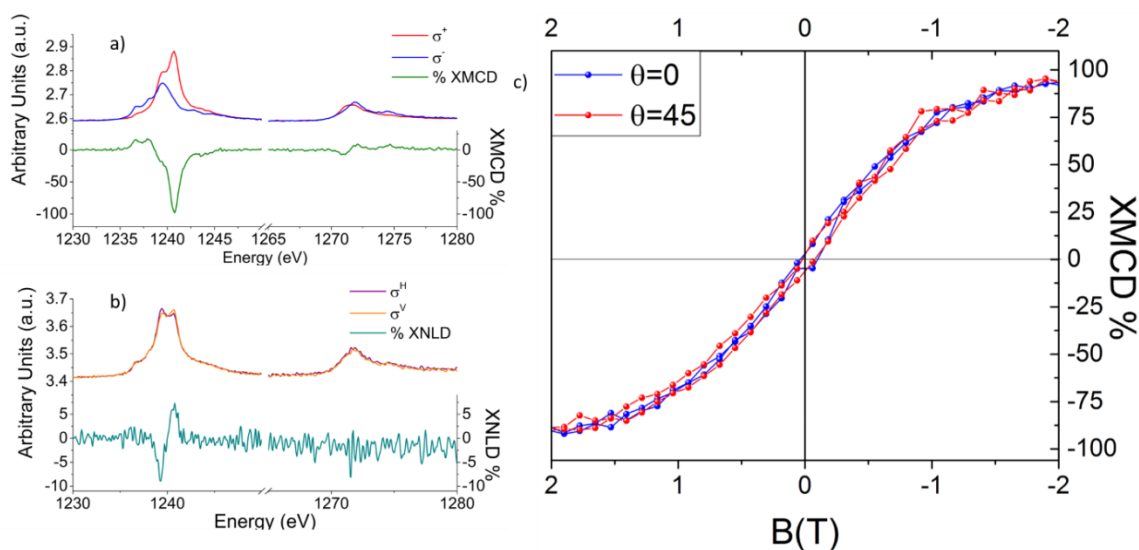
The deposition of Tb[Pc(PO<sub>3</sub>Et<sub>2</sub>)<sub>2</sub>] on LSMO has been achieved by implementing the same procedure previously described for the self-assembly of nitronyl nitroxide radicals functionalized with the diethyl-phosphonate group.<sup>[22]</sup> In parallel, also the deposition of a  $\omega$ -iodo alkyl-phosphonate, the diethyl(11-iodoundecyl)phosphonate, has been performed to obtain a reference diamagnetic layer to be used in the following steps (see SI for details). Chemisorption of these molecular layers (see Methods for details and SI) has been verified by XPS. Focusing on the grafting of Tb[Pc(PO<sub>3</sub>Et<sub>2</sub>)<sub>2</sub>] this spectroscopic characterization (See Fig. S8) confirms the intactness of the molecular layer. Due to the presence of interfering signals, only the Tb3d<sub>3/2</sub> (at 1277.7 eV and a shake-up at 1282.7 eV)<sup>[37,38]</sup> and N1s signals have been used for this analysis. The N/Tb ratio is  $16.7 \pm 1.0$ , perfectly in line with the expected value (16); additionally, the N1s peak fitting reveals two components at 398.5 eV and at 400.2 eV. The first peak is directly attributable to a nitrogen in the bulk TbPc<sub>2</sub><sup>[39]</sup> while the other one at higher energy (400.2 eV) suggests that part of the chemisorbed molecules are influenced by the substrate, in analogy to what observed for similar complexes chemisorbed on Si.<sup>[21]</sup>

To characterize the magnetic behaviour of the hybrid system an X-ray absorption spectroscopy (XAS)-based study using circularly polarized light has been performed to extract the XMCD contribution and its magnetic field dependence at low temperature ( $2.2 \pm 0.2$  K) for both substrate and molecular layer. Absorption and dichroic spectra measured at the L<sub>2,3</sub> edges of Mn (Fig. S9) exhibit the standard LSMO features in perfect agreement with previous reports.<sup>[40,41]</sup> Analogously the XAS and XMCD investigations at Tb M<sub>4,5</sub> edges, reported in Fig. 2, show the expected TbPc<sub>2</sub> spectral features<sup>[31]</sup> and the “edge jump” analysis<sup>[42]</sup> of the derived isotropic spectrum confirms the formation of a deposit of the order of 0.8 monolayer if compared to a monolayer deposit of TbPc<sub>2</sub> sublimated on LSMO.<sup>[43]</sup>



The magnetization curves extracted for the  $L_3$  edge of Mn (Fig. S9) show the typical angular dependence of LSMO thin films with in-plane magnetic anisotropy.

