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Self-Assembly of TbPc₂ Single-Molecule Magnets on Surface through Multiple Hydrogen Bonding

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The complexation between 2-ureido-4[1H]-pyrimidinone (UPy) and 2,7-diamido-1,8-naphthyridine (NaPy) has been used to promote the mild chemisorption of a UPy-functionalized terbium(III) double decker system on silicon surface. The adopted strategy allows to maintain the SMM properties of the system unaltered on the surface.

Introduction

Single-molecule magnets (SMMs)¹ are transition metal and/or rare earth ion(s)-based systems featuring magnetic bistability of purely molecular origin,^{2,3} coupled with size-related quantum effects. These peculiar properties make SMMs highly appealing for the development of novel spintronic devices.^{4–6} The optimization of the organization of these magnetic objects at the nanoscale is strongly required, with the specific assembling of molecules at the “spinterface” being a crucial point for the development of novel spin-transport based devices.⁷ The challenge is therefore to devise new strategies for the preparation of SMMs-based assemblies on surfaces with a careful evaluation of the substrate effect on their molecular properties.⁸

Among SMMs, bis(phthalocyaninato)lanthanide(III) double decker complexes (LnPc₂) have been widely studied as they couple elevated blocking temperatures with high thermal and chemical stability.^{9,10} In particular, sub-monolayer deposition of LnPc₂ on different substrates *via* sublimation under Ultra-High Vacuum has been largely investigated.^{11–16} Despite their stability, LnPc₂ magnetic behaviour was found to be influenced by the deposition process. Magnetization dynamics can be strongly affected^{13,17} or enhanced^{15,18} by the specific interaction with the substrate, thus strongly deviating from the characteristic SMM behaviour observed in bulk samples.

Perturbations on the double decker structure arising from molecule–surface interactions may also occur using wet-chemistry based grafting protocols: recently we reported that TbPc₂ covalently grafted on silicon surface *via* hydrosilylation reaction shows an enhancement of the magnetic bistability compared to the bulk.¹⁸ Photoelectron spectroscopy and theoretical analyses evidenced the non-innocent role played by this surface in stabilizing cationic [TbPc₂]⁺ species formed during the harsh conditions of the grafting reaction. This result highlights the needs for the development of alternative chemisorption approaches. So far, most of the activity of TbPc₂ assembling has been focused on the non-covalent anchoring through π - π interactions^{19–21} and *via* S-Au monolayer assembling.²² However, these protocols suffer from the inherent low stability of the resulting layer due to the weakness of the interactions involved. For instance, the efficiency of the TbPc₂ grafting on graphene is rather low, assuring the presence of the SMM in only few devices over the tested ones.²¹ To overcome this limitation as well as to introduce a more versatile anchoring strategy, herein we present a novel protocol based on the complexation between 2-ureido-4[1H]-pyrimidinone (UPy) and 2,7-diamido-1,8-naphthyridine (NaPy). This concept has been earlier applied to supramolecular polymers assembly/disassembly²³ as well as to the reversible hierarchical self-assembly of complex architectures on silicon surface.²⁴

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Fig 1. Sketch of the UPy-NaPy self-assembly mode used in this work for TbPc₂ anchoring on silicon surface (top left) and structures of the two components involved.

