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Investigation of the Slow Relaxation of the Magnetization Dynamics in Homoleptic Ene-Diamido Organodysprosium(III) Complexes with K’/Arene Interactions

Jérôme Long*, a Aleksei O. Tolpygin, b Anton V. Cherkasov, b Konstantin A. Lyssenko, c,d Yannick Guarti, a Joulia Larionova, a Alexander A. Trifonov a,b,c

We report the synthesis, structure and magnetic investigations of two new DyIII homoleptic complexes based on different ene-diamido ligands [K(THF)][Dy(DAD)3]2 (R = H (1), Me (2)) DAD = [2,6-iPr2C6H3-N=CH–NC6H4–iPr2-2,6] showing K’/Arene interactions. Magnetic investigations reveal that both compounds exhibit a zero-field Single-Molecule Magnetic relaxation mainly governed by a Raman process.

Introduction

The ability of some mononuclear lanthanide complexes to exhibit slow relaxation of their magnetization possibly associated with magnetic bistability at the molecular scale opens exciting avenues for the information storage or spin-based computing.1-4 In these so-called Single-Molecule Magnets (SMMs), the optimum balance between the specific 4f electronic density of defined lanthanide ions with the coordinated ligands engenders a crystal-field splitting which could lead to the appearance of an anisotropic barrier, Δ, separating opposite orientations (± mI) of the magnetic moments.5-8 It is generally recognized that in efficient genuine SMMs, the energy barrier should be as large as possible and the retention of the magnetization (with hysteresis effect) should be achieved in zero magnetic field below a blocking temperature, which should be the highest possible.9 The theoretical modelling predicted, some years ago, that the most efficient strategy to fulfill such objectives consists in stabilizing the oblate electronic density of DyIII ion by an axial crystal-field generated by the presence of two negatively charged ligands along an axis with short bond lengths and no coordinated species in the equatorial plane.5-10 This targeted environment permits to maximize the crystal-field splitting when a suitable symmetry is achieved. Such approach has been nicely demonstrated in both, coordination complexes11-18 and organometallic metallocene complexes19-20 with magnetic hysteresis observed up to 80 K.21 Yet, these studies point out that additional processes, such as the Quantum Tunnelling of the Magnetization (QTM), as well as Raman and direct relaxations, may greatly complicate the overall relaxation mechanism by creating underbarrier pathways, reducing the SMMs hallmarks.22-23 For instance, the exceptional magnetic performances of dysprosium metallocene family could be ascribed, not only to the tailored coordination environment, but also to the reduced molecular vibrations (vibrational modes) imposed by the rigid cyclopentadienyl ligands.20-21, 23-25 It appears therefore critical, with the aim to ultimately optimize the SMMs, to gain deeper insights on the parameters affecting such spin-phonon coupling.

Following this idea, we have recently investigated the use of diazabutadiene ligands for the design of lanthanide SMMs.26-27 These doubly negatively charged ligands could act both, as n and π-electron donors, while benefiting from a great tunability with respect to their steric and electronic features. Hence, we have previously shown that an homoleptic [Li(DME)][Dy(DAD)3Cl] complex (DAD = [2,6-iPr2C6H3-N=CH–NC6H4–iPr2-2,6], DME = dimethoxyethane) exhibit a genuine SMM behaviour with a significant axial crystal-field.27 However, despite this noticeable crystal-field splitting generated by the DAD ligands, the Raman process was found to dominate the relaxation dynamics. In order to increase the rigidity of the system and circumvent such Raman relaxation, half-sandwich heteroleptic complexes [Dy(DADMe2)Cp*Cl] and [Li(THF)][Dy(DADMe2)Cp*Cl] (DADMe2 = [2,6-iPr2C6H3-N=CMe–CMe–NC6H4–iPr2-2,6], Cp* = C5Me5) were also designed by associating DAD-type ligands providing short Dy-N distances with a rigid Cp* moiety.28 However, in the previous examples, an additional ligand (Cl or THF) was coordinated in the equatorial plane that in turn decreases the axiality. Encouraged by these results, we continued to explore the potential of the DAD ligands. We report here, the synthesis, structure and magnetic investigations of two cationic homoleptic complexes of DyIII based on distinct dianionic DAD ligands with unusual K’/arene interactions and exhibiting a zero-field SMM behaviour. Remarkably, although the nature of the substituent on the DAD ligand and counter-ion directly affects the DyIII coordination sphere, the magnetization is found to relax mainly via a Raman process.
Experimental

Materials and Methods

General Procedures

All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. THF and toluene were purified by distillation from sodium/benzophenone ketyl and degassed thoroughly. Hexane was dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. DyCl₃ was dried by distillation from sodium/triglyme and toluene were purified by distillation from sodium. All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox.