On the other hand, the magnetization curves obtained at the Tb  $M_5$  edge (Fig. 2c) do not follow the behaviour of the LSMO substrate excluding the presence of a strong magnetic coupling between the molecular layer and the ferromagnetic substrate in contrast to what found in other hybrid TbPc<sub>2</sub>-based assemblies.<sup>[44–46]</sup> It has to be noticed that the presence of the small hysteresis confirms the persistence of the SMM behaviour even if, independently to the orientation of the sample, it is characterized by a much narrower opening than the one recorded by either conventional magnetometry (Fig. 1c) or XMCD (Fig. S10) in the bulk phase. Analogies of this behaviour with earlier reports<sup>[31,32,43]</sup> are evident and can be partially justified by distortion of the molecular structure induced by the chemisorption on the LSMO substrate.



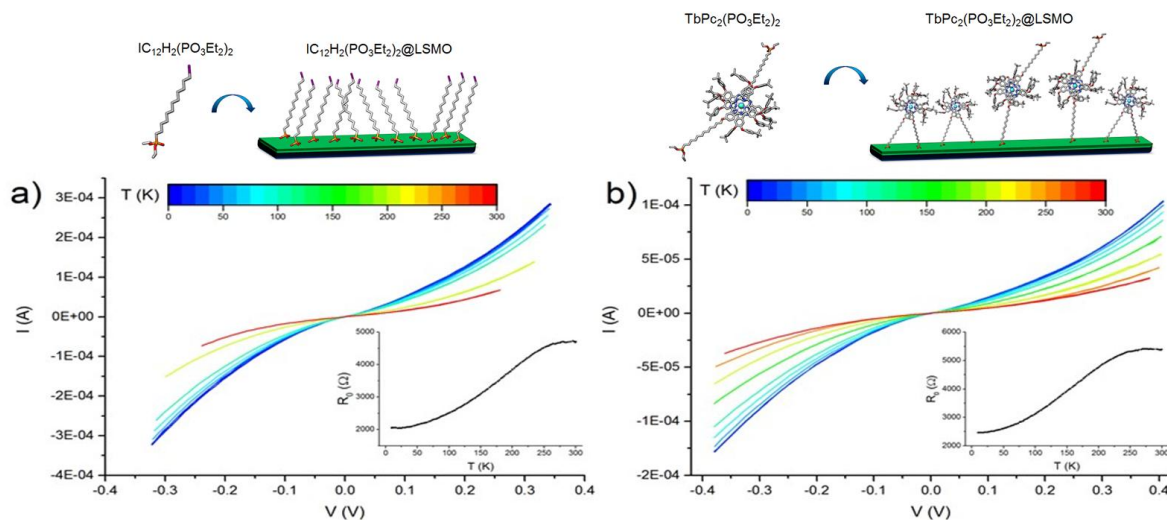
**Figure 2.** a) XMCD measurements at  $2.2 \pm 0.2$  K under a 30 kOe magnetic (green line is obtained from the difference of the left ( $\sigma^+$ , red line) and right ( $\sigma^-$ , blue line) polarized light and b) XNLD measurements for TbPc<sub>2</sub>@LSMO performed at  $2.2 \pm 0.2$  K under a 30 kOe magnetic field to enhance detection sensitivity. XNLD (dark green line) is obtained from the difference of the horizontally ( $\sigma^H$ , purple line) and vertically ( $\sigma^V$ , orange line) polarized light. c) Field dependence of the XMCD signal measured at the maximum of the dichroic signal at

the  $M_5$  edge for  $TbPc_2@LSMO$ . The curves are reported at two angles,  $\theta$ , between the magnetic field and the surface normal ( $\theta = 0^\circ$  and  $\theta = 45^\circ$ ).

Linearly polarized light was also used in order to get information about the orientation of the molecules with respect to the surface. The derived X-ray Natural Linear Dichroism (XNLD) spectrum measured at  $\theta = 45^\circ$  (Fig. 2b) shows a small dichroic contribution indicative of a slightly preferential molecular orientation on the surface with the phthalocyanine rings parallel to the plane of the LSMO surface. We notice the opposite trend with respect to unfunctionalized  $TbPc_2$  molecules deposited by sublimation on LSMO that tend to assemble with a standing configuration.<sup>[43]</sup>

### 2.3. Device preparation and characterization

The effects induced by the SMM layer on the spin injection process have been investigated by the direct comparison of two specially designed organic spin valve devices (OSV) differing only by the presence or the absence of the  $TbPc_2$ , while keeping similar all the other parameters. Vertical cross-bar geometry has been employed with LSMO as bottom and Co as top electrodes, 40 nm of tris(8-hydroxyquinoline) Gallium(III) ( $Gaq_3$ ) as charge/spin transport layer, and an Aluminium oxide buffer layer between the  $Gaq_3$  and Co.<sup>[47,48]</sup> The two ferromagnetic electrodes are characterized by different coercive field values allowing the achievement of parallel and antiparallel relative orientations of their magnetic moments and enabling the spin valve functionality.<sup>[49]</sup> In both sets the LSMO electrode has been functionalized by chemisorbing a single layer of alkyl-phosphonate molecules. The first set contained the  $\omega$ -iodo alkyl-phosphonate to chemically tailor the bottom injecting interface, while the second set has been additionally characterized by the presence of SMM centres (see Fig. 1a).