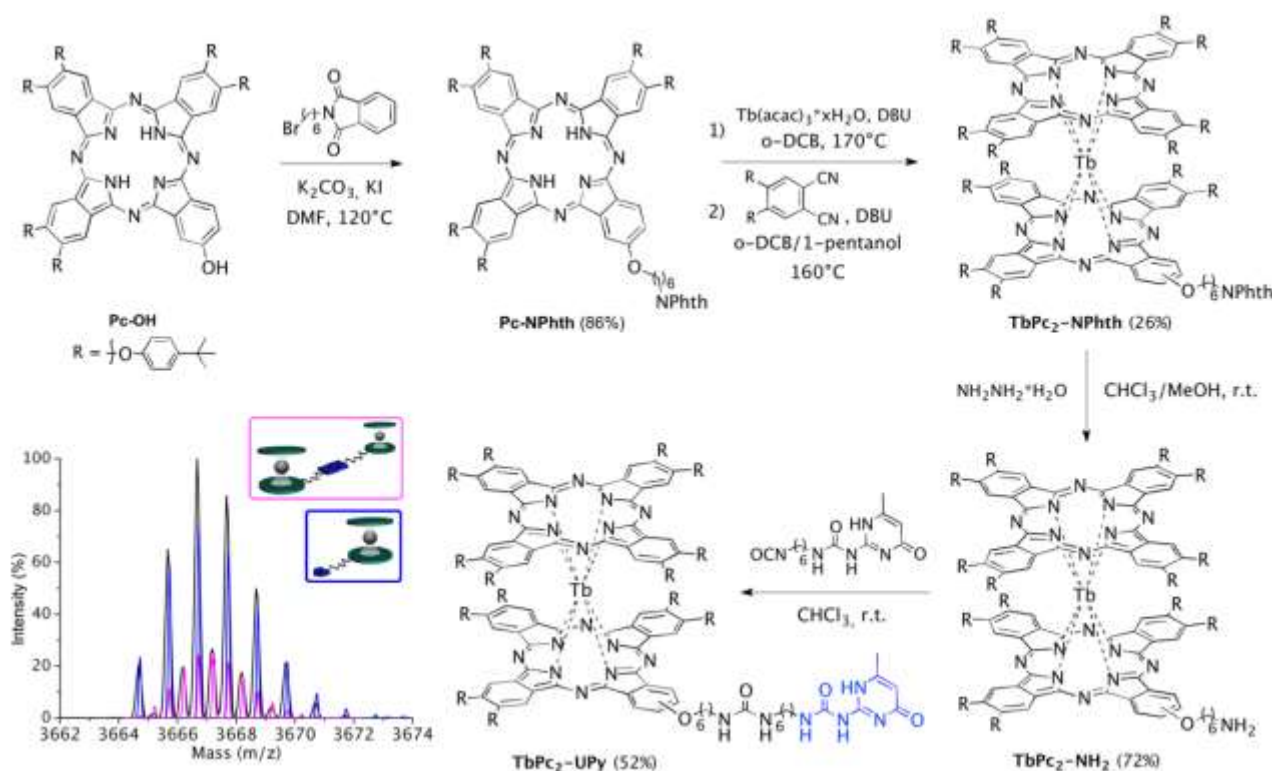


Fig 2. Synthesis (top and right) and High-resolution ESI Q-Orbitrap MS (bottom left) of **TbPc₂-UPy**. The experimental (black line), theoretical [M]⁺ (blue line) and theoretical [2M]²⁺ (magenta line) isotopic distributions are reported.

The functionalization of **TbPc₂** with UPy (**TbPc₂-UPy**) allows the reversible interaction^{25,26} with a complementary NaPy functionalized silicon surface, obtained by grafting of the terminal double bond-derivatized NaPy unit (**NaPy-DB**, Figure 1). The anchoring of SMMs is guaranteed by the strong association constant of the multiple hydrogen bonds UPy•NaPy complex.²⁷ Compared to the previously reported **TbPc₂** non-covalent anchoring, this approach can guarantee a long-term stability related to the hydrogen bond architecture, as well as the possibility to easily extend this strategy to different surfaces by chemically tailoring the NaPy structure.

RESULTS AND DISCUSSION

UPy-Functionalized **TbPc₂** Synthesis and Characterization

In the design of functionalized terbium(III) bisphthalocyaninato double decker, both homoleptic or heteroleptic complexes can be targeted.²⁸ In the first case, a minimum of two functionalities are introduced on the double decker scaffold.