Synthesis of \([K(THF)]_2[Dy(2,6-iPr₂C₆H₃NCHCHNC₆H₃iPr₂-2,6)_2]\) (1).

A solution of \(K_{2}[2,6-iPr₂C₆H₃NCHCHNC₆H₃iPr₂-2,6]\) in situ prepared from \(2,6-iPr₂C₆H₃NCHCHNC₆H₃iPr₂-2,6\) (0.78 g, 0.67 mmol, 68% yield) and \(K\) shavings (0.16 g, 3.98 mmol) in 30 mL of THF was slowly added to a suspension of \(DyCl₃\) (0.27 g, 0.99 mmol) in 5 mL of THF. The reaction mixture was stirred for 12 h at ambient temperature. The volatiles were removed in vacuum. Recrystallization of the resulting solid from THF/hexane mixture at 20 °C afforded orange crystals of 1 (0.68 g, 0.62 mmol, 62% yield). Elemental analysis calcd. (%) for \(C_{46}H_{88}DyK_{12}O_{4}\): C, 58.56; H, 8.07; Dy, 14.79; N, 5.10; found (%): C, 58.78; H, 7.93; Dy, 14.90; N, 5.21. IR (Nujol, KBr) \(v/\text{cm}^{-1}\): 2091 (w), 1919 (w), 1855 (w), 1836 (w), 1794 (w), 1628 (s), 1581 (s), 1563 (m), 1530 (s), 1429 (s), 1368 (s), 1334 (s), 1309 (s), 1265 (s), 1224 (s), 1208 (s), 1178 (s), 1151 (m), 1114 (m), 1074 (s), 1050 (s), 1005 (s), 922 (s), 890 (s), 871 (s), 819 (s), 796 (s), 770 (s), 760 (s), 744 (s).

Synthesis of \([K(THF)]_2[Dy(2,6-iPr₂C₆H₃N(CMe)CMeNC₆H₃iPr₂-2,6)_2]\) (2).

A solution of \(K_{2}[2,6-iPr₂C₆H₃NCMeCMeNC₆H₃iPr₂-2,6]\) in situ prepared from \(2,6-iPr₂C₆H₃NCMeCMeNC₆H₃iPr₂-2,6\) (0.80 g, 1.98 mmol) and \(K\) shavings (0.15 g, 3.95 mmol) in 30 mL of THF was slowly added to a suspension of \(DyCl₃\) (0.27 g, 0.99 mmol) in THF (5 mL) at room temperature. The reaction mixture was stirred for 12 h at ambient temperature. The volatiles were evaporated and the solid residue was extracted with toluene (40 mL). The toluene extract was filtered, toluene was removed in vacuum. Recrystallization of the resulting solid from THF/hexane mixture at 20 °C afforded orange crystals of 2 (0.78 g, 0.67 mmol, 68% yield). Elemental analysis calcd. (%) for \(C_{44}H_{86}DyK_{12}O_{4}\): C, 66.55; H, 8.38; Dy, 14.07; N, 4.85; found (%): C, 66.81; H, 8.11; Dy, 14.00; N, 4.69. IR (Nujol, KBr) \(v/\text{cm}^{-1}\): 1914 (w), 1882 (w), 1835 (w), 1786 (w), 1645 (s), 1583 (s), 1560 (m), 1425 (s), 1362 (s), 1337 (s), 1254 (s), 1204 (s), 1156 (c), 1138 (s), 1111 (s), 1049 (s), 936 (s), 887 (s), 863 (s), 818 (s), 799 (m), 789 (m), 775 (s), 758 (s), 744 (s).

