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Molecular order in buried layers of TbPc₂ Single-Molecule Magnets detected by torque magnetometry

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Structural order and molecular orientation play a fundamental role in determining the physical properties of functional molecular materials used in devices such as organic field effect transistors and photovoltaic cells.^[1] Similarly, for the development of new molecule-based devices like molecular spin-valves, molecular orientation needs to be deeply investigated and controlled. Some molecular magnetic materials may exhibit structural polymorphs which differ dramatically by the magnitude^[2] or the sign^[3] of the exchange coupling interaction. Single-Molecule Magnets are strongly sensitive to structural order^[4] and a different orientation of the magnetic anisotropy can allow a different coupling with a functional substrate thus altering the magnetism of the hybrid molecular system in addition to its transport properties.^[5]

The crystallinity and the texture, i.e. the preferential crystallographic orientation, of thermally deposited thin films can be tuned by choosing the deposition conditions, like the deposition rate, the substrate type and its temperature during the film growth.^[1b,1d,6] Weakly interacting substrates, such as amorphous or disordered oxides, induce an almost standing orientation of planar aromatic molecules where the conjugated system is nearly perpendicular to the substrate, favouring π interactions.^[1b, 7] On the contrary, crystalline metallic substrates, such as the Au(111) surface, can strongly interact with electron rich rings favouring a flat (lying) arrangement of the aromatic system;^[4b,8] however the surface reactivity, or other factors such as substrate polycrystallinity or roughness, can decouple the first monolayer (ML) from the rest of the film, resulting in the loss of the lying orientation within a few MLs.^[4b,9] Some inorganic and organic materials can be employed to modify the order of the molecular overlayer through a templating effect, thus tuning the crystal orientation to suit a specific application.^[10] Among the large class of conjugated organic molecules that can act as templating agents, the archetypal templating molecule perylene-3,4,9,10-tetracarboxylic dianhydride, PTCDA, is particularly useful to pin planar aromatic systems, such as phthalocyanines (Pc),^[1d,11] in the lying configuration.

The information about the order and orientation is not always easily accessed in soft materials. Indeed, XRD measurements are very challenging when crystallites are smaller than about 10-20 nm and only provides average lattice parameters across the entire film thickness.^[12] Optical methods such as ellipsometry^[13] have been used to characterize the average orientations of organic films,^[14] but are less efficient in the case of multi-layered structures, including those that are based on a single type of molecule but adopt different properties as a function of thickness.^[12, 15] In these conditions detailed information about the order of a specific layer of anisotropic molecules can be obtained from a series of samples of different thickness using the element and surface selectivity of synchrotron radiation.^[4b] Efforts have been made to develop lab-based techniques to access the orientation and aggregation of Pc using electron paramagnetic resonance,^[11a] but again spatial selectivity is lacking, while local probes such as transmission electron microscopy provide detailed information but require extensive and aggressive sample preparation.^[16]

If the investigated molecule, or one isostructural analogue, possesses magnetic anisotropy, the orientation can be detected by measuring the torque exerted by an external magnetic field. Sensitive torqueimeters are based on miniaturized cantilevers and on the capacitive detection of the deflection (see Figure S1a). Cantilever torque magnetometry (CTM) is thus a simple and relatively inexpensive technique, usually employed to investigate the magnetic anisotropy of single crystals.^[17] Here we exploit at best the high sensitivity of the technique to investigate the growth of films of the widely investigated Single Molecule Magnet Tb^{III} bis-phthalocyaninato neutral

complex (TbPc_2) on different substrates. The molecular structure of TbPc_2 is reported in **Figure 1a**: two phthalocyaninato rings are coordinated to a Tb^{III} ion in a double-decker structure that is known to present a very large magnetic anisotropy with the easy axis of magnetization perpendicular to the plane of the Pc ligands (pink axis in **Figure 1a**). A detailed depth-dependence of the molecular orientation of the film has been accessed here by depositing pure films or intercalating ultra-thin layers of TbPc_2 during the growth of an isomorphous YPc_2 film, suggesting that the CTM technique can outperform much more expensive and time-demanding techniques based on synchrotron radiation.