If we consider UPy capability to form highly stable intramolecular homodimers,^{29–31} the presence of more than one UPy unit on the **TbPc₂** structure might hamper the subsequent UPy-NaPy heterodimerization process. Following these considerations, we focused on the synthesis of monofunctionalized heteroleptic complex **TbPc₂-UPy**. The 2-ureido-4[1H]-pyrimidinone unit was found to be unstable under the harsh reaction conditions for both phthalocyanine and **TbPc₂** synthesis, therefore its introduction after complex formation (post-functionalization) is mandatory. To insert a single functionality on the **TbPc₂** scaffold the complex was prepared starting from A₃B-type³² phthalocyaninato ligand **Pc-NPhth** (Figure 2). Since phthalimide, used as protecting group for the amine, is known to be unstable under phthalocyanine formation conditions,³³ this functionality was introduced *via* Williamson reaction of the mono-hydroxyl phthalocyanine **Pc-OH**. This asymmetric phthalocyanine was prepared following similar procedures reported in literature (See Scheme S1).^{34,35} The ether group was chosen for its stability under **TbPc₂** formation conditions, while the hexyl spacers guarantees a

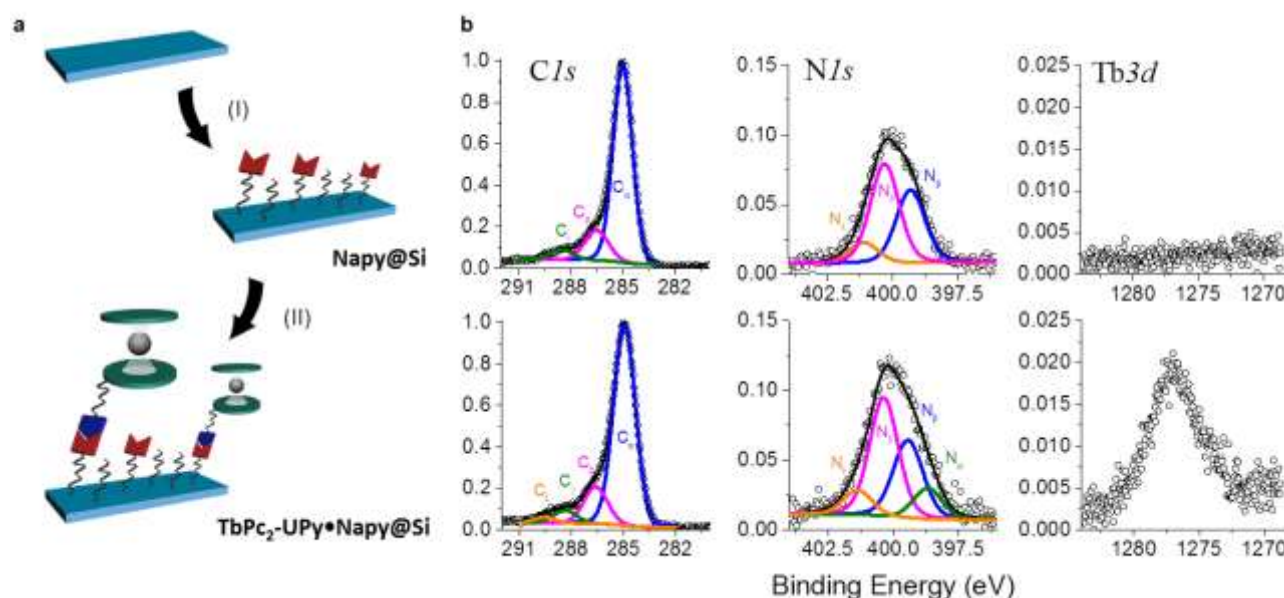


Fig 3. a) Sketched view of the **TbPc₂-UPy•Napy@Si** preparation (I) hydrosilylation reaction promoting the chemisorption of the dodecene/**NapyDB** mixture and (II) the subsequent **TbPc₂-UPy** incubation. b) High resolution XPS analysis of the C1s, N1s and Tb3d_{3/2} regions of the results samples from (I) and (II) respectively. In C1s and N1s spectra the results of the fitting analysis is reported (see ESI for details).