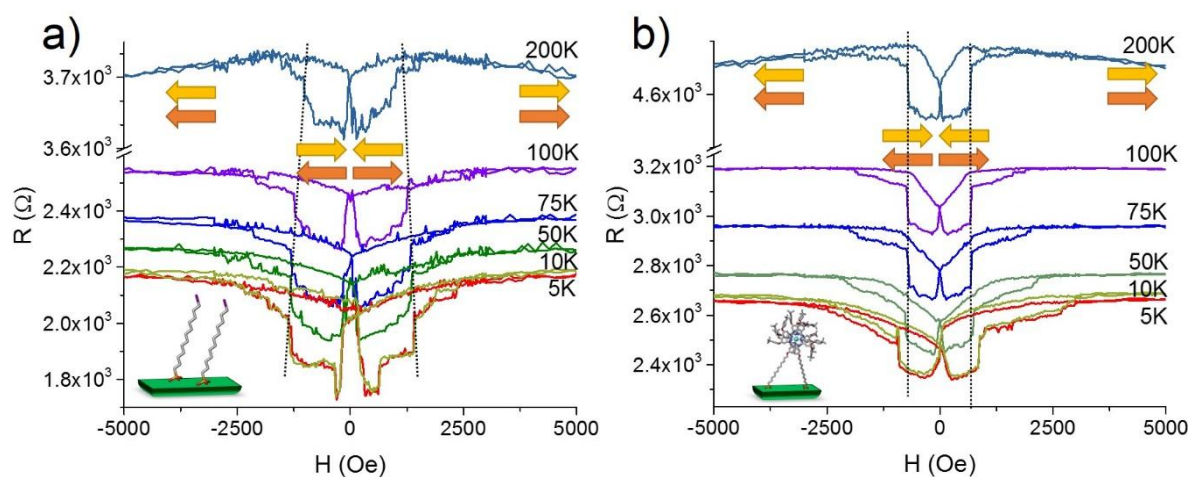
**Figure 3.** I-V characteristics for OSV functionalized with  $\omega$ -iodo alkyl-phosphonate (a) and with  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)_2]_2$  (b) at different temperatures (colour scale in the inset). In the insets is also reported the values of resistance (measured at  $I = 0.5 \mu\text{A}$  and with no magnetic field present) as function of temperature in the range 3 – 300 K. On top of both I-V curves the chemisorption on LSMO of the two molecules is depicted.

Fig. 3 reports the I-V characteristics measured at different temperatures in the range 3 – 300 K for the devices bearing respectively the  $\omega$ -iodo alkyl-phosphonate and  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)_2]_2$ . The two different functionalizations sketched in Fig. 3 do not induce qualitative modifications: both sets show typical trends for this geometry and electrodes<sup>[7,50]</sup> and can be tentatively described by transport via both the LUMO (or HOMO) level<sup>[51]</sup> or the impurity band.<sup>[52]</sup> The observed increase in the resistivity values when  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)_2]_2$  is present could be reasonably attributed to an increased thickness of the chemisorbed layer or to a different transport efficiency of the embedded system.

The magnetoresistance (MR) detected for the two sets of devices for the 5 – 200 K temperature interval is presented in Fig. 4. The in-plane magnetic field was swept from -1 T to +1 T and *vice versa* while measuring the device resistance in a four-point probes configuration at a fixed 0.5  $\mu\text{A}$  applied current.

Both types of devices feature inverse spin-valve effect, *i.e.* the lower resistance corresponds to antiparallel Co and LSMO magnetizations (see the cartoons in Fig. 4). This behaviour is typical for OSV devices based on LSMO-quinolines-Co systems and was confirmed for a number of spin valve devices.<sup>[7,8,22,50]</sup> It is generally accepted that the fundamental contribution to this inversion comes from the interfacial hybridization between one or both magnetic electrodes and the organic molecules (the so called spinterface effect).<sup>[22,53]</sup> We thus note that the performed functionalization does not induce qualitative changes to this generally established picture.

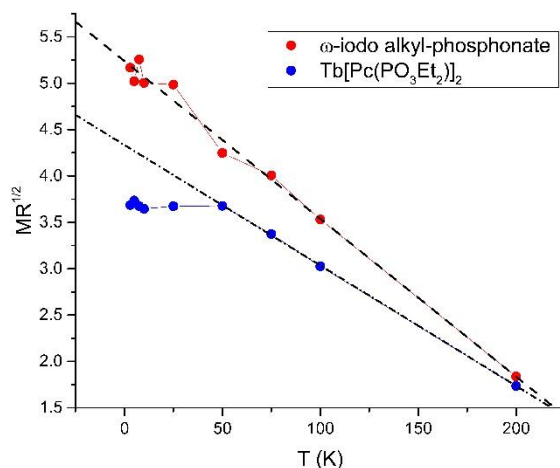
We also observe a fine structure for the antiparallel resistive section detected at low temperatures for the  $\omega$ -iodo alkyl-phosphonate set of measurements. Such features are quite typical for OSV and even inorganic devices and are basically attributed to local imperfections of electrodes, an effect which is beyond the scope of this paper.



