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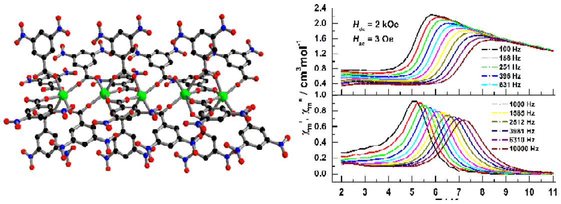

A simple route to 1D ferromagnetic Dy-containing compound showing magnetic relaxation behaviour

Wen-Hua Zhu,* Yan Zhang, Zhen Guo, Shen Wang, Juan Wang, Yan-Li Huang, Li Liu, Yu-Qiao Fan, Feng Cao, and Su-Wei Xiang

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paper

A simple route to 1D ferromagnetic Dy-containing compound showing magnetic relaxation behaviour

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Two well-isolated rare earth ions-based one-dimensional (1D) compounds with the general formulae $[RE(3,5\text{-}DNBz)_3(H_2O)_2](H_2O)$ (RE = Y(**1**) and Dy(**2**); 3,5-DNBz = 3,5-dinitrobenzoic acid) have been assembled under hydrothermal conditions with the bulky ligand 3,5-DNBz and structurally characterized by single-crystal X-ray diffraction technique, IR, TG–DTA, and elemental analysis. **1** and **2** are isostructural and possess a chain structure bridged alternatively by double and quadruple carboxylic groups of the 3,5-DNBz anions. For **2**, the rare earth ion center surrounded by six 3,5-DNBz anions and two water molecules is in an intermediate coordination geometry between the ideal square anti-prism (SAP) and bicapped trigonal prism (BTP). Magnetic investigation using direct-current (dc) measurement revealed weak ferromagnetic intra-chain interaction in the Dy analogue **2**. In the alternating-current (ac) susceptibility measurements, **2** was revealed dominating quantum tunnelling relaxation under zero dc field, while it exhibited the coexistence of quantum tunnelling and thermal activated relaxations (with an energy barrier U_{eff}/k of 77.8 K) in 300 Oe dc field, and the quenching of quantum tunnelling and an almost pure thermal magnetic relaxation (U_{eff}/k = 90.9 K) in 2 kOe dc field.

Introduction

Since the discovery of Mn12 acetate as the first single molecule magnet (SMM) in 1990s,[1] considerable research efforts have been devoted to the transition metal ions-based SMMs and single chain magnets (SCMs), namely anisotropic V^{III}, Mn^{III}, Fe^{III}, Co^{II} and Ni^{II},[2] exhibiting many interesting characteristics such as magnetic hysteresis, slow thermal magnetic relaxation and quantum tunnelling of magnetization (QTM).[3] These unique magnetic properties originate from a high-spin ground state (S) and a large uni-axial anisotropy (D), which leads to an energy barrier for the reversal of magnetic moment, $U_{\mathrm{eff}} = |D|S^2$.

In the last decade, triggered by the remarkable single ion magnetic (SIMs, Single Ion Magnets) behaviour of $[Pc_2Tb]^-\cdot TBA^+$ with a large thermal energy barrier of *ca*. 331 K for the reversal of magnetic moment,[4a] the synthesis of SMMs has also been extended to the lanthanide ions, especially Tb^{III}, Dy^{III}, Ho^{III}, Er^{III} ions,[4] which have been predicted by a simple model developed by J. R. Long, *et al*.[5] to be the best candidates for the design of stronger SMMs under particular crystal field environment. The energy barrier to reverse the magnetic moment has been refreshed continuously, e.g. the energy barrier of Ishikawa's SIMs, $[\{Pc(OEt)_8\}_2Tb]^+\cdot(SbCl_6)^-$ cationic complex, have reached 792 K;[4h] Winpenny and co-workers have reported a polynuclear Dy-based SMMs with an energy barrier of 530 K;[4i] Coronado and co-workers have achieved a record barrier to date of 939 K in a heteroleptic [Tb(Pc)(Pc')] system.[4j] The high magnetic moment and large spin-orbit coupling (except for Gd^{III}) to bring large intrinsic single-ion anisotropy of lanthanide ions are critical for the construction of SIMs, SMMs and SCMs, collectively known as low-dimensional magnets (LDMs). Noticeably, the Dy^{III}-containing family, including mononuclear,[6] polynuclear,[7] 1D,[8] or magnetic secondary building unit in 2D,[9] and 3D structural compounds,[10] is the largest one of rare earth ions-based LDMs.