Figure 1. a) Molecular structure of MPc_2 ($M=\text{Tb}$ or Y). Colour code: M-pink (Tb) or grey (Y), C-black, N-blue, H omitted for clarity. The pink axis is the easy direction of the magnetization. b) Representation of the model distribution of tilt angles α of the TbPc_2 easy axis in a sample,

characterized by an average angle α_0 with respect to the normal and an isotropic in-plane orientation. The spread of α values is modelled by a Gaussian distribution with standard deviation σ . The magnetic field $\mathbf{B}$ forms an angle θ with the substrate. c) Schematic representation of the structure of investigated samples (violet spheres: TbPc₂, grey spheres: YPc₂). The values of σ extracted from CTM data on the different substrates are reported as histograms on top of the scheme of each investigated multilayer. Vertical and horizontal filling patterns of the histograms represent the *standing* ($\alpha_0=90^\circ$) and *lying* ($\alpha_0=0^\circ$) orientation used in the fit, respectively.

The classical definition of the torque moment ($\boldsymbol{\tau}$) that is exerted on a sample inside a homogenous magnetic field ($\mathbf{B}$) is the vector product between the magnetization ($\mathbf{M}$) and $\mathbf{B}$. Taking into account that in a capacitive-detection setup only one component of $\boldsymbol{\tau}$ can be detected, say τ_y in the XYZ laboratory reference frame, we can write:

$$\tau_y = M_z B_x - M_x B_z = B^2 \sin\varphi \cos\varphi (\chi_{zz} - \chi_{xx}) \quad (1)$$

where χ is the magnetic susceptibility tensor and φ is the angle between $\mathbf{B}$ and the projection of the easiest direction of magnetization in the XZ plane, which can be varied by rotating the cantilever along the Y axis inside the magnetic field. In Figure S1 we report a sketch of the experimental setup; note that the angle θ of rotation, corresponding to the angle of the magnetic field with the plane of the substrate (**Figure 1b**) only in special cases coincides with the φ angle of equation (1). The period of the torque signal is reduced to 180° (unlike in permanent magnets) and the zero points corresponds to $\mathbf{B}$ being parallel to the axis of easy magnetization (easy zero) or perpendicular to it (hard zero). However, equation (1) is only valid if $\mathbf{M}$ is linear with $\mathbf{B}$, i.e. for a paramagnet in a weak magnetic field when the thermal energy is sufficiently larger than the Zeeman energy. The application of stronger fields deforms this torque profile inducing a rapid variation of τ when the field is applied along the direction of hard magnetization as shown in **Figure 2a**, reporting the simulation of the torque in the non-linear regime for a film of collinear TbPc₂ molecules in a *standing* (easy anisotropy axis parallel to the film plane, black line) and in a *lying* configuration (easy anisotropy axis perpendicular to the film plane, grey line). The simulations were obtained using the Spin Hamiltonian:

$$\mathcal{H} = g_L \mu_B \hat{\mathbf{J}} \cdot \mathbf{B} + \sum_{k=2,4,6} B_k^0 \hat{\mathcal{O}}_k^0 \quad (2)$$

in which the crystal field (CF) effects are described by the O_k^0 Stevens operators acting on the ground $J=6$ multiplet of the 7F_6 state of Tb^{III} with B_k^0 parameters taken from literature data^[18] (see ESI for a more complete set of calculations showing a weak dependence from the CF parameters as long as the strong uniaxial character of the system is maintained).

Figure 2. a) Simulation of the torque profile of a $TbPc_2$ film in a perfectly *standing* (black line) and *lying* (grey line) orientation. In the other panels the experimental (symbols) and fitted curves (lines) for all the investigated samples depicted in Figure 1 at $T=2K$ and $B=12T$. Data renormalized to the height of the peak of a perfect lying configuration.