good accessibility of the amino group in post-derivatization reactions. The presence of bulky *tert*-butylphenol groups on peripheral positions increases Pcs solubility, reducing at the same time their tendency to aggregate. **Pc-NPhth** was then reacted with an equimolar amount of terbium acetylacetonate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The reaction afforded a half-sandwich complex, which was directly used as a template for the subsequent cyclotetramerization. The crude was treated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to partially oxidize the aliquot of reduced double decker formed during the reaction. **TbPc₂-NPhth** was deprotected with hydrazine hydrate affording heteroleptic double decker **TbPc₂-NH₂**. Being hydrazine a well-known reducing agent for these complexes, the product was initially obtained in its anionic form and then re-oxidized in air before purification. **TbPc₂-NH₂** was finally reacted with 2(6-isocyanatohexylamino-carbonylamino)-6-methyl-4[1H]-pyrimidinone affording **TbPc₂-UPy**. The resulting urea group guarantees the stability of the introduced functionality and its interference in the final hydrogen bond-driven UPy•Napy complexation can be considered marginal.

The formation of the designed heteroleptic TbPc₂ was confirmed by the presence of the molecular peak, with an isotopic distribution in agreement with the theoretical one, in the ESI Q-Orbitrap MS spectrum (Figure 2 bottom left). The

signal of the double charged **TbPc₂-UPy•TbPc₂-UPy** homodimer was detected under the dominant [M]⁻ molecular ion, remarking UPy tendency to dimerize.²⁹ **TbPc₂-UPy** was characterized also by MALDI-TOF spectrometry (Figure S1) and ¹H NMR spectroscopy (Figure S2). All the attempts to assign NMR signals were prevented by the typical perturbation of the signals caused by TbPc₂ magnetic dipolar term. UV-Vis spectrum (Figure S3) is characteristic of a double decker system, featuring an intense Q-band at 682 nm, two broad absorption bands, attributed to radical Pc ligands, at 490 and 919 nm and a split Soret band around 300 nm. The shoulder of the Q-band at 615 nm has been reported to be due to the weak π-π interactions between the two Pc ligands.³⁶

Magnetic properties of **TbPc₂-UPy** were tested in the bulk *via* standard DC magnetometry. Hysteresis measurements were performed at 3 K with a Quantum Design PPMS setup equipped with a Vibrating Sample Magnetometer (VSM) unit (see Figure 5). As clearly observable, the introduction of the UPy functionalization on the double decker scaffold does not alter significantly the SMM behaviour of the complex. This is confirmed by AC susceptometry measurements (see Figure S4-S7) revealing a linear trend in the ln(τ) vs. 1/T plot at high temperature (above 35 K) that is in line with the expected relaxation behaviour of a TbPc₂ system due to a thermally-assisted process.^{9,10,37} Below this temperature, relaxation is

dominated by resonant tunnelling when measuring without an external magnetic field while the thermally activated process is maintained to lower temperature when measuring in a 5 kOe static field. The best fit parameters for the Arrhenius behaviour $\tau_0 = 5.8 \cdot 10^{-12}$ s and $U_{eff}/k_B = 760$ K are in line with the expected ones for $TbPc_2$.^{9,10}

Silicon Functionalization and $TbPc_2$ -UPy Self-Assembly.

The anchoring of $TbPc_2$ -UPy on silicon has been obtained with a two-steps procedure (Figure 3a), see ESI for details. Initially H-terminated Si(100) has been treated at 453 K with a 4:1 mixture of dodecene and 2-(10-Undecenylamino)-7-acetylamino-1,8-naphthyridine (**NaPy-DB**), synthesized according to a literature procedure.³⁸ Grafting of these molecules on the freshly etched silicon wafers occurs *via* thermal hydrosilylation of the double bond.^{39–41} Then, $TbPc_2$ -UPy was assembled on the NaPy functionalised surface (**NaPy@Si**) by dipping the slab in a dilute $TbPc_2$ -UPy solution ($CHCl_3$, 10^{-5} M).

X-ray photoelectron spectroscopy (XPS) was used to monitor each reaction step by the analysis of C1s, N1s and $Tb3d_{3/2}$ XPS regions (Figure 3b). These regions were also used to evaluate the atomic compositions of the $TbPc_2$ functionalised surface (Table 1).