In comparison to single-ion and polynuclear Dy^{III}-based LDMs, the development of 1D chain Dy-containing compounds showing magnetic relaxation behaviour is at its early stage. As far as the reported examples of 1D Dy^{III} chains bridged by carboxy1ic groups were concerned, some of them were attributed to exhibit antiferromagnetic interactions despite the intrinsic magnetic characteristics of large magnetic anisotropy and spin-orbit coupling of Dy^{III} ions,[8d,e] others were revealed to show weak ferromagnetic interactions.[8a,b,g,h,i,k] However, it was obvious that slow magnetic relaxation behaviour could be observed in the examples from the two aspects. Due to the unpaired electrons in the *4f* orbitals well shielded by outer *s* and *p* electrons, the exchange interaction between the Ln^{III} ions and other neighbouring spin carriers is very weak, usually 2 orders of magnitude lower than the energy splittings,[8a] and it becomes a secondary factor to influence the low-dimensional magnetic behaviour. Therefore, the magnetic properties of Dy^{III}-containing LDMs mainly originate from crystal field effect and are closely related to the coordination geometry of the Dy^{III} ions,[5,11] such as distorted square antiprism,[6d,j,k,8i] distorted dodecahedron,[6e,u,8f] bicapped trigonal prism,[6e] distorted trigonal prism,[10a] tricapped trigonal prism,[6f] distorted monocapped trigonal prism,[6h] pentagonal bipyramid,[6l,q] trigonal prism,[6m] which provides a uni-axial anisotropy for generating high energy barrier to relax the magnetization.

Herein, two new well-isolated rare earth 1D chain compounds, [RE(3,5-DNBz)$_3$(H$_2$O)$_2$](H$_2$O) (RE = Y(**1**); RE = Dy(**2**)) were successfully assembled under hydrothermal conditions by intentionally choosing the bulky ligand 3,5-DNBz with large steric hindrance. And a reported Dy-carboxylate chain structure, Dy(4-NBz)$_3$(H$_2$O) (**3**, 4-NBz = 4-nitrobenzoic acid) was prepared by a simple new method for comparison of magnetic properties.[8c] The compounds have been structurally characterized, in which the local coordination geometry of the Dy^{III} ions of **2** and **3** is an intermediate geometry between ideal SAP and BTP, and distorted square antiprism, respectively. Magnetic analyses indicate that weak ferromagnetic intra-chain interactions propagate in complex **2**, which displays dominating quantum tunnelling relaxation in zero dc field, and enhanced field-induced thermal magnetic relaxation under external field in the alternating-current susceptibility measurements. The Dy-carboxylate chain compound **2** represents one of the rare examples that belong to 1D ferromagnetic Dy-containing compounds showing magnetic relaxation behaviour.

Experimental section

Materials and physical techniques

All chemicals were of reagent grade and used as purchased without further purification. Elemental analyses of C, H and N were carried out on a Vario Micro Cube elemental analyzer (Elementar Aanlysensysteme GmbH, Germany). IR spectra were recorded on a Perkin Elmer Spectrum one spectrophotometer in the range of 4000–400 cm^{-1} using KBr pellets. The TG–DTA thermal analyses were performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of 10 °C/min under flowing nitrogen atmosphere. Static magnetic measurements including temperature-dependent magnetic susceptibility in the range 2–300 K, field-dependent magnetization and hysteresis loop at 2 K of **2** were carried out on a Quantum Design MPMS-7 SQUID magnetometer. Alternating current susceptibilities of **2** and **3** were measured using a Quantum Design PPMS magnetometer. All of the magnetic measurements were performed on polycrystalline samples tightly packed and sealed with a capsule to avoid the anisotropic orientation. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Synthesis of [Y(3,5-DNBz)$_3$(H$_2$O)$_2$](H$_2$O) (1)