**Figure 4.** Inverse spin-valve effect measured sourcing a constant current  $I = 0.5\mu\text{A}$  for a)  $\omega$ -iodo alkyl-phosphonate and b)  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)_2]_2$  based OSV in the temperature range 5 – 200 K: the high and low resistance states correspond to parallel and antiparallel configurations respectively (see the cartoons). Dotted lines are guides to the eyes to follow the temperature dependence of high switching fields.

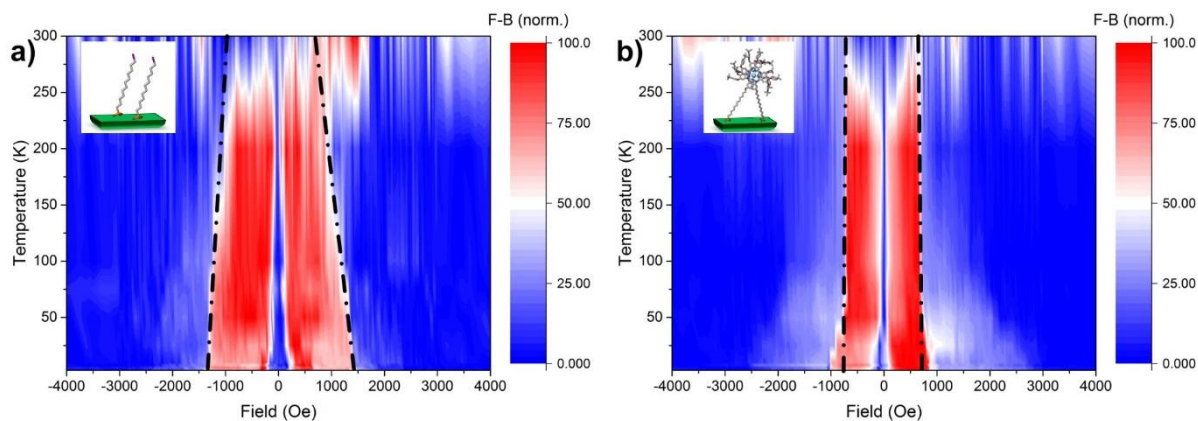
In order to unveil the contribution of the SMM layer to the interfacial effects a quantitative analysis of data has to be employed. The first statistically relevant difference between the two sets is noticeable for the switching fields. The low switching fields in both types of devices closely correspond to the coercive fields of Co electrodes (see SI, Fig. S11). Conversely, the high switching fields significantly exceed those of the manganite electrodes (see SI, Fig. S12), and can be tentatively attributed to the hybrid LSMO-PO<sub>3</sub>Et<sub>2</sub> bilayers, similarly to previously reported chemisorbed interfaces,<sup>[2,54]</sup> resulting as the most sensitive region of the field scan to the alterations we operated. In fact these switching fields feature a remarkably different behaviour: when the LSMO is functionalized with the alkyl-phosphonate layer, the external switching fields increase by decreasing the temperature as expected for ferromagnetic thin films (see Fig. 4a).<sup>[55]</sup> On the other hand, when the TbPc<sub>2</sub> molecule is integrated at the interface, the standard magnetic behaviour is no longer detected for LSMO based electrode: the switching fields surprisingly become temperature independent above 50 K (see Fig. 4b).

The same temperature of about 50 K separates two different regimes also for the strength of magnetoresistance as function of temperature. Fig. 5a shows the square root of the MR versus T. The MR<sup>1/2</sup>(T) plot is linear in standard LSMO based spin valves (without additional functionalization), whose temperature dependence is mainly governed by LSMO surface spin polarization.<sup>[22]</sup> While the ω-iodo alkyl-phosphonate set generally obeys this standard temperature dependence (red dots in Fig. 5), a clear deviation from linear behaviour for T < 50 K is visible for samples with LSMO electrodes functionalized with the TbPc<sub>2</sub> (blue dots).