Table 1. Atomic concentration estimated by XPS

	N	C	Tb	C/N	N/Tb
NaPy@Si	5.9	94.1	-	15.9	-
$TbPc_2$-UPy•NaPy@Si	7.4	92.1	~0.2 ^a	12.4	~37

^a Tb value has been corrected assuming that $TbPc_2$ is confined on the top of the layer having 0.5 nm thickness.⁴²

In the **NaPy@Si** assembled system the N1s region features two main components of equal intensity (Figure 3b, top-middle) at 400.3 eV and 399.2 eV (49.5% and 40.1% respectively) assigned to the two amidic nitrogen atoms and to the naphthyridine ring respectively.^{43,44} In addition a third component at 401.6 eV (10.4%) is present due to N atoms protonated or forming hydrogen bond.^{45,46} The line shape of C1s band is consistent with the chemical formula of the grafted NaPy molecule (Figure 3b, top left). The peak deconvolution figures out a main component at 285.0 eV (82%), related to the aliphatic carbons of the hydrocarbon chain, and a broad shoulder component around 286.5 eV (12.5%), due to carbon atoms bonded to N and O atoms. At 288.3 eV (5.3%) is present another component due to the carbon of amide groups (see Table S1 and S2 for fitting details for N1s and C1s respectively). The C/N ratio of **NaPy@Si** (Table 1) is in agreement with the presence of a mixed NaPy/dodecene layer with a NaPy percentage on the surface of about 25%. The presence of $Tb3d_{3/2}$ signal is diagnostic of the formation of the **$TbPc_2$ -UPy • NaPy@Si** complex on the surface. The $Tb3d_{3/2}$ component is the only one suited to evaluate the presence of Tb due to the overlap of the $3d_{5/2}$ component with the KVV Auger peak of C, while the $Tb4d$ peak is hidden by the Si2s signal. In particular, the energy of $Tb3d_{3/2}$

peak at 1277.0 eV (Figure 3b, top right) is consistent with the presence of a Tb^{3+} system.^{18,47} Unfortunately, due to the large difference between kinetic energies of $Tb 3d_{3/2}$ and N1s photoelectrons the evaluation of Tb concentration is strongly dependent on both Tb in-depth distribution and adventitious carbon overlayers (see ESI). For this reason, only qualitative information can be inferred from the $Tb3d_{3/2}$ band. However, by assuming a model in which $TbPc_2$ moieties are confined on the upper part of the layer according to the scheme on Figure 3a, it is possible to find an estimated value of Tb atomic content (Table 1). After the assembly of **$TbPc_2$ -UPy** on the **NaPy**-functionalized surface, instead of the expected N/Tb ratio of 26, corresponding to the complete reaction of **$TbPc_2$ -UPy** with all the **NaPy** groups present on surface, a larger value was found (37). Within the limits of our approximations (the adopted XPS sensitivity factor for Tb depends on the layer organization, see ESI), this suggests that about 1 out of 4 NaPy molecule is directly connected to **$TbPc_2$ -UPy**. A more detailed analysis of the N1s region of **$TbPc_2$ -UPy•NaPy@Si** (see Figure 3b and Table S1) gives further indications on $TbPc_2$ complexation. Indeed the fitting procedure in the region of N1s band shows the presence of the three main components at 399.3 eV, 400.3 eV and 401.4eV already present in the same spectral region for **NaPy@Si**. Moreover, in this self-assembled system a fourth component centred at 398.4 eV is present and can be assigned to the nitrogen atoms of the $TbPc_2$ moiety of **$TbPc_2$ -UPy** (Figure 3b, middle bottom). This assignment is supported by comparison with XPS data of drop-casted alkyl chain functionalized $TbPc_2$ molecules on Si surface (Figure S8). The N1s region of this reference sample featuring only the N atoms of the Tb-double decker shows a main peak centred at 398.3 eV,^{18,48} while low intensity components observed at higher B.E. are usually assigned to the satellite peaks.^{48,49} The C1s region (Figure 3b, bottom left) of **$TbPc_2$ -UPy•NaPy@Si** shows only little differences compared to **NaPy@Si**. The typical C components of the Pc rings (pyrrole carbons at 286.5 eV and its shake-up at 288.5 eV)^{48,50} overlap with C components of NaPy moiety. However, we notice that a low band at 299.3 eV is evidenced, diagnostic of the presence of ureidic carbon atoms in the UPy chain.