A mixture of Y(NO$_3$)$_3$·6H$_2$O (0.0958 g, 0.25 mmol), 3,5-DNBz (0.1060 g, 0.5 mmol), TEA (0.05 mL), and H$_2$O (10 mL) was heated in a 25 mL capacity stainless-steel reactor lined with Teflon at 150 °C for 3 days, and then cooled to room temperature overnight. Yellow block-shaped crystals of **1** were obtained. The yield (0.0470 g) was about 30.6% based on Y^{III} ion. Anal. (%) Calcd for C$_{21}$H$_{15}$N$_6$O$_{21}$Y: C, 32.49; H, 1.95; N, 10.83. Found: C, 32.85; H, 1.68; N, 11.09.

Synthesis of [Dy(3,5-DNBz)$_3$(H$_2$O)$_2$](H$_2$O) (2)

A similar procedure was adopted for the synthesis of **2** except that Y(NO$_3$)$_3$·6H$_2$O was replaced by Dy(NO$_3$)$_3$·6H$_2$O (0.1142 g, 0.25 mmol). Yellow block-shaped crystals of **2** were obtained in 24.7% yield (0.0525 g) based on Dy^{III} ion. Anal. (%) Calcd for C$_{21}$H$_{15}$N$_6$O$_{21}$Dy: C, 29.68; H, 1.78; N, 9.89. Found: C, 28.94; H, 1.78; N, 9.55. IR (cm^{-1}, KBr pellet): 3632 (m), 3571 (s), 3095 (s), 1676 (m), 1607 (vs), 1572 (vs), 1548 (vs), 1466 (vs), 1415 (vs), 1343 (vs), 1098 (m), 1076 (m), 933 (w), 918 (m), 793 (s), 725 (s), 525 (m).

Table 1 Crystallographic data for the compounds **1** and **2**

	1	2
Empirical fromula	C$_{21}$H$_{15}$N$_6$O$_{21}$Y	C$_{21}$H$_{15}$N$_6$O$_{21}$Dy
Formula weight	776.30	849.89
Temperature/K	296	296
Crystal system	triclinic	triclinic
Space group	$P-1$	$P-1$
a [Å]	9.2897(10)	9.2791(11)
b [Å]	11.5182(13)	11.4893(14)
c [Å]	13.7146(15)	13.7207(16)
α [°]	107.747(2)	107.5990(10)
β [°]	90.548(2)	90.4890(10)
γ [°]	93.464(2)	93.625(2)
Volume [Å^3]	1394.5(3)	1390.9(3)
Z	2	2
D_c [g cm^{-3}]	1.849	2.029
μ (Mo $K\alpha$) [mm^{-1}]	2.202	2.797
F (000)	780	834
Crystal size, mm^3	0.20×0.20×0.22	0.08×0.12×0.25
Max. and min. transmission	0.667, 0.643	0.807, 0.542
θ_{min}, θ_{max} [°]	2.66, 24.57	2.66, 29.76
Total reflections collected	10156	9789
Uniq reflections (R_{int})	6544 (0.0240)	7107 (0.0284)
Observed reflections [I≥2σ(I)]	5275	6421
No. of refined parameters	467	467
$R1$,w$R2$ [I≥2σ(I)]	0.0380, 0.0755	0.0315, 0.0825
$R1$,w$R2$ (all data)	0.0552, 0.0821	0.0355, 0.0855
Goodness of fit	1.029	1.009
Max. and min. residual density, e/Å^3	0.473, –0.439	1.325, –1.431
Max. and mean shift/sigma	0.001, 0.000	0.001, 0.000

X-ray crystallography

Determination of the unit cell and data collection for complexes **1** and **2** were performed on a Bruker Smart APEX II CCD area detector diffractometer with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). All of the diffraction data were collected at room temperature and corrected for Lorentz and polarization effects. Adsorption corrections were performed by SADABS method.[12] The structures were solved by direct methods of SHELXS-97 program and refined by the full-matrix least-squares techniques based on F^2 using SHELXL-97 program.[13a,b] All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, except those of the hydroxy groups, were introduced in calculated positions, and refined with isotropic thermal parameters and a fixed geometry (e.g. O–H 0.96 Å) riding on their parent atoms.[13c,d] The crystal data and structural refinement details of **1** and **2** are summarized in Table 1. The selected bond lengths and angles are listed in

Tables S1 and S3 in the ESI.