**Figure 5.** Square root of the MR as function of temperature for representative devices from the two sets. Red circles represent the OSV with LSMO functionalized with the  $\omega$ -iodo alkyl-phosphonate while blue circle the ones functionalized  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)]_2$ . The black lines are guides to the eye

A pictorial comprehensive representation of the OSV behaviour is proposed in Fig. 6 as an useful approach to describe the temperature dependence of the magneto-transport behaviour of the devices. Here we show the maps of the absolute value of normalized differences between the MR measurements obtained sweeping the magnetic field from negative to positive values and those obtained in the way back, for two representative devices from the two batches. The device with the monolayer of  $\omega$ -iodo alkyl-phosphonate is characterized by a temperature dependent hysteresis (with coercive fields that vary linearly from 1400 Oe at 3 K to 1000 Oe at 250 K). On the opposite,  $\text{TbPc}_2$  based OSV, above 50 K, shows a narrower and temperature independent hysteretic behaviour (coercive field is 700 Oe in almost the entire temperature range covered). This confirms the evidence from Fig. 4 and represents an alternative way to figure out the information. Although in Fig. 6 we cannot see each singular MR measurement, we can grasp at a glance the comprehensive trend. We reckon this as a useful pictorial device oriented representation.



**Figure 6.** Colormap of the normalized (to 100) difference between the MR measurements obtained by sweeping the magnetic forward and backward in the range of temperature 3 – 300 K for the OSV functionalized with  $\omega$ -iodo alkyl-phosphonate a) and with  $\text{Tb}[\text{Pc}(\text{PO}_3\text{Et}_2)_2]$  b). The dashed and dotted black lines are only guides to the eye following the coercive fields.

### 3. Discussion

Analysing the coercive field and magnetoresistance trends in temperature, it becomes clear that the former parameter is mainly altered above the 50 K, while the latter below this temperature. This indicates a conceptually different contribution of Tb double decker on the two different parameters. To understand these effects it is necessary to analyse the process of the spin injection that governs the magnetoresistance and related measurable parameters and, on the other hand, to consider the magnetic properties of the added molecule. Starting from the MR we can limit our analysis to the case when LSMO injects carriers and spins; inverting the current, *i.e.* collecting spins with LSMO, does not change the physical picture. The charge-spin injecting interface represents a complex system, where the injecting surface is composed of the last metallic layer strongly hybridised with the first molecular layer; this is followed by partly modified second molecular layer and further by the three-dimensional van der Waals molecular solid.<sup>[56]</sup> It is widely agreed that the injection of carriers proceeds via a

two-step process: the tunnelling event from the injecting surface into the first non-hybridised layer and the subsequent diffusion of carriers (polarons) into the bulk of molecular solid.<sup>[57]</sup> There the transport proceeds via hopping processes, where the carriers “jump back and forth” gradually moving the polaron to the neighbouring site.<sup>[58]</sup> In our case the injecting surface is represented by the LSMO-alkylphosphonate bilayer, while the first non-hybridised molecular layer is the TbPc<sub>2</sub>, with its strong paramagnetic behaviour at these temperatures. The last injecting step is then represented by the diffusion from the double decker to the bulk of Gaq<sub>3</sub>. It is clear that, as far as the spin transfer is concerned, the injection process can be strongly affected by the paramagnetic scattering. The decrease of the MR with respect to the expected temperature trend may be explained by an additional spin scattering induced by TbPc<sub>2</sub> molecules. This scattering is supposed to proceed via a partial transfer of the magnetic momentum from incoming charges and localised impurities, like in doped inorganic semiconductors.<sup>[59]</sup> The scattering is thus expected to depend on the interaction with these magnetic centers and their magnetic dynamics. On the basis of earlier descriptions of the TbPc<sub>2</sub> electronic structure<sup>[60]</sup> we can exclude a direct involvement of the localized 4f orbitals of Tb<sup>3+</sup> ion in the transport process. More probably charge transfer can occur here through the singly occupied molecular orbital (SOMO) delocalized on the phthalocyaninato ligands. Carriers can feel the magnetic moment of the SMM through space (dipolar interaction) or through a weak, bond-mediated, exchange interaction.<sup>[61,62]</sup> We remind that the TbPc<sub>2</sub> system has its own intrinsic dynamics defined by its characteristic relaxation time  $\tau$  introduced in paragraph 2.1. At 50 K the relaxation time value is, also in presence of magnetic fields of the order of those experienced in the device, of the order of 10  $\mu$ s (see Fig. 1d) and this parameter is extraordinary close to the carrier diffusion time ( $\tau_d$ ) in Gaq<sub>3</sub>. Indeed the mobility in the quinolines is notably in the interval of  $10^{-4} - 10^{-5}$  cm<sup>2</sup>/Vs with corresponding diffusion times between 1  $\mu$ s and 10  $\mu$ s respectively, as evaluated from the Einstein equation.<sup>[63]</sup> From the



model of charge injection described above, it is clear that the diffusion inside Gaq<sub>3</sub> represents the “escape channel” (or the “arrival gate”, according to the polarity) for carriers localized in the frontier orbitals of TbPc<sub>2</sub>. This diffusion process defines the time along which the injected spins (or the collected ones) are exposed to the magnetic scattering interaction