Figure 2b reports the experimental data recorded at $T=2 K$ and $B=12 T$ for films of $TbPc_2$ evaporated on three different substrates: Au(111) (red), glass (blue) and PTCDA (green). The height of the film, estimated by atomic force microscopy (AFM) measurements, was 80(10) nm on Au and glass and 110(15) nm on PTCDA. Comparing the experimental data with the simulations in **Figure 2a** it is trivial to identify at first glance that the preferential order of the molecules is *lying* on PTCDA and *standing* on glass and Au. A templating effect of PTCDA forcing the Pc to lie flat on the substrate was previously reported for simpler MPc and $TbPc_2$, though the templating efficiency was quickly reduced with increasing film thickness for $TbPc_2$.^[11a,13b] The presence of a distribution in the orientation of $TbPc_2$ molecules in the films is evidenced in our experiment by the shape of the measured curves, which show a rounded feature of the peaks compared to the simulations in **Figure 2a**.

To have an estimation of the degree of the disorder we assumed the model distribution depicted in **Figure 1b**. The angular distribution of the molecules on the substrate is assumed to be isotropic in the plane of the substrate with a most favourable orientation defined by the polar angle α_0 that the easy axis forms with the normal to the substrate. A Gaussian distribution centred on α_0 characterized by a standard deviation σ is then assumed. To simulate the torque we have sampled a hemisphere (see Figure S3) taking into account also the azimuthal angle β defining all possible orientations of a uniaxial system like TbPc₂ with respect to the magnetic field and the Y direction (see Figure S4). The calculated torque curve for each set of α and β was then multiplied by a weight factor that depends only on $|\alpha - \alpha_0|$ and σ (see Figure S5). Data are satisfactorily reproduced (solid lines in **Figure 2b**) by assuming $\alpha_0 = 0^\circ$ for molecules on PTCDA and $\alpha_0 = 90^\circ$ for Au and glass with the corresponding relatively narrow σ ($5^\circ < \sigma < 12^\circ$) reported in Figure 1c; a scale factor f_{sc} was used to compensate for deviations from the nominal thickness of TbPc₂ layers (see experimental). Letting α_0 free to vary does not improve the fit and best-fit values are, within error, coincident with 0° and 90° (see ESI and Figure S6 for additional simulations).

The successful characterization of films of pure TbPc₂ confirmed the spontaneous standing orientation typical of thick films on Au and glass.^[4a,b] The observed σ for films grown on PTCDA, of the order of 10° , actually corresponds to an average deviation from the lying orientation of $\pm 8^\circ$ and evidences an exceptionally strong templating effect of the organic layer, in contrast to recent findings that showed a significant rearrangement of TbPc₂ molecules.^[13b] To have a clearer picture of the templating effect and to provide a *proof-of-concept* of the exceptional potentialities of the CTM technique we realized multi-layered deposits based on a YPc₂ matrix and containing a buried layer of TbPc₂ embedded in the Y-based film at different height, thus using TbPc₂ as a local probe of the orientation at different depths in the film. In fact, even if YPc₂ molecules carry an unpaired electron, their response is fully isotropic and no torque is exerted on them (see Figure S7).

We analysed four samples, whose structure is sketched in Figure 1c, named in relation to the position of the TbPc₂ layer (see Figure 1c): TOP (≈ 10 nm of TbPc₂ on top of ≈ 50 nm of YPc₂), MIDDLE (≈ 17 nm of TbPc₂ on top of ≈ 20 nm of YPc₂), BOTTOM (≈ 5 nm of TbPc₂ covered by >20 nm of YPc₂) and ULTRA BOTTOM (≈ 3 nm of TbPc₂ covered by >25 nm of YPc₂). The experimental results and simulations using the model previously developed are reported in **Figure 2**, while the corresponding best-fit σ are gathered in Figure 1c on top of the corresponding film structures. In all samples grown on glass the molecules assume a standing configuration that is maintained from a few nm up to 80 nm. The values of σ , reported in **Figure 1b**, show a clear trend, σ decreasing on increasing the distance from the substrate. The standing configuration is also

characteristic of molecules on Au for all the investigated samples, except for the ULTRA BOTTOM that had no torque signal at all. As the torque signal for the BOTTOM sample indicates a preferential standing configuration we concluded that the reorientation from the lying orientation typical of mono and bilayers of TbPc₂ on Au occurs in very few layers,^[9b] as observed in CuPc films on polycrystalline Au,^[9a] with a disordered phase. Notice that in the non-linear regime of torque detection the simultaneous presence of ordered lying and standing orientations could be detected (see Figure S8).^[17b] Also the standard deviation σ supports this conclusion since it decreases on increasing the distance from the substrate.