Results and discussion

Crystal structure of 1 and 2

Since complex **1** is isostructural to complex **2**, only the structural details of complex **2** will be described herein. As listed in Table 1, complex **2** crystallizes in the *P*−1 space group. Generally, the chain structure of complex **2** is similar in many aspects to complex **3**. As depicted in Fig. S1a, the asymmetric unit for **2** contains one crystallographically independent Dy^{III} ion, three deprotonated 3,5-DNBz ligands, two coordinated and one lattice water molecules (the water molecules have been omitted for clarity). The uniq Dy^{III} ion is 8-fold coordinated with the donor oxygen atoms from six 3,5-DNBz anions and two H_2O molecules. The Dy–O bond distances range from 2.292 (2) to 2.512 (3) Å, which are comparable to the lengths in other Dy–carboxylate compounds.[8] It is noteworthy that the Y–O bond distances for complex **1**, varying from 2.278 (2) to 2.496 (2) Å, are extremely similar to the Dy–O bond distances in **2**.

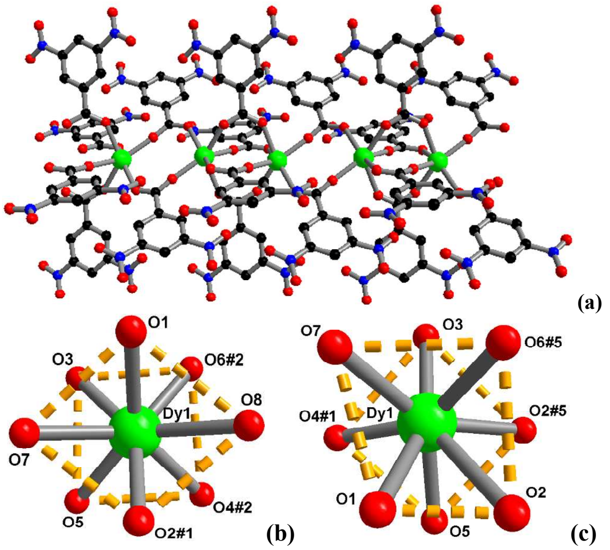

Fig. 1 (a) View of the 1D chain structure bridged by double and quadruple 3,5-dinitrobenzoato carboxylic groups along *a* axis in complex 2. (b) The coordination geometry around the Dy^{III} ion of complex 2. Symmetry codes: #1 –x, –y, –z; #2 –x+1, –y, –z. (c) The coordination geometry of the Dy^{III} ion for complex 3. Symmetry codes: #1 –x, –y, –z; #5 –x+1, –y, –z.

As shown in Fig. 1a, the carboxylic groups of the 3,5-DNBz anions adopting μ^2–η^1:η^1 coordination mode doubly and quadruply bridge the Dy^{III} ions alternatively to form a 1D chain structure along *a* axis, which gives rise to two different intra-chain Dy···Dy distances of 4.27 and 5.05 Å, respectively. The packing pattern is displayed in Fig. S1b with the shortest inter-chain Dy···Dy distance being 11.49 Å. As listed in Table S4, there are extensive H–bonds between the O atoms of the coordination water molecules, the lattice water molecules, and the COO groups of the 3,5-DNBz ligands. π–π interactions also exist among the neighbouring chains with a center-to-face distance of 3.403 Å (the center of the phenyl ring C9~C14 to the least-square plane of the phenyl ring C9#3~C14#3, #3 1–x, 1–y, –z), the slippage of 0.770 Å and the dihedral angle of about 0° between the two stacking phenyl rings.