The sizeable reduction of the magnetoresistance with respect to the case without the SMM monolayer (Fig. 5a) can thus be attributed to an additional scattering. Although a description of the microscopic mechanisms of such scattering is still lacking, some possible general trends can be figured out from the involved time scales and their temperature dependences by considering two limit cases, namely  $\tau_d \ll \tau$  and  $\tau_d \gg \tau$ . In the first case, the magnetic dynamics of the TbPc<sub>2</sub> molecule is slower than the charge diffusion process through the Gaq<sub>3</sub>: this means that its magnetic moment may be considered fixed with respect to the moving carrier. The latter will thus experience, each time it interacts during its diffusive walk with a TbPc<sub>2</sub> molecule, the molecular magnetic moment as an additional local static field, the precession around which will partially modify its spin, inducing an additional decrease of magnetoresistance (Fig. 5a). In the opposite case,  $\tau_d \gg \tau$ , the dynamics of TbPc<sub>2</sub> is faster than the charge carrier diffusion time and the spin scattering channel cannot be established: the MR is again fully governed by the manganite spin polarisation. This model allows to describe the MR(T) behaviour observed in the OSVs studied: when  $T > 50$  K we are in the  $\tau_d \gg \tau$  case (see Fig. 1d) and MR(T) follows the surface magnetization of the LSMO electrode being linearized in the  $MR^{1/2}$  vs T plot.<sup>[50]</sup> Once temperature is lower than 50 K the system enters in the  $\tau_d \ll \tau$  regime: a new scattering channel is present which constitutes a bottleneck for spin polarized currents leading to the plateau observed in MR(T) curves of OSV comprising TbPc<sub>2</sub> molecules. Devices functionalized with  $\omega$ -iodo alkyl-phosphonate are instead not affected by this additional magnetic scattering channel and their MR(T) is indeed determined only by manganite spin polarization.

Considering the coercive fields and their trend with temperature, we note that this parameter is strongly modified, in contrast to MR, above 50 K, that is in the pure paramagnetic regime of TbPc<sub>2</sub>. The coercive field  $H_C$  represents the applied field value for which half of the magnetic volume has switched its magnetization direction and is strongly related to the dynamics of the domain wall motion.<sup>[64]</sup> In a magnetoresistance experiment the sensing probe is the spin of the charge carriers, i.e. these magnetic processes are seen from the carriers' perspective. The coercive fields ascribed to the LSMO interface are higher than those measured directly on manganite films. This is a typical scenario in OSVs and can be ascribed to the modification of the surface magnetism of LSMO (or other electrode) via the hybridisation with grafting molecules of the SAM.<sup>[54]</sup> It is reasonable to assume that a layer of fast relaxing TbPc<sub>2</sub> magnetic moments in contact with this hybridised interfacial layer, may modify the magnetic dynamics of the latter. We can suppose that considering separately the spinterface, i.e. the bilayer formed by the surface of LSMO and the alkyl-phosphonate, is not sufficient to describe the magnetic reversal process because of the additional dipolar interaction of this ultrathin layer with the magnetic molecules. Nevertheless, to the best of our knowledge there are no available models able to treat these effects. The presence of a strong magnetic layer in the vicinity of the spin injecting surface may represent a powerful tool for the investigation of the magnetic dynamics and other key magnetic parameters and we believe that understanding this from both experimental and theoretical point of view is crucially important.

#### 4. Conclusions

A new derivative of TbPc<sub>2</sub> engineered for the LSMO functionalization has been produced and used to create an additional spinterface in a vertical organic spin valve. The behaviour of this hybrid spin valve has been compared with that of a similar device fabricated by the chemisorption of a diamagnetic alkyl-phosphonate system in order to disentangle the role of

the chemisorbing agent from the additional effects due to the introduction of an almost decoupled SMM which behaviour has been preliminarily evaluated by XAS-based techniques.

The crafted spinterface plays an active role establishing an additional spin-scattering layer able to control directly the MR strength. This regime is active below a threshold temperature that can be correlated to the characteristic timescale of the dynamics of the SMMs. Above this critical temperature an unusual effect of freezing the coercive fields of the vicinal to SMM magnetic electrode was detected. The observed results open novel perspectives on the use of these molecular layers with a controlled magnetism for a functional tailoring of the spinterface, although a deeper understanding of the interaction between the carriers' spins and single molecule magnets is strongly required.