$TbPc_2$ -UPy•NaPy@Si structural and magnetic characterization

The $TbPc_2$ -functionalized surface has been investigated by using X-ray Absorption Spectroscopy (XAS) based techniques at the DEIMOS beamline at SOLEIL synchrotron (France)⁵¹ to evaluate the orientation of the SMM unit and to assess if the magnetic behaviour^{11–16} is retained upon assembly. Linear and circular polarization-dependent X-ray absorption experiments have been carried out profiting of the element selectivity of the XAS-based technique that guarantees to probe selectively molecular properties by focusing the measurements at the $M_{4,5}$ absorption edges of Tb using Total Electron Yield (TEY) detection mode.⁵² From the estimated XAS edge-jump we can assume that the silicon surface is covered by 0.8 monolayers of equivalent $TbPc_2$.¹⁸ The absorption spectra recorded at 2.5 ± 0.5 K with horizontally (σ^H) and vertically (σ^V) polarized

light were measured with k X-Ray propagation vector at 45° with respect to the normal n to the surface. Figure 4 reports the extracted X-ray Natural Linear Dichroism (XNLD) of the Tb $M_{4,5}$ edges estimated as the difference ($\sigma^V - \sigma^H$). The normalization of the XNLD with respect to the isotropic spectrum ($\sigma_{\text{iso}} = 1/3 \sigma^V + 2/3 \sigma^H$) indicates, following the analysis method described elsewhere,^{13,18,53} that less than 15% of the molecules are preferentially oriented in a lying down configuration (with the Pc rings parallel to the surface). This partial disorder level can be attributed easily to the elevated mobility of the alkyl chains present in the **TbPc₂-UPy•NaPy** system.

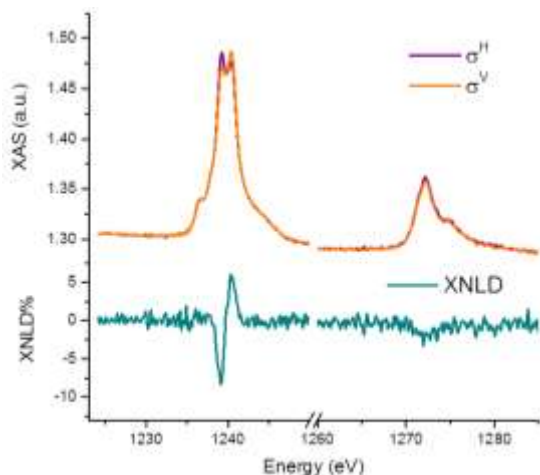


Fig. 4. XNLD measurements for **TbPc₂-UPy•NaPy@Si** performed at 2.5 K under a 30 kOe magnetic field to enhance TEY sensitivity. XNLD (dark green line) is obtained from the difference of the horizontally (σ^H , purple line) and vertically (σ^V , orange line) polarized light.

X-ray absorption experiments under a 30 kOe magnetic field parallel to the X-ray light propagation vector, and left (σ^+) and right (σ^-) circularly polarized light allowed also to extract the X-ray Magnetic Circular Dichroism (XMCD) defined as ($\sigma^- - \sigma^+$). In Figure 5a is reported the XMCD spectra acquired at 2.5 ± 0.5 K for the **TbPc₂-UPy•NaPy@Si** system. The detected features and the intensity of the dichroic signal are in line with the ones expected for a Tb^{3+} system characterized by total angular momentum $J = 6$, $g_J = 3/2$ with a powder-like behaviour. Thanks to the field dependence of the maximum of the XMCD in the Tb edge, normalised with the isotropic spectra, it is possible to follow the magnetization dependence of the self-assembled complex with the magnetic field (Figure 5b) revealing clearly that the **TbPc₂** behaviour is essentially unaltered with respect to the bulk sample measured in similar conditions. The adopted procedure allows to transfer unaltered the SMMs properties to the Si surface, an uncommon result for a monolayer of **TbPc₂** which properties are often affected by the nanostructuring procedure excluding non-covalent interaction of pyrene-functionalized units with graphene substrates. The multi-technique characterization protocol we adopted suggests that the multiple hydrogen bonding strategy can allow a mild and controlled chemisorption of the molecular layer that could be extended also to other surfaces in the future allowing in all