According to the classification by Muetterties, the stereochemical distribution of eight-coordinated compounds is dominated by the low-energy polyhedra, namely square antiprism (SAP), dodecahedron (DD), bicapped trigonal prism (BTP) and intermediate geometries.[14] The semi-quantitative method is applied to determine the coordination geometry of the Dy^{III} ion. The characterizing δ and φ dihedral angles of the coordination polyhedron of the Dy^{III} ion for complex **2** and **3** are summarized in Table S5. In the case of **3**, the corresponding δ values of 5.71, 2.75, 51.97, 54.75° and φ values of 37.38, 23.32° are very close to the parameters of the ideal SAP geometry, indicative of a slightly distorted square antiprism (Fig. 1c). For **2**, the δ values of 3.87, 17.34, 44.68, 44.39° and φ values of 23.40, 27.22° are intermediated between the parameters of the ideal SAP and BTP geometry, which originates from the relatively long Dy–O7 of 2.438 (3) Å and Dy–O8 of 2.512 (3) Å (comprising the two caps of the BTP geometry) to other Dy–O bond lengths (Fig. 1b). This suggests an intermediate coordination geometry between SAP and BTP around the Dy^{III} ion of **2**, comparing to the slightly distorted square anti-prism geometry in **3**.

Thermal stability of 2

As depicted in Fig. S2, the thermal stability of complex **2** has been investigated by TG–DTA instrument under nitrogen atmosphere. The compound experienced three thermal processes of weight loss. The former two endothermic processes with the total weight loss of 5.9% (calcd 6.3%) in the temperature of 50–170 °C are the release of the lattice and coordination water molecules. Regarding to the relatively long Dy–O8 distance of 2.512 (3) Å and weak coordination of this water molecule, the first weight loss of 3.9% (calcd 4.2%) at 50–90 °C corresponds to the departure of this coordination water along with the lattice water. The second one (2.0%, calcd 2.1%) occurs at 130–170 °C is in agreement with the escape of another coordination water molecule. The third exothermic process from 390 to 450 °C is the decomposition of 3,5-DNBz ligands, leaving the final residues of Dy_2O_3 with the weight of 20.1% (calcd 21.9%).

Magnetic properties of 2

The direct-current magnetic susceptibility of **2** was measured in the temperature range of 2–300 K in an external magnetic field of 1 kOe. As shown in Fig. 2, the $\chi_M T$ value of 14.22 cm^3 mol^{-1} K at 300 K is slightly larger than the expected value of 14.17 cm^3 mol^{-1} K for one non-interacted Dy^{III} ion (S = 5/2, L = 5, $^6H_{15/2}$, J = 15/2, g = 4/3).[15] Upon cooling, the $\chi_M T$ value decreases until 14 K with a minimum value of 12.08 cm^3 mol^{-1} K, and then increases sharply with decreasing temperature until 2 K with a value of 14.05 cm^3 mol^{-1} K. Such behaviour is similar with that of compound **3**.[8c] The best Curie–Weiss law fitting of χ_M^{-1} vs. T at 300–30 K gives the Curie constant C = 14.45 cm^3 mol^{-1} K and the Weiss constant θ = –3.85 K. The negative Weiss constant as well as the decrease of $\chi_M T$ value with decreasing temperature may presumably be ascribed to the crystal field effect, the large magnetic anisotropy and the progressive thermal depopulation of the excited Stark sublevels of the Dy^{III} ions. And the increase of $\chi_M T$ value at 14–2 K may be attributed to the intra-chain ferromagnetic magnetic exchange.[8c,16]

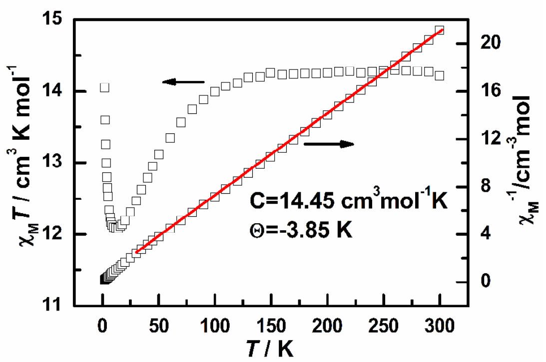

Fig. 2 Temperature dependency of $\chi_M T$ and χ_M^{-1} in the range of 2–300 K in 1 kOe dc field for 2.

