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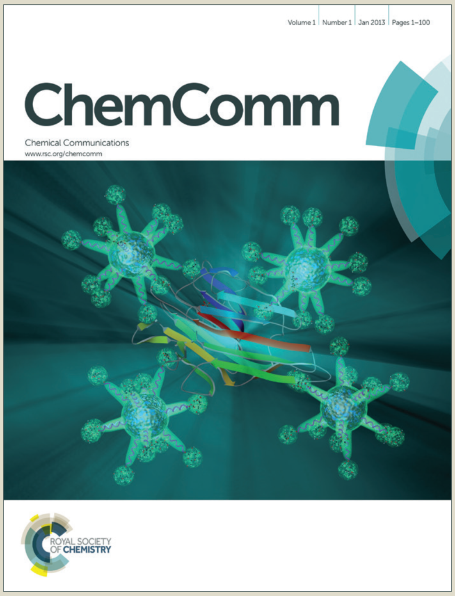

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Experimental and theoretical evidences that electrostatics governs easy-axis orientation in Dy^{III}-based molecular chains

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Magnetic slow relaxation is observed on a Dy^{III}-based molecular chain and magnetic easy-axis is determined via single-crystal magnetometry. ab initio calculations confirm its orientation and highlight that the latter is governed neither by coordination polyhedron symmetry nor by chain direction but rather by single-ion electrostatic environment, a feature that is confirmed by similar theoretical analysis on other Dy^{III} chains.

The design of materials that can retain magnetic information is an important issue for the scientific community.[1] Among all magnetic materials, one-dimensional (1-D) molecular chains form a peculiar class of compounds, not only because of their structural elegance and rareness, but also because they can be used as textbook examples to validate theories or concepts. For example non-compensation of the magnetic moment in 1-D magnetic edifices alimented the whole theory of magnetic exchange interaction[2] and combination of 4f ions with radical ligands permitted several achievements such as the verification of Villain's conjecture[3] or the presence of Glauber's dynamics in molecular chains.[4] Such magnetic material can be seen as an assembly of magnetic sub-units that interact more or less strongly.[5] The challenge is then to untangle their contribution to the global behaviour of the compound as weak interactions between the building blocks can affect the magnetic relaxation.[6] Single-crystal rotating magnetometry has experimentally permitted to provide figures to sustain these assumptions and confrontation with ab-initio calculations has been found to be particularly fruitful allowing for a rationalization of the observed behaviours.[6a, 7]

In ethylene glycol (EG), the reaction of Dy-based precursors (either $[Dy_6O(OH)_8(NO_3)_6(H_2O)_{12}]\cdot 2NO_3\cdot 2H_2O)$[8] or $DyCl_3\cdot 6H_2O$ with benzoic acid (PhCOOH) gives rise to $\{Dy(PhCOO)_3(EG)\}_n$, a molecular chain made of octacoordinated Dy^{III} ions (Fig. 1). This compound crystallizes in the P-1 triclinic space group (N°2) (Table S1) with only one crystallographically independent Dy^{III} that is coordinated by two oxygen atoms from an EG molecule and six oxygen atoms from five $PhCOO^-$ anions. The $Dy\text{-}O_{(PhCOO)}$ and the $Dy\text{-}O_{(EG)}$ bond lengths are in the range 2.24(4)-2.47(7) Å and 2.44(8)-2.45(9) Å, respectively (Table S2). Four $PhCOO^-$ ligands behave as mono-dentate $\mu\text{-}\eta_1\eta_1$ bridging ligands and one as bi-dentate capping ligand. It induces a large deformation of the coordination polyhedron (Table S3). Inversion centres located between two consecutive Dy atoms create the chain of formula $\{Dy(PhCOO)_3(EG)\}_n$ (Fig. 1 and S1). The Dy-Dy direction is almost along the *a* axis with homogenous Dy-Dy distances within the chain (4.83(1) Å and 4.86(2) Å). Chains are isolated from each other and the shortest interchain Dy-Dy distance is 10.09 Å.