The case of the PTCDA substrate is completely different. All samples show clearly the preferential lying orientation, even when only the top layer is sampled. Only a mild weakening of the template effect on distance from the substrate is observed, in agreement with the result for the pure TbPc₂ film, but in contrast with previous finding.^[13b]

Being this the first report of CTM use to investigate molecular order in evaporated films, we employed synchrotron radiation at the M_{4,5} edge of Tb to validate the procedure by recording the natural linear dichroism (XNLD) in a few representative TbPc₂ films on gold and PTCDA. Stark differences between the absorption cross-sections in the directions perpendicular and parallel to the TbPc₂ phthalocyanine plane result in a clear dichroic signature of both preferential orientations of the molecular assemblies (Figure S11a). XNLD, defined as the difference of absorption between vertically and horizontally polarized light ($\sigma_V - \sigma_H$) is reported as the percentage of the edge jump of the isotropic spectrum,^[19] $\sigma_{\text{Iso}} = (1/3 \sigma_V + 2/3 \sigma_H)$.^[20] As CTM measurements evidenced a rapid reorientation of TbPc₂ molecules on gold we studied by XNLD three samples: a 5 nm TbPc₂, a 13nm TbPc₂ on 20 nm YPc₂, and a 100nm TbPc₂ film. Due to the sampling depth limit of about 5 nm of the Total Electron Yield detection mode, these *ex situ* prepared films were not capped with YPc₂. The samples are therefore not directly comparable to those of the CTM investigation but can be considered representative of the BOTTOM, MIDDLE and TOP structures discussed before, based on the distance from the substrate of the probed layer. To confirm the long range order templating effect of PTCDA detected by torque magnetometry we recorded XNLD spectra of a pure TbPc₂ film of 20 nm and a 10 nm TbPc₂ layer sublimated on 52 nm YPc₂ film both deposited on a 20 nm PTCDA layer on a Si(100) wafer covered by native oxide, which are equivalent to the MIDDLE and TOP structures on PTCDA studied by CTM.

In **Figure 3** we summarize the results, while spectra of all investigated samples are reported in Figures S9 and S10. The two samples exhibit XNLD spectra of opposite sign that, according to literature,^[4b] indicate preferential standing orientation on gold and lying orientation on PTCDA, in agreement with the conclusions of the CTM study. A trend in the magnitude of the dichroic signal

can be observed in the films on gold, as seen in **Figure 3b**, where the % of dichroic signal at its maximum is reported. For comparison literature values for an *in situ* deposited monolayer on Au(111) and a thick film on aluminium foil from our previous investigations are also reported.^[4b] A qualitative agreement is observed though the XNLD intensity for films on PTCDA is significantly lower than that of a monolayer on gold. Sample calculations using the model distribution of **Figure 1b** and the XAS calculated cross-sections^[4b] (Figure S11a) show that XNLD is significantly reduced only when σ is larger than 15° (Figure S11b). This indicates that at the surface the lying orientation induced by PTCDA is less robust than the spontaneous standing configuration.

Figure 3 a) XAS spectra at $M_{4,5}$ Tb edge of 10 nm TbPc₂ on 52 nm YPc₂ on 20 nm PTCDA/Si (TOP structure) in vertical and horizontal polarization with the substrate tilted at 45° from the photons direction, and XNLD spectrum (green) of the same sample compared to the XNLD spectrum (red) of 100 nm TbPc₂ film on gold. b) Maximum value of XNLD for different positions of the TbPc₂ layer in the film on different substrates (colour code in the legend). The open squares refer to literature data taken in the same conditions.^[4b]