The field dependency of magnetization for complex **2** has been determined at 2.0 K in the field range of 0–70 kOe (Fig. S3). The magnetization rises abruptly at low fields and the magnetization of 7.82 $N\beta$ at 70 kOe does not reach the theoretical saturation value ($g_J \times J = 4/3 \times 15/2 = 10\ N\beta$), indicating the presence of magnetic anisotropy or low-lying excited states in the system. The hysteresis loop of the magnetization of **2** was collected at 2.0 K in the range of –20–20 kOe (inset of Fig. S3). No hysteresis effect was observed at 2.0 K with the sweep rates used in a Quantum Design MPMS-7 SQUID magnetometer.

There are only a few examples reported to date of Dy-containing chain-like complexes with ferromagnetic intra-chain interactions.[8a,b,g,h,i,k] For complex **3**, the evaluation of the intra-chain magnetic interaction by non-critical scaling theory had been demonstrated to be ferromagnetic.[8c,16,17] The ac susceptibilities had been explored to show **3** displaying field-induced slow magnetic relaxation.[8d] Herein, the temperature and frequency dependence of the ac susceptibilities of **3** were carried out under zero applied static magnetic field and 3.0 Oe oscillating ac field with higher frequencies to 10000 Hz and shorter time scale to validate more distinctly the slow magnetic relaxation process. The ferromagnetic exchange and the similar chain-like structure with complex **3** prompted us to investigate the ac magnetic properties of **2**. Under zero dc field and 3 Oe of ac field (Fig. 3), both χ' and χ'' components of the ac susceptibility increase with decreasing temperature and show clear frequency dependence with no peaks in the temperature range of 2.0 to 8.0 K due to QTM effect, which is quite similar to the magnetic relaxation behaviour of complex **3**.

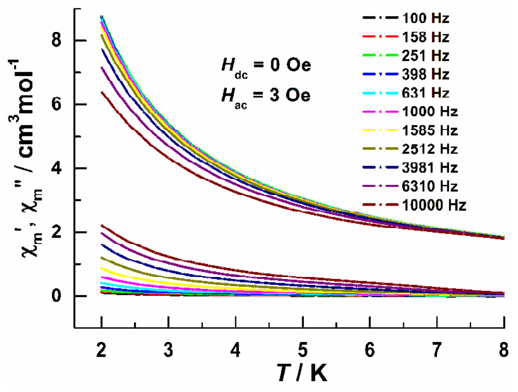

Fig. 3 Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibilities of compound 2 under zero dc field.

A suitable dc field may be used to weaken the QTM effect. In this direction, a field-dependent ac susceptibility measurement was performed from 0–10 kOe with f = 1000 Hz (f is the oscillating frequency of ac field). As depicted in Fig. S4, a peak field of the out-of-phase ac susceptibility appeared at 300 Oe, which was considered as a dc field to be exerted to reduce the QTM effect. When a dc field of 300 Oe was applied (Fig. 4), for both in-phase and out-of-phase ac susceptibilities broad peaks appeared at ac fields with relatively high frequencies, suggesting the existence of slow magnetic relaxation behaviour, and the curves upturned at further decreasing temperature rather than went down with the trend to zero value, indicating that the QTM effect existing at zero dc field was notably suppressed but not eliminated even under this dc field. This suggests the coexistence of two distinct magnetic relaxation pathways including thermal activated and quantum tunnelling relaxations, which has been observed in Dy-containing SIMs and poly-nuclear systems.[6d]

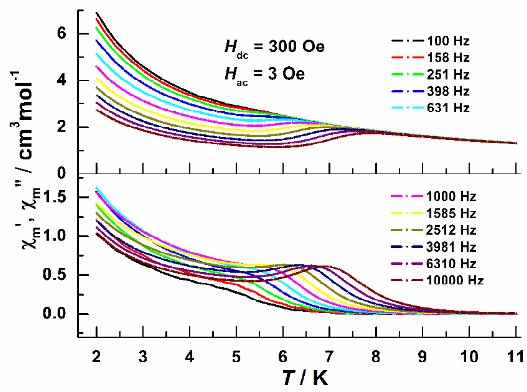

Fig. 4 Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibilities of compound 2 under 300 Oe dc field.