X-Ray crystallography

The X-ray data for 1 and 2 were collected with Bruker Smart Apex II (1) and Rigaku OD Xcalibur (2) diffractometers (MoKα radiation, ω-scans technique, λ = 0.71073 Å) using APEX3 and CrystalsAlis Pro software packages. The structures were solved by direct methods and were refined by full-matrix least squares on \(F^2\) for all data using SHELX and SCALE3 ABSPACK scaling algorithm implemented in CrystalsAlis Pro were used to perform absorption corrections. All non-hydrogen atoms in 1 and 2 and hydrogen atoms of NCCN fragments in 1 were found from Fourier syntheses of electron density (all non-hydrogen atoms were refined anisotropically). All other hydrogen atoms were placed in calculated positions and were refined in the “riding” model with \(U(H)_{\text{iso}} = 1.2U_{eq}\) of their parent atoms (\(U(H)_{\text{iso}} = 1.5U_{eq}\) for methyl groups). Disordered fragments in both structures were restrained using AFIX, DFIX, SADI and FLAT instructions. Displacement parameters of non-hydrogen atoms of disordered fragments in 1 and all non-hydrogen atoms in 2 were restrained using RIGU instruction.

Magnetic Measurements

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working in the range 1.8–300 K with the magnetic field up to 7 Tesla. The samples were prepared in a glove box. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal’s constants. The AC magnetic susceptibility measurements were carried out in the presence of a 3 Oe oscillating field in zero or applied external DC field.
**Results and Discussions**

**Synthesis and crystal structures**

The synthetic strategy to design the targeted homoleptic ate-complexes relies on the salt metathesis reactions of anhydrous DyCl₃ with two-fold amounts of [K(THF)ₙ][DAD₂] (R = H, Me), in situ prepared from DAD and potassium shavings and giving [K(THF)₂][Dy(DAD₂)] (X = H (1), Me (2)) (Scheme 1). The reactions were carried out at 25 °C in THF solution within 24 h. After recrystallization from a THF/hexane mixture, complexes 1 and 2 were isolated as orange crystals in 62 and 68% yields, respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dy-N distances / Å</th>
<th>DAD-DyDAD Angle NCCN centroids / °</th>
<th>Trans N-Dy-N angles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.239(2) 2.248(2) 2.266(2) 2.268(2)</td>
<td>164.5</td>
<td>109.34(5) 152.85(5)</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>2.231(2) 2.238(2) 2.248(2) 2.259(2)</td>
<td>177.5</td>
<td>126.39(6) 128.78(6)</td>
<td>This work</td>
</tr>
<tr>
<td>3</td>
<td>2.221(3) 2.226(4) 2.246(3) 2.256(3)</td>
<td>172.2</td>
<td>125.01(7) 138.27(7)</td>
<td>27</td>
</tr>
</tbody>
</table>

The X-ray diffraction study revealed that the homoleptic complexes crystallize in the triclinic P̅I (1) and monoclinic P2₁/n (2) space groups, respectively, with one molecule of ate-complex in the asymmetric unit (Fig. 1, Table S1). The Dy³⁺ cation presents a comparable lanthanide coordination environment, reminiscent to the recently described [Li(DME)₃][Dy(DAD₂)₂] (3) complex.²⁷ It simply consists of two 2σ:η²-coordinated dianionic DAD ligands, the overall negative charge being compensated by a coordinated potassium ion in proximity with the Dy³⁺, the shortest Dy³⁺-K distances being equal to 3.6548(8) and 4.6851(7) Å for 1 and 2, respectively. The K⁺ cation interacts with one phenyl ring of each DAD ligand and completes its coordination sphere with two THF molecules. It is worthy of note that the two K···Ar centre (Ar for aryl substituent of DAD) distances in 1 are equal to 3.5071(9) and 4.0800(9) Å and are much longer compared to those found in 2 (2.978(8) and 3.26(2) Å). Accordingly, different types of coordination of aryl substituents to potassium ion are observed in these complexes. Thus in 1, the K⁺ is η²-coordinated by one aryl fragment resulting in short K···C distances (1:3.071(2), 3.135(2) Å, while only one K···C short contact (3.249(2) Å) is observed for the second phenyl ring (K···C distances > 3.5 Å are declared as not bonding). In 2, the potassium ion is η⁴-coordinated by one aryl fragment (3.175(2)-3.445(2) Å), whereas the interaction with the second one can be classified rather as η⁶ (K···C: 3.175(2)-3.450(2) Å). The Dy-N distances are in the ranges 2.239(2)-2.268(2) Å in 1 and 2.231(2)-2.259(2) Å in 2 (Table 1). Additionally, the presence of short Dy-C contacts (1:2.622(2)-2.671(2) Å; 2:2.675(2)-2.699(2) Å) is indicative of η²-coordination of C=C bond to Dy³⁺. The Dy-N distances in 1 and 2 are slightly longer than those measured in the lithium analogue 3 (shortest distance is 2.221(3) Å, Table 1). The nature of the substituents by the imino carbons in the NCCN fragment affects the angle defined by the Dy³⁺ ion and the NCCN centroids of each DAD ligands ranging from 164.5 (complex 1) to 177.5° (complex 2) (Table 1). The shortest intermolecular Dy-Dy distances found by the analysis of the crystal packing (Fig. S1) are equal to 10.196(7) and 10.947(7) Å for 1 and 2, respectively, indicating that the complexes are relatively well isolated.