In conclusion, we have demonstrated that CTM can be successfully employed to detect the molecular orientation of the archetypal single molecular magnet TbPc₂. The selectivity of the

technique enables unprecedented depth resolution of the structure and shows both relaxation to a *standing* orientation following disordered interfacial layers on Au and a robust templating to a *lying* orientation on PTCDA. This insight into the distinct behaviour of a buried interface compared to the bulk sample is particularly important in the context of molecular spintronics, where the “spinterface” plays a key role,^[21] and our characterisation methodology can be generalised to a wide range of topical materials. The only requirement is the existence of an anisotropic paramagnetic analogue, which is the case for many metallo-macrocycles systems.^[22] Going beyond materials characterisation, recent work on effect of gas adsorption on the spin states of porphyrins^[23] highlights that torque magnetometry could also be used as a dynamic sensing.

Experimental Section

Microcrystalline powders of the neutral TbPc₂ and YPc₂ complexes were prepared following procedure of Weiss et al.^[24] Borosilicate glasses were sonicated in acetone and then in isopropanol, dried with nitrogen and then used as a substrates; the same procedure was used for cleaning Si(100). Polycrystalline gold films (≈ 100 nm) with preferential (111) orientation were thermally evaporated on glass substrates at a pressure of about 10^{-6} mbar and at a rate c.a. $2 \text{ \AA}/\text{min}$ monitored by a quartz microbalance (QCM). The PTCDA films (≈ 20 nm) were deposited on glass or Si(100) by Organic Molecular Beam Deposition with a Kurt J Lesker SPECTROS system at pressure $< 10^{-6}$ mbar and a rate of $0.2 \text{ \AA}/\text{s}$. Depositions of the YPc₂ and TbPc₂ layers were obtained by using a home-built twinned sublimation setup allowing to deposit them on the same substrate without moving the sample and without breaking the vacuum. Powders were degassed for several days before sample preparation. The base pressure during the sublimation was $< 10^{-6}$ mbar and the deposition rate was about $0.2 \text{ \AA}/\text{min}$, as measured by QCM before exposing the substrates. The thickness of each deposition was checked by AFM imaging (NT-MDT P47-PRO) on a shadow masked redundant sample. Scale factors in the simulation of the torque data provided effective thickness in reasonably good agreement ($\pm 30\%$) with AFM evaluations. A CuBe cantilever was employed in an Oxford Instrument MAG2000 platform equipped with a 12 T magnet. The capacitance was detected with an Andeen-Hagerling 2550A automatic capacitance bridge.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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Cantilever Torque Magnetometry is used to elucidate the orientation of magnetic molecules in **thin films**. The technique allows depth-resolved investigations by intercalating a layer of anisotropic magnetic molecules in a film of its isotropic analogues. The proof-of-concept is here demonstrated with the single-molecule magnet TbPc_2 evidencing also an exceptional long range templating effect on substrates coated by the organic molecule PTCDA.

Keywords: Magnetic anisotropy, Terbium phthalocyanine, thin films, cantilever torque magnetometry, synchrotron radiation

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Molecular order in buried layers of TbPc_2 Single-Molecule Magnets detected by torque magnetometry

Abstract

The organization of magnetic molecules in 3D architectures is a fundamental prerequisite for the development of devices for molecular spintronics and quantum computation based on molecules. Here we show that Cantilever Torque Magnetometry (CTM) can be used to elucidate the orientation of magnetic molecules in thin films. The high sensitivity and selectivity furthermore enables us to identify any changes of orientation as a function of depth within the film. The strength of the methodology was demonstrated in the investigation of the molecular orientation in Terbium Phthalocyaninate (TbPc_2) films grown by thermal sublimation on three different substrates. The magnetic anisotropy of TbPc_2 is used as a local probe to map the orientation of a thin layer of molecules intercalated in a YPc_2 matrix at different distance from the substrate. The results, confirmed by synchrotron investigations, show that the standing orientation is favoured on glass and does not depend much on the height in the film, while on Au the lying configuration observable by scanning tunnelling microscopy in monolayers is already lost for a film thickness of 3 nm. Moreover, the lying orientation is adopted on a film of the conjugated organic molecule perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and, in contrast to what happens on gold, the strong templating effect of PTCDA is remarkably effective also in films of about 100 nm.