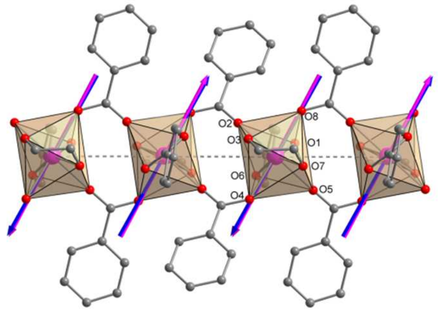

Fig.1 Representation of $\{Dy(PhCOO)_3(EG)\}_n$ with experimental (pink) and calculated (blue) easy magnetization axes.

Static and dynamic magnetic properties have been measured on a polycrystalline sample of $\{Dy(PhCOO)_3(EG)\}_n$ as a pellet (Fig. S2). The $\chi_M T$ room temperature value is 14.12 emu.K.mol^{-1}, in agreement with the expected 14.17 emu.K.mol^{-1} for an isolated Dy^{III} ion (g_J=4/3; J=15/2). As the temperature is lowered the $\chi_M T$ value decreases to reach 9.82 emu.K.mol^{-1} at 2K (Fig. S3). This is a consequence of the depopulation of the M_J sublevels of the J=15/2 manifold.

On the dynamic point of view, $\{Dy(PhCOO)_3(EG)\}_n$ depicts frequency dependence of the out-of phase susceptibility (χ_M'') above 1500 Hz in zero-field and below if an external dc field H_{dc}=1600 Oe is applied (Fig. 2 and S4-S5). Above 5 K a thermally activated magnetic relaxation according to an Arrhenius law ($\tau=\tau_0\exp(\Delta/kT)$ with τ_0 the characteristic relaxation time and Δ the activation energy for spin reversal) is observed (Fig. 2, Table S4) and $\tau_0=4.4(\pm0.5)\times10^{-8}$ s, Δ=38(±2)

cm^{-1} (~54 K). The distribution of the relaxation time is quite small as evidenced on normalized Cole-Cole[9] plots (Fig. S6) where α is found between 0.19 and 0.13 in the 3.5-7 K temperature range (Table S5). Almost all the sample is able to relax slowly as low χ_s/χ_T values are observed (around 0.2). At low temperature, quantum tunnelling mechanisms overcome phonons contribution and at 2K the activation energy is zero and τ=0.067s (2.36 Hz).

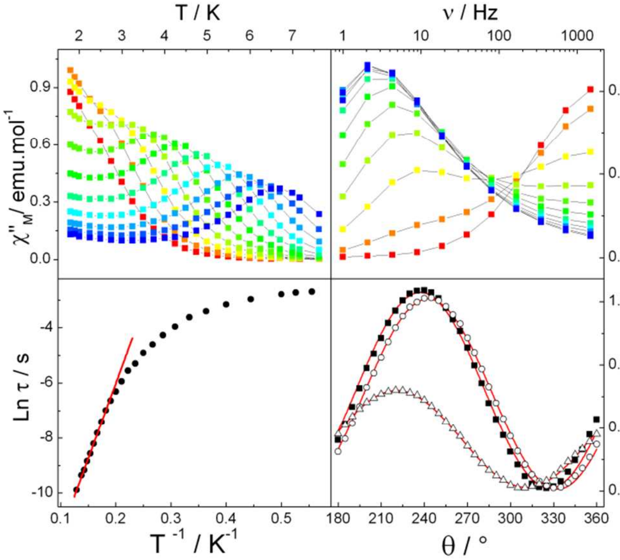

Fig. 2 Temperature dependence of χ_M'' with frequency ranging from 1 (red) to 1500 Hz (blue) measured with a 1600 Oe dc field (Left top). Arrhenius plot with best fit (left bottom). Field dependence of χ_M'' with field ranging from 0 (red) to 2000 Oe (blue) (top right). Single-crystal angular dependence of χ_M along XY (squares), YZ (circles) and XZ directions (triangles) (bottom right).