![Fig. 1. Molecular structure of 1 and 2 and 3.²⁷ Color code: orange, Dy; red, O; grey, C; purple, K. Hydrogen atoms and Li⁺ ion (for 3) have been omitted for clarity.](image-url)
Magnetic Properties

The magnetic properties were investigated in both, static and dynamic modes by using a SQUID MPMS-XL. The room temperature $\chi T$ values of 13.12, and 13.42 cm$^3$.K.mol$^{-1}$ for 1 and 2, respectively, are slightly lower than the value of 14.17 cm$^3$.K.mol$^{-1}$, expected for a unique Dy$^{3+}$ ion using the free-ion approximation (Fig. 2). These lower experimental $\chi T$ values may be rationalized by a significant crystal-field splitting.\(^6\)

![Fig. 2: Temperature dependence of $\chi T$ under an applied magnetic field of 1000 Oe for 1 and 2. Inset: field dependence of the magnetization at 1.8 K for 1 and 2.](image)

Upon cooling, both samples exhibit a similar decrease of $\chi T$ due to the thermal depopulation of the Stark sub-levels, while the field dependence of the magnetization at 1.8 K reveals the typical unsaturated curves with the values of 5.81 and 4.90 N$\beta$ under 70 kOe for 1 and 2, respectively (Fig. 2). A clear opening in the hysteresis loops could be observed at low temperature for both compounds (Fig. S2), suggesting the occurrence of a slow relaxation of the magnetization.

This was further confirmed by using alternate currents (ac) measurements to study the relaxation dynamics. Both samples exhibit a clear frequency dependence of the in-phase ($\chi'$) and out-of-phase ($\chi''$) components of the magnetic susceptibility (Fig. 3, Fig. S3-S4) indicating a SMM behavior. While for 1, a single frequency dependent peak could be observed, 2 exhibits a broad peak at low temperature with the appearance of a plateau at high frequency upon increasing temperatures. Noticeably, such broad signals of $\chi''$ have also been observed in heteroleptic dysprosium DAD$_{2}$M/Cp* complexes with the same DAD$_{2}$M ligand.\(^28\) The corresponding Cole-Cole plots for 1 and 2 (Fig. 4) could be fitted with a generalized Debye model (Tables S2-S3), but this treatment gives large values for the $\alpha$ parameter, especially for 2 (about 0.4) indicating a large distribution of the relaxation times.\(^38\) This could result in large uncertainties in the determination of the relaxation time, $\tau$. Consequently, the program CC-FIT2, recently developed by Reta and Chilton,\(^39\) was utilized to extract the $\tau$ values and the corresponding uncertainties from the underlying distribution function.

![Fig. 3: Frequency dependence of the out-of-phase susceptibility component, $\chi''$, for 1 and 2 under a zero dc-field.](image)