## 5. Experimental Section

*Synthesis details:* Reagents used as starting materials and commercial solvents were used as received without further purification. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Silica column chromatography was performed using silica gel 60 (Fluka 230–400 mesh or Merck 70–230 mesh). NMR spectra were obtained using a Bruker AVANCE 300 (300 MHz) and a Bruker AVANCE 400 (400 MHz) spectrometer at 25 °C. All chemical shifts ( $\delta$ ) in  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR were reported in ppm relative respectively to the proton resonances resulting from incomplete deuteration of the NMR solvents and to external 85%  $\text{H}_3\text{PO}_4$  at 0.00 ppm. High-resolution MALDI-TOF mass spectrometry was performed on an AB SCIEX MALDI TOF–TOF 4800 Plus (matrix: *a*-cyano-4- hydroxycinnamic acid). UV–vis spectra were collected using a Thermo Scientific Evolution 260 Bio spectrophotometer equipped with a Peltier water-cooled

cell changer device, using matched quartz cells of 1 cm path length. Phthalocyanine **Pc(OPMB)** was prepared according to modified published procedures.<sup>[30]</sup>

**Diethyl 12-bromododecylphosphonate (DBDP)**. A mixture of 1,12-dibromododecane (2.0 g, 6.1 mmol) and triethylphosphite (0.35 mL, 2.0 mmol) was stirred at 220 °C under microwave irradiation for 5 minutes. The resulting solution was dried under vacuum and the residue was purified by flash column chromatography (ethyl acetate/hexane 7:3) to give **PBDP** (0.7 g, 1.8 mmol, 90%) as a colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 4.08 (q, 4H, *J* = 6.1 Hz, POCH<sub>2</sub>), 3.39 (t, 2H, *J* = 6.7 Hz, BrCH<sub>2</sub>), 1.83 (q, 2H, *J* = 6.9 Hz, CH<sub>2</sub>), 1.70 (m, 2H, CH<sub>2</sub>P=O), 1.57 (m, 2H, CH<sub>2</sub>), 1.42-1.25 (m, 22H, CH<sub>2</sub> and CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}NMR (162 MHz, CDCl<sub>3</sub>, δ): 32.7 (s, P=O); ESI-MS *m/z*: 385.2 [M+H]<sup>+</sup>, 407.4 [M+Na]<sup>+</sup>, 425.1 [M+K]<sup>+</sup>.

**Tb[Pc(OPMB)]<sub>2</sub>**. To a dispersion of **Pc(OPMB)** (0.127 g, 0.08 mmol) in 0.8 g of 1-exadecanol, [Tb(acac)<sub>3</sub>]*n*H<sub>2</sub>O (0.018 g, 0.04 mmol) and MeOLi (0.009 g, 0.24 mmol) were added. The resulting mixture was stirred at 180 °C for 1 h. The dark-green residue was dissolved in CHCl<sub>3</sub>, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 0.009 g, 0.04 mmol) was added, and the reaction was stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure and the solid was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane 6:4) to give **Tb[Pc(OPMB)]<sub>2</sub>** as a green solid (0.046 g, 0.014 mmol, 35%). UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 921, 682, 615, 479, 360, 331; MALDI-TOF *m/z*: [M]<sup>+</sup> calcd for C<sub>200</sub>H<sub>192</sub>N<sub>16</sub>O<sub>16</sub>Tb, 3232.396; found, 3232.352.

**Tb[Pc(OH)]<sub>2</sub>**. Trifluoroacetic acid (3 mL) was added to a solution of **Tb[Pc(OPMB)]<sub>2</sub>** (0.046 g, 0.014 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred at room temperature for 5 h. The solvent was evaporated to yield **Tb[Pc(OH)]<sub>2</sub>** (0.043 g, 0.014 mmol, quant.), that was used without further purification for the next step. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 918, 681, 613, 491, 363, 330; MALDI-TOF *m/z*: [M]<sup>+</sup> calcd for C<sub>184</sub>H<sub>176</sub>N<sub>16</sub>O<sub>14</sub>Tb, 2992.281; found, 2992.250.

**Tb[Pc(PO<sub>3</sub>Et<sub>2</sub>)<sub>2</sub>]**. To a solution of **Tb[Pc(OH)]<sub>2</sub>** (0.035 g, 0.012 mmol) in 10 mL of DMF, **PBDP** (0.018 g, 0.048 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.017 g, 0.12 mmol) were added. The reaction mixture was stirred overnight at 90 °C. The solvent was removed under reduced pressure and the crude was purified by flash column chromatography (CHCl<sub>3</sub>/MeOH 98:2) to give **Tb[Pc(PO<sub>3</sub>Et<sub>2</sub>)<sub>2</sub>]** as a green solid (0.021 g, 0.005 mmol, 48%). <sup>31</sup>P{<sup>1</sup>H}NMR (162 MHz, CDCl<sub>3</sub>, δ): 31.5 (s, P=O); UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> = 926, 680, 615, 469, 360, 330; MALDI-TOF *m/z*: [M]<sup>+</sup> calcd for C<sub>216</sub>H<sub>242</sub>N<sub>16</sub>O<sub>20</sub>P<sub>2</sub>Tb, 3600.714; found, 3600.705.