Orientation of the easy magnetic axis of such compounds has been shown to be affected by subtle changes in the coordination sphere of lanthanide ions[6b, 10] but the effect of close neighbouring of lanthanides in pure 4f systems is not fully understood.[11] In fact, if the library of 0-D Dy-based SMMs is quite extended nowadays,[12] their corresponding 1-D molecular architectures are less common. Then, theoretical approaches, that are very efficient on mononuclear lanthanide-based compounds, are less straightforward for polynuclear entities[6a, 13] and even less on infinite structures.[6b, 14] Last and surprisingly, confrontation and validation of these theoretical findings with single-crystal measurements are style scarce.[6a, 12a]

$\{Dy(PhCOO)_3(EG)\}_n$ is an example of 1-D arrangement of Single Ion Magnets (SIM) that permits the investigation of neighbours influence on the magnetic anisotropy. It crystallizes in the P-1 space group, and consequently allows performing easily rotating single-crystal magnetometry (Fig. 2). Fitting of these data leads to an Ising-type magnetic anisotropy (χ_{zz}>>χ_{xx}, χ_{yy}) with g_{xx}=1.32, g_{yy}=2.18 and g_{zz}=17.63 in the effective spin ½ approximation as already observed on similar Dy^{III}-based compounds.[6b] These values do not exactly fit with a pure Ising system (g_{xx}=g_{yy}=0 and g_{zz}=20) because of the angular resolution of the technique, that does not permit the measurement of very small g values, and also because of the antiferromagnetic inter-site interactions which operate at 2K and significantly decrease the effective magnetic moment. The orientation of the axis does not coincide with the pseudo-C_2 axis of the coordination polyhedron of the Dy^{III} ion that is also the chain direction (Fig. 1). Ising axis lies at 62.3° of the Dy-Dy direction.[15] Given this value the dipolar interaction J_{dd} between magnetic moments in a chain can then be calculated[11] at -0.535 cm^{-1} in the Ising limit and the effective spin ½ approximation.

For a deeper analysis of the neighbours influence on the magnetic anisotropy of $\{Dy(PhCOO)_3(EG)\}_n$, *ab-initio* wavefunction-based calculations were performed on two different fragments of the chain (see ESI). The first fragment (model **A**) consisted of one Dy^{III} ion together with its EG and $PhCOO^-$ bidentate ligands and 4 bridging $PhCOO^-$ ligands. At this level, the influence of the neighbouring Dy^{III} ions is thus neglected. In the second fragment (model **B**), to properly account for the dipolar coupling evidenced experimentally, the neighbouring Dy^{III} ions are considered explicitly. However, due to the lack of symmetry in the system and to computational limitations, it is not possible to treat them as open-shell units. The latter are thus replaced by point charges. To avoid meaningless charges in the system, the surrounding ligands of the neighbouring Dy^{III} ions are also accounted for by means of point charges that are extracted from a single point calculation on the ground state of model **A**, and converged for model **B** by a single iteration. For both models, the energy barrier, *i.e.* the energy difference between the ground and first excited states is basically similar (Table S6), lying around 100 cm^{-1} (± 20 cm^{-1}) while the overall splitting is around 450 cm^{-1}. The slight differences in the energy spectrum of the ground multiplet for both models do not lead to any significant changes in the magnetic susceptibility (Fig. S3) since both curves are superimposed and do not reproduce the experimental magnetic susceptibility at low temperature. This difference can be corrected in taking into account Dy-Dy interactions in the calculations. The dipolar interaction J_{dd} determined from single crystal magnetometry is introduced with an excellent agreement between simulated and experimental $\chi_M T$ vs. T curves (Fig. S3). Magnetic exchange (J_{ex}) seems then to be negligible in a J= J_{ex}+J_{dd} scheme and this is in agreement with the μ-$\eta_1\eta_1$ bridging mode of the carboxylate ligands that is not supposed to transmit sizeable superexchange interaction. Similarly, no fundamental differences are observed in the anisotropy tensors. For both models, the g_z value is close to 20 while g_x and g_y are close to zero (Table S6). The ground state is composed by approx. 98% of the |±15/2> eigenstates. Finally, for both models the computed easy-axis is lying less than 10° from the experimental one and coincides with the most "charged" direction of the coordination polyhedron, i.e. almost perpendicular to the plane defined by Dy^{III} and the oxygen atoms of EG (87.8°).