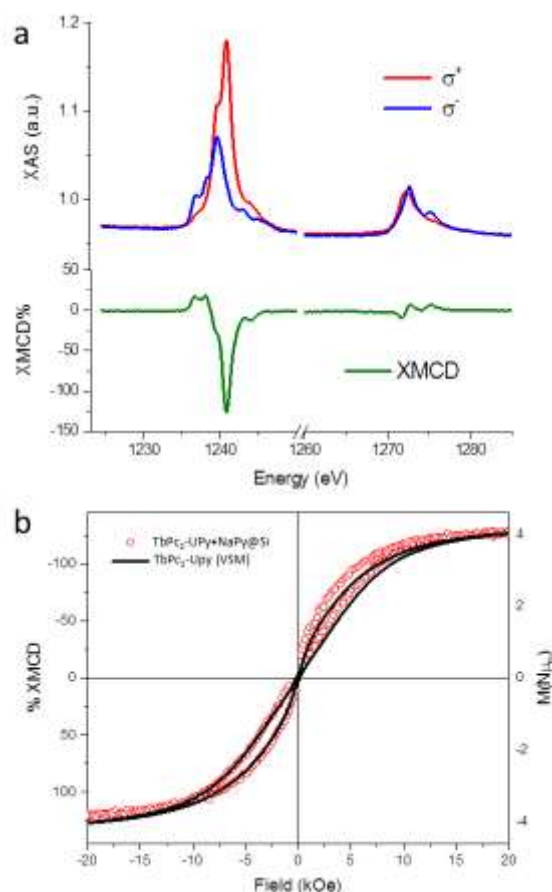


Fig. 5. XMCD measurements (a) and field dependence of Tb M_5 edge XMCD maximum (b) for **TbPc₂-UPy•NaPy@Si** monolayer measured at 2.5 ± 0.5 K. XMCD (green line) is obtained from the difference of the left (σ^+ , red line) and right (σ^- , blue line) polarized light. The magnetic characterization of the monolayer (red circles) compared with VSM data (black line) measured at 3 K. Both measurements have been obtained with 50 Oe/s scan speed. A more precise comparison is obtained by calculating in both cases the hysteresis opening for both curves referred to the saturation field of 30 kOe.

cases an efficient decoupling of the SMM core from the surface.

Conclusions

A two-steps protocol for the anchoring of **TbPc₂** SMMs on silicon surface is presented, applying the **UPy•NaPy** self-assembly procedure to surface modification. To this purpose, a heteroleptic **TbPc₂-UPy** was synthesized and anchored on a **NaPy** covalently decorated silicon substrate (**NaPy@Si**). The formation of Si–C bonds *via* hydrosilylation reaction guarantees an elevated stability of the **NaPy** system, while the multiple H-bond system ensures robust **TbPc₂** anchoring. The whole protocol assures the efficient deposition of intact **TbPc₂** on silicon wafers, as proven by extensive XPS analyses. XAS-based techniques evidenced that the SMM unit is forming a submonolayer of unaligned molecules that maintain the behaviour of the pristine bulk system without being influenced by the presence of the silicon substrate. The assembling strategy proposed here can be used in the future for the development of novel spintronic devices in which the **TbPc₂** layer can be operated independently to the underlying surface.

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Notes and references

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Author Contributions: The manuscript was written through contributions of all authors. MM and ED designed the project. AP, MT and FB made the synthesis, MS achieved the mass spectrometry characterization; MM performed the bulk magnetic characterization; CT, AEG and GGC prepared the self-assembled monolayers and performed the XPS characterization, MM, LP, IC, EO, PO and PS performed the synchrotron experiments. All authors have given approval to the final version of the manuscript.

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