The shift parameter of the peak temperature of χ', $\varphi = (\Delta T_p/T_p)/\Delta(\log f)$, is approximately 0.20, which is a normal value in the range of super-paramagnets ($0.1 \leqslant \varphi \leqslant 0.3$) but out of the range commonly observed in spin glasses ($0.007 \leqslant \varphi \leqslant 0.05$).[18] Below 1585 Hz, no peaks appeared in the curves of χ''–T and the magnetization relaxation time τ can be derived from the frequency dependence measurements (Fig. S5). In the range of 1585–10000 Hz the pre-exponential factor τ_0 and anisotropic energy barrier U_{eff} to reverse the magnetization can be inferred from the analysis of the frequency dependence of the χ'' peak temperature, T_p, through Arrhenius law ($\tau = \tau_0 \exp(U_{eff}/kT_p)$), where $\tau = 1/2\pi f$). As shown in Fig. 5, the best fitting based on $\ln\tau = \ln\tau_0 + U_{eff}/kT_p$ affords the magnetization parameters τ_0 of 3.4×10^{-10} s and U_{eff}/k of 77.8 K, which are comparable to those of Dy-based SMMs (in the range of ~10^{-6}–10^{-11} s).[6–10,19] Below 2 K, the magnetization relaxation time τ become temperature independent with a value of 2.6×10^{-4} s as expected in a dominating quantum regime.[20] Between 2 and 6 K, the magnetization relaxation dynamics of **2** was the coexistence of QTM and thermally activated relaxation. Similar behaviour was also reported by Cosquer et al. for the mononuclear [Dy(hfac)$_3$(L)] complex.[6n] Above 6 K, the magnetization relaxation process was dominated by thermal relaxation (Arrhenius-like behaviour), which becomes faster than quantum relaxation in this temperature regime.

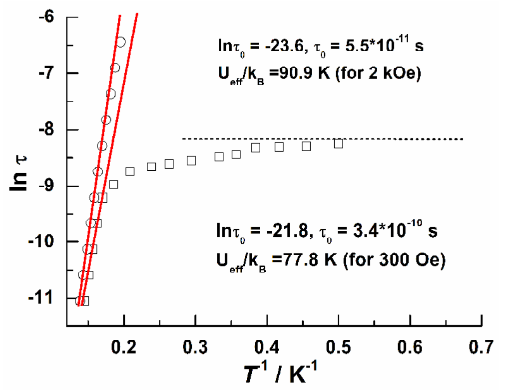

Fig. 5 The natural logarithm of magnetization relaxation time vs. reciprocal temperature, lnτ vs. T^{-1} plot for complex 2 in 300 Oe (□) and 2 kOe (○) dc field. The solid line is fitted with the Arrhenius law.

At several fixed temperatures such as 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 K, the plots of the out-of-phase (χ'') vs. the in-phase (χ') components of the ac susceptibility (the Cole–Cole diagram)[21] displayed nearly semi-circle shape (Fig. 6), which were best fitted by the generalized Debye model giving the distribution coefficient α value (Table S6) of 0.44–0.34 (between 2.0 and 5.0 K) and 0.04–0.05 (between 6.0 and 7.0 K).[22] The relatively large α values below 5.0 K are consistent with the coexistence of QTM and thermally activated relaxation processes. Above 6.0 K, the parameter α decreasing abruptly to a very small value (0.04 at 6.0 K) indicates that in this temperature regime the quantum relaxation is eliminated and the magnetization relaxation is dominated by a single thermally activated pathway. The least-square fitting of the frequency dependence of χ' and χ'' gives rise to the relaxation parameters (Fig. S8 & Table S6). The fitting τ relaxation parameters are in good agreement with the relaxation times derived from the frequency dependence measurements (Fig. S5).

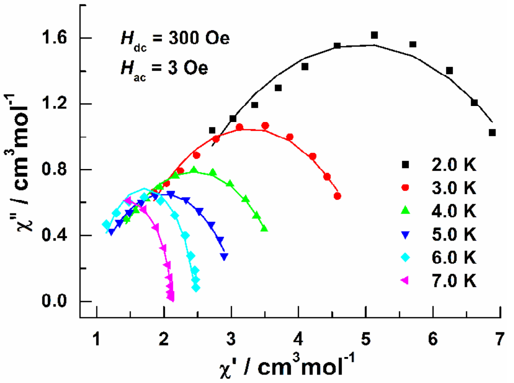

Fig. 6 The Cole–Cole plots of χ'' vs. χ' at 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 K for compound 2 under 300 Oe dc field. The solid lines are the least-square fitting of the data to a distribution of single relaxation processes.