The $\tau$ vs. $T$ plot (Fig. 5, Fig. S5) reveals a clear deviation at low temperatures, indicating the presence of several relaxation processes. It could be noticed that for 2, the large values of the $\alpha$ parameter leads to important uncertainties for $\tau$. For the three investigated compounds, the fitting was performed by considering the following equation: $\tau^{-1} = \tau_0^{-1}\exp(-\Delta/kT) + CT^\alpha + \tau^{-1}_{QM}$ (Eq. 1),\(^40\) for which the first term accounts for a thermally activated process, while the second and third ones stand for two-phonon Raman and QTM, respectively. This however leads to small $\Delta$ barriers and/or large uncertainties (Table S4), suggesting that, as previously observed for 3, the thermally activated Orbach process is not dominant or even not involved in the relaxation.\(^27\) Consequently, the temperature dependence of the relaxation time was fitted with only a combination of Raman and QTM: $\tau^{-1} = CT^\alpha + \tau^{-1}_{QM}$ (Eq. 2). The best fit parameters could be found in Table 2. Despite the nice apparent fittings for all compounds (Fig. 5), the large uncertainties on the fit parameters obtained from the CC-FIT2 software suggest that such analysis could only be considered as qualitative. For comparison, the fitting parameters by considering solely the extracted $\tau$ values (without taking into account the distribution of relaxation times) could be found in Table S5.
For all compounds, the relaxation time becomes temperature independent at low temperature pointing out a significant QTM that could be shortcut by applying a dc magnetic field. Thus, the field dependence of the ac susceptibilities was monitored (Fig. S8, for 3 please refer to ref.25). For 2, a second relaxation process could be discerned at high frequency upon applying dc fields but without a maximum.

Table 2: Fit parameters of the temperature dependence of the relaxation time for 1 and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>$C$ (s$^{-1}$ K$^{-m}$)</th>
<th>$\tau_{QTM}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (0 Oe)</td>
<td>5(2)</td>
<td>$10^{-10.21}$</td>
<td>$10^{-2.81}$</td>
</tr>
<tr>
<td>1 (1000 Oe)</td>
<td>4.8(3)</td>
<td>$10^{-1.04}$</td>
<td>-</td>
</tr>
<tr>
<td>2 (0 Oe)</td>
<td>4(7)</td>
<td>$10^{-10.21}$</td>
<td>$10^{-2.11}$</td>
</tr>
<tr>
<td>3 (0 Oe)</td>
<td>4(2)</td>
<td>$10^{-10.21}$</td>
<td>$10^{-2.11}$</td>
</tr>
<tr>
<td>3 (3500 Oe)</td>
<td>4.8(7)</td>
<td>$10^{-2.23}$</td>
<td>-</td>
</tr>
</tbody>
</table>

The corresponding field dependences of the relaxation time can be modelled with the equation, $\tau^{-1} = DH^2T + B_1/(1+B_2H^2) + K$ (Eq. 3), for which the first term accounts for the direct process (for Kramers-ion), the second one for the QTM, while the $K$ constant accounts for Raman and thermally activated processes (Fig. S7, Table S6). The optimum field for which the relaxation time is the greatest is estimated at 1000 Oe and 2000 Oe for 1 and 2, respectively. The ac susceptibilities measured under these fields (Fig. 18) corroborate the decrease of the QTM contribution, while the corresponding Cole-Cole plots (Fig. S8, Tables S7-S8) unambiguously confirm the occurrence of a second relaxation process for 2. These Cole-Cole plots were therefore fitted with a generalized Debye model and with a sum of two modified Debye functions26 for 1 and 2, respectively. Noticeably, a strong decrease in the $\tau$ parameter values for 1 ($< 0.05$) is observed, indicating that the magnetic field causes a dramatic effect on the distribution of the relaxation times. Thus, a pertinent fitting of the temperature dependence of the relaxation time could be achieved for 1 and 3 using CC-FIT2 and by considering solely a Raman process, $\tau^{-1} = CT^{-m}$ (Table 2, Fig. 6 and S10), taken into account that the direct process should be inoperative for such weak values of the magnetic field. Remarkably, the obtained parameters are comparable with those obtained in zero dc fields (Table 2), but the associated small uncertainties indicate that, this in-field analysis for 1 and 3 could be considered as quantitative. Nevertheless, it was not possible to obtain a relevant fit with realistic parameters for 2, which could be ascribed to the presence of two relaxations.
complex 3 is rather symmetrical regarding the two DAD
ligands and the N-Dy-N angles strongly deviate from linearity
(ranging from 120 and 139°). Consequently, it appears that
the K'/arene interaction results in the alteration of the DAD
ligands repartition in the coordination sphere of the Dy
ion. Similarly than for 3, the N1-Dy-N4 and N2-Dy-N3 angles in 2
are comparable and equal to 126 and 129°. In that case, the
anisotropic axis is found to pass roughly through the
barycentre of each DAD ligands (Fig. S11) which could be
explained by a lesser electrostatic influence of the K' ion
caused by a greater Dy-K+ distance.