Since both models perform similarly, model **A** was used to investigate the orientation of the easy-axis in other Dy^{III}-based chains of SIMs. The selected chains, i.e. $\{Dy(4\text{-methyl-3-nitrobenzoate})_3(H_2O)(CH_3OH)\}_n$ (**DyNitro**)[16] $\{[Dy(HPA)_2(NO_3)_2]NO_3\}_n$ (**DyHPA**)[17] and $\{Dy(2\text{-fur})_3(HOCH_2CH_2OH)\}_n$ (**DyFur**)[6b] contain Dy^{III} ions in a O_8 environment, but with various symmetries of the coordination polyhedron (see ESI for the description of the chains). For **DyNitro** and **DyFur**, results are very similar to those obtained for $\{Dy(PhCOO)_3(EG)\}_n$ *i.e.* the energy barrier is around 170 cm^{-1} and g_z is close to 20 while g_x and g_y are close to zero (Table S7), meaning that the ground state of these systems is highly axially anisotropic and mainly composed of the |±15/2> eigenstates. In these two systems the easy-axis is more or less perpendicular to the chain and is lying in the mean plane defined by the 4 oxygen atoms of the bridging ligands (Fig. 3). For **DyHPA** the first excited state is very close in energy to the ground state (~10 cm^{-1}) and has a magnetic anisotropy tensor very similar to that of the ground state with g_x, g_y and g_z around

0.1, 3.6 and 15.6 respectively. This suggests that even at low temperature the first excited state is populated and contributes to the magnetic properties of the system. Thus, rather than an Ising-type magnetic anisotropy, we may expect **DyHPA** to have a magnetic easy-plane. The latter corresponds to the mean plane defined by the g_z directions of both the ground and first excited states which are 90° from each other (Fig. 3), *i.e.* is defined by the 4 oxygen atoms from the bridging ligands. In the end, whatever the system, the direction of the magnetic easy-axis (or easy-plane in the case of **DyHPA**) does not follow the direction predicted by coordination polyhedron site symmetry considerations but always lies in the plane where the electrostatic potentials of the first neighbouring oxygen atoms on the Dy^{III} centre are the strongest (Table S8)[18]. This corresponds to the mean plane defined by the four oxygens atoms of the bridging ligands ("$O_{bridging}$" in Table S8; Fig. 3). For a given Dy-O distance, spatial distribution of the charges is as important as their values and can create (as for $\{Dy(PhCOO)_3(EG)\}_n$, **DyFur** or **DyNitro**) or annihilate (for **DyHPA**) Ising anisotropy.

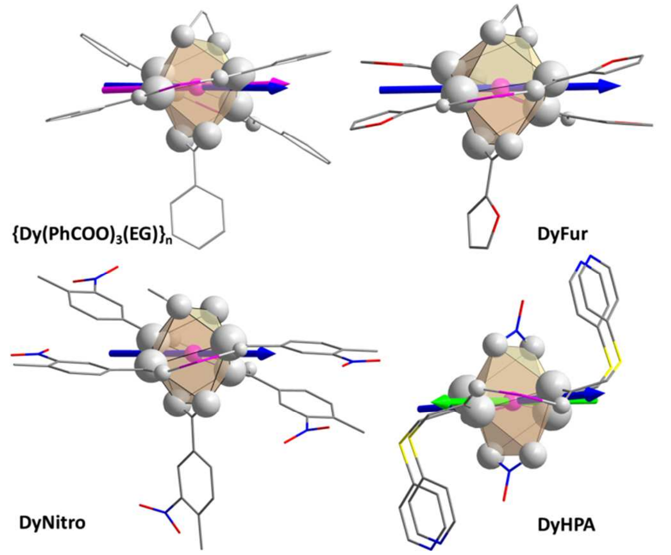

Fig. 3 Representation along the chain direction of calculated ground state anisotropy axes for $\{Dy(PhCOO)3(EG)\}_n$, DyFur, DyNitro and DyHPA in blue (for DyHPA first excited state anisotropy axis in green). Fragments are depicted with the electrostatic potential created by oxygen atoms on the Dy^{III} centre as scaled grey balls (values in ESI).

In this study, single-crystal rotating magnetometry has been performed directly on a molecular chain, without going through monomeric analogies.[19] It permits to assess the robustness of the ab-initio methodology and to extrapolate our theoretical treatment to various Dy^{III}-based chains. We thus provide experimental and theoretical evidences that magnetic properties of single-ion magnets even if organized in chains, are not governed by the overall chain structure but by electrostatic potentials. An optimization of the magnetic relaxation in such chains would thus require an arrangement of all the magnetic axes not only collinear but along the chain direction. On the molecular point of view, and given the oblate nature of the Dy^{III} ion, this requires a confinement of ligand's electronic density along the chain direction.

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