For better understanding of the magnetic relaxation behaviour of complex **2**, a larger dc field of 2 kOe was applied to reduce the QTM effect more completely, and better peak shapes were detected in both χ' and χ'' components of the ac susceptibility in the frequency region of 100–10000 Hz. As shown in Fig. 7, the χ' and χ'' signals strongly depend on the frequencies of ac field and the QTM effect is almost quenched under 2 kOe dc field, which is the typical field-induced magnetic relaxation characteristics for single molecule or single chain magnets.[6d] The shift parameter φ of the peak temperature of χ' is in the range of SMMs ($0.1 \leqslant \varphi \leqslant 0.3$) with a value of about 0.18.

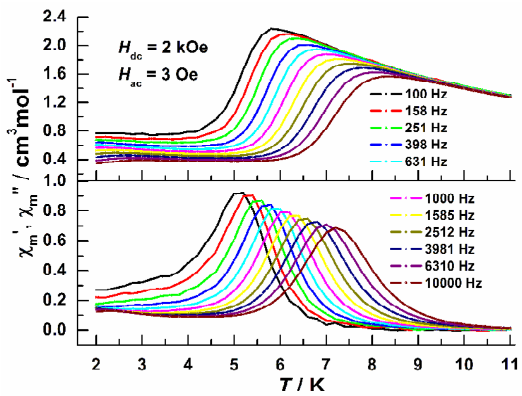

Fig. 7 Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibilities of compound 2 under 2 kOe dc field.

As can be seen from Fig. 5, the relaxation time is significantly increased under 2 kOe relative to 300 Oe dc field in the temperature range of 2.0–6.0 K where the QTM is effective. However, τ changes a little above 6.0 K in the thermally activated region. In the temperature range 5.1–7.2 K of the magnetization relaxation, lnτ vs. $1/T_p$ follows Arrhenius law basically, which is in agreement with the minimization of QTM and an almost pure thermal relaxation. The best fitting of the data gives the parameters τ_0 of 5.5×10^{-11} s and U_{eff}/k of 90.9 K. The data of χ'' vs. χ' at 5.0, 6.0 and 7.0 K were selected to draw the Cole–Cole diagram (Fig. S7), the best fitting of which by the generalized Debye model presented the distribution coefficient α values of 0.34, 0.14 and 0.14 (Fig. S9 & Table S7). The small α values beyond 5.0 K indicate the narrow distribution of relaxation time correlating with the almost pure thermal magnetic relaxation. The fitting τ relaxation parameters are consistent with the relaxation times derived from the frequency dependence measurements (Fig. S6).

Conclusions

In conclusion, two well-isolated rare earth ions-based 1D chain compounds, Y(**1**) and Dy(**2**), have been generated by hydrothermal method with a deliberately chosen bulky ligand 3,5-dinitrobenzoic acid to provide relatively large steric hindrance between neighbouring chains and structurally characterized by various methods, in which the Dy^{III} center of the Dy analogue is in an intermediate coordination geometry between regular SAP and BTP geometry. The dc and ac magnetic properties of the Dy-based compound have been measured and discussed in detail with a similar Dy-containing carboxylate chain compound Dy(**3**) as a contrast. The full magnetic investigation of Dy(**2**) indicates weak ferromagnetic intra-chain interaction, zero-field dominating quantum tunnelling, the coexistence of QTM and thermally activated relaxation under intermediate external field, and almost pure field-induced thermal magnetic relaxation with an optimum dc field. Therefore, it demonstrates that the utilization of lanthanide ions with high magnetic moment and large intrinsic anisotropy, and single carboxylate ligands with huge steric hindrance represents a promising simple route to achieve the rarely investigated 1D ferromagnetic lanthanide chain compound with interesting slow magnetic relaxation behaviour, which is beneficial for the study of the construction and the magnetic relaxation mechanism of lanthanide ions-based SIMs, SMMs and SCMs.

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Notes and references

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, PR China. Tel: +86 27 88662747; E-mail: zhuwenhua@pku.org.cn

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