It appears that in these homoleptic complexes, the
magnetic relaxation is dominated by the Raman process, which
clearly shortcut the Orbach relaxation, despite a noticeable
crystal-field splitting. Determining the influence of the
Raman relaxation is relatively complex since this process is
known to depend on numerous parameters, such as the crystal
density, the speed of sound in the solid and the strength of
spin-phonon interactions. Recently, the decisive role of
vibrational modes on the Raman parameters has been
evidenced. Therefore, the decision of the Raman relaxation;
ii) introduction of methyl substituents on the DAD ligands does
not alter specifically also the Raman relaxation. Consequently,
the series based on the DAD ligands, the
Raman process seems to be mainly controlled by vibrational
modes in the close vicinity of the Dy ion and most likely
involves metal-ligand modes.

Analyzing the exact effect of the K'-arene interactions over the
slow relaxation is however far to be unequivocal due to very
subtle structural effects and the predominance of the Raman
relaxation. Yet, the possibility to alter the coordination sphere
of the Dy ion and in turn the orientation of the anisotropic
axis through the electrostatic influence of the K' ion may
provide new synthetic strategies to design high energy barriers
SMMs involving a thermally activated relaxation.

Conclusions
In summary, we have reported here two new homoleptic Dy
complexes based on DAD ligands bearing different substitution
groups and involving K'/arene interactions. Both compounds
exhibit a zero-field slow relaxation of the magnetization arising
from a SMM behaviour. Although they differ by the nature of
the substituent (H vs. Me) on the DAD ligands, both
compounds exhibit comparable slow relaxation of the
magnetization dynamics despite the observed changes in the
Dy-N distances and the N-Dy-N sequence. In addition to the
role of the substituent, the presence of K'/arene interactions
provides also a route to tune the coordination environment of
the Dy ion. Detailed magnetic analysis indicates that, in this
series, the magnetic relaxation is governed by a Raman
process, which only depends on molecular vibrations in the

Fig. 6. Temperature dependence of the relaxation time for 1-3 using the ac susceptibility data in the presence of a dc field. The solid lines represent the fit with a Raman process.

Hence, the comparison between 1 and 3 for the in-field data
clearly shows almost identical (within the standard deviation)
n and C parameters. These parameters are however found
slightly altered without considering the distribution of
relaxation times (Table S5). Nevertheless the superposition on
the τ vs. T plot for all compounds shows that they obviously
follow the same trend (Fig. S10).

Magneto-structural correlations
At the exception of the large distribution of relaxation times
for 2, the magnetic analysis indicates therefore a comparable
behaviour of the slow relaxation of the magnetization in 1-3
despite the slightly different structures. To get further insights,
the orientation of the anisotropic axes of the ground Kramer's
doublets was evaluated by using the MAGELLAN software.
A negative charge on each nitrogen atom of the DAD ligand was
considered. For 1, the anisotropic axis does not pass through
the center of the two DAD ligands but is almost collinear
(deviation of 16 and 18°) to the N2-Dy-N4 string (Fig. S11). The
distance Dy-N2 is the second shortest one and is equal to
2.248(2) Å, while the Dy-N4 is longer 2.268(2) Å. However, the
N2-Dy-N4 angle of 152.85° is closer to the linearity than any
other N-Dy-N angles ranging from 109–119°. This may explain
the deviation of the anisotropic axis with respect to the
barycenter of the DAD ligand. Moreover, the electrostatic
influence of the K' ion most likely impacts the orientation of
the anisotropic axis. In comparison, the anisotropic axis in
complex 3 obtained with the same ligand, but with an
uncoordinated Li ion, passes through the middle of each DAD
ligand (Fig. S11). This could be rationalized by the fact that the

Detailed magnetic analysis indicates that, in this
series, the magnetic relaxation is governed by a Raman
process, which only depends on molecular vibrations in the

5 10 15 20
10
-4
10
-3
10
-2
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-1
10
-4
10
-3
10
-2
10
-1
3500 Oe 3
 
 
T / K
 
 
 / s
2000 Oe 2 
 
 
 
11000 Oe
close vicinity of the Dy$^{3+}$ ion. This confirms that the in-depth understanding of the parameters affecting the Raman relaxation would be the key to improve the SMM features and achieve a high-temperature magnetic bistability.

**Conflicts of Interest**

There are no conflicts to declare.

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**Notes and references**