*LSMO preparation and functionalization*: The LSMO films have been grown on Neodymium-Gallium Oxide (NGO) single crystals by using the channel spark ablation (CSA) technique.<sup>[64]</sup> **Morphology of the electrodes has been evaluated by Atomic Force Microscopy (See Fig S13) prior the functionalization.** These surfaces have been cleaned using a protocol described elsewhere<sup>[65]</sup> and incubated at about 60 °C for 20 h in a 2 mM solution of **Tb[Pc(PO<sub>3</sub>Et<sub>2</sub>)<sub>2</sub>]** or diethyl(11-iodoundecyl)phosphonate in a mixture 3:1 of MeOH/CH<sub>2</sub>Cl<sub>2</sub>. The slides were rinsed several times with pure solvents, sonicated in the solvents solution for 30 minutes, rinsed a second time and dried under nitrogen flux in order to assure the removal of the molecules not directly interacting with the LSMO.

*XPS characterization*: XPS experiments were carried out in a UHV apparatus with a base pressure in the 10<sup>-10</sup> mbar range. Monochromatized Al Kα radiation was used for XPS measurements (1486.6 eV, 100 W). The detector was a SPECS PHOIBOS 150 hemispherical analyser mounting a 1D-DLD detector, the angle between the analyser axis and the X-ray source was 54.44°. The XPS spectra were measured with a fixed pass energy of 100 eV. The binding energy (BE) scale was calibrated setting the C1s signal of the substrate at 284.5 eV. In order to minimize air exposure and atmospheric contamination, samples were mounted on sample holder under dry nitrogen environment in a portable glove bag which was then connected to the fast-entry lock system of the XPS chamber. Spectral analysis consisted in a

linear background subtraction and deconvolution using a mixed Gaussian and Lorentzian lineshapes for each spectral component (See SI for further details)

*Synchrotron characterization:* The XAS/XMCD experiments have been performed on monolayer samples at the DEIMOS beamline<sup>[66]</sup> of the SOLEIL Synchrotron facility. The density of photon from the X-ray beam has been reduced to prevent any radiation damage. None have been observed. A magnetic field up to 30 kOe was applied along the photon propagation at variable angle with the normal to the surface. The reported XAS spectra have been acquired at the  $L_{2,3}$  edges of Mn and  $M_{4,5}$  edges of Tb edges under 30 kOe of magnetic field (applied parallel to the X-ray propagation vector) and using the two circular polarization (left,  $\sigma^+$  and right,  $\sigma^-$ ) at normal incidence ( $\theta = 0^\circ$ ) and rotating the sample plane  $\theta = 45^\circ$  respect to the X-ray propagation vector. XMCD is extracted as the difference  $\sigma^- - \sigma^+$ . The XNLD spectrum is the difference between vertically and horizontally polarized light absorption, both measured at  $\theta = 45^\circ$ . All the spectra have been normalized following the procedures described in earlier reports,<sup>[31,67]</sup> The field dependence of the XMCD signal for both the Tb  $M_5$  edge and Mn  $L_3$  edge were recorded at  $\theta = 0^\circ$  and  $45^\circ$ .

*Spin-valve preparation:* The typical vertical devices were realized following the procedure described on earlier reports<sup>[9,22]</sup> using the LSMO electrodes patterned over a STO substrate and functionalized with monolayers of  $Tb[Pc(PO_3Et_2)]_2$  with alkyl-phosphonate or  $\omega$ -iodo alkyl-phosphonate. Subsequently, a 40 nm thick molecular film of  $Ga_3$  was thermally evaporated on the functionalized LSMO surface. A cobalt electrode was then deposited together with an additional tunnelling barrier constituted by a 2 nm thick  $AlO_x$  layer at the  $Ga_3/Co$  interface in order to avoid cobalt inter-diffusion inside the OSC which could led to pinholes creation between the two electrodes.<sup>[50]</sup> **Using this strategy we prepared three identical devices with an active area of 1 mm x 0.1 mm.**

*Transport measurements:* Transport measurements were performed in 4-point probes configuration using a 2601 Keithley SMU to supply current and a 2182A Keithley nanovoltmeter for voltage reading. The instrumentation was interfaced with a Quantum Design PPMS in order to perform measurements at cryogenics temperatures (down to 2.5 K) and in presence of magnetic fields (up to 7 T). The reported characterization has been carried out subsequently in each of the three devices obtained on the STO substrates for each kind of OSV revealing similar qualitative behaviour.

**Supporting Information.** Supporting Information is available from the Wiley Online Library or from the author.

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**Spinterface tuning of a vertical spin-valve**, is achieved by the chemical functionalization of the spin-injecting electrode with a Terbium(III) bis(phthalocyaninato) monolayer grafted from solution. Comparing the results obtained with a similar device fabricated including a diamagnetic layer it has been possible to evidence that the SMMs film constitute an additional spin-scattering layer able to control directly the MR strength.

Keyword: Molecular spintronics.

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Title: **Tuning of a vertical spin valve with a monolayer of single molecule magnets**

ToC figure:

