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SUPPORTING INFORMATION

Synthesis, structure and magnetic properties of tris(pyrazolyl)methane lanthanide complexes: effect of the anion over the slow relaxation of the magnetization

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Experimental Section

Syntheses

The synthesis of complexes **1–6** was performed under aerobic conditions. Acetonitrile was distilled prior to use. Tris(3,5-dimethylpyrazolyl)methane (Tpm) was prepared according to the literature procedure.[1] IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. The N, C, H elemental analyses were carried out in the microanalytical laboratory of the IOMC by means of a Carlo Erba Model 1106 elemental analyser with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Lanthanide metal analysis was carried out by complexonometric titration.[2]

Synthesis of [Ln(Tpm)(NO_3)$_3$]·MeCN

[Tb(Tpm)(NO_3)$_3$]·MeCN (1): MeCN (30 mL) was added to a mixture of $Tb(NO_3)_3(H_2O)_6$ (0.380 g, 0.839 mmol) and Tpm (0.275 g, 0.923 mmol) and the resulting suspension was heated at 80 °C for 10 min to give a clear pale yellow solution. Cooling the solution to room temperature resulted in the formation of **1** as colourless cubic crystals. The mother liquid was decanted and the crystals were washed twice with MeCN (5 mL). Crystals of **1** were dried in vacuum for 10 min.

Complexes **[Dy(Tpm)(NO_3)$_3$]·MeCN** (**2**) and **[Et(Tpm)(NO_3)$_3$]·MeCN** (**3**) were prepared following the similar procedure and were isolated as colorless (**2**) or pale pink (**3**) crystals. Complexes **1–3** were isolated in 78, 82 and 74% yields respectively.

Characterization of **[Tb(Tpm)(NO_3)$_3$]·MeCN** (**1**)**:** Complex **1** crystallizes as a solvate **[Tb(Tpm)(NO_3)$_3$]·MeCN**. Elemental analysis calcd. (%) for $C_{18}H_{25}N_{10}O_9Tb$: C, 31.59; H, 3.68; N, 20.47; Tb, 23.22; found (%): C, 31.28; H, 3.49; N, 20.13; Tb, 23.35. IR (Nujol, KBr) ν/cm^{-1}: 485 (m), 635 (w), 705 (s), 745 (s), 800 (m), 810 (s), 820 (w), 835 (m), 860 (s), 865 (s), 905 (s), 985 (m), 1025 (s), 1040 (s), 1110 (m), 1155 (w), 1170 (w), 1275 (s), 1305 (s), 1415 (m), 1515 (s), 1530 (m), 1570 (s), 1730 (w), 1770 (w), 1975 (w), 2045 (w), 2250 (m), 2290 (w), 2530 (w).

Characterization of **[Dy(Tpm)(NO_3)$_3$]·MeCN** (**2**): Complex **2** crystallizes as a solvate **[Dy(Tpm)(NO_3)$_3$]·MeCN**. Elemental analysis calcd. (%) for $C_{18}H_{25}DyN_{10}O_9$: C, 31.43; H, 3.66; Dy, 23.62; N, 20.36; found (%): C, 31.30; H, 3.30; Dy, 23.52; N, 20.20. IR (Nujol, KBr) ν/cm^{-1}: 485 (m), 635 (w), 705 (s), 750 (s), 800 (m), 810 (s), 820 (w), 835 (m), 860 (s), 865 (s), 905 (s), 985 (m), 1025 (s), 1040 (s), 1110 (m), 1155 (w), 1170 (w), 1275 (s), 1305 (s), 1415 (m), 1515 (s), 1530 (m), 1570 (s), 1730 (w), 1770 (w), 1975 (w), 2045 (w), 2250 (m), 2290 (w), 2530 (w).

Characterization of **[Er(Tpm)(NO_3)$_3$]·MeCN** (**3**): Complex **3** crystallizes as a solvate **[Dy(Tpm)(NO_3)$_3$]·MeCN**. Elemental analysis calcd. (%) for $C_{18}H_{25}ErN_{10}O_9$: C, 31.21; H, 3.64; Er, 24.15; N, 20.22; found: C, 31.08; H, 3.40; Er, 23.96; N, 20.18. IR (Nujol, KBr) ν/cm^{-1}: 485 (m), 635 (w), 705 (s), 755 (s), 800 (m), 810 (s), 820 (w), 835 (m), 860 (s), 865 (s), 905 (s), 985 (m), 1025 (s), 1040 (s), 1110 (m), 1155 (w), 1170 (w), 1280 (s), 1305 (s), 1415 (m), 1515 (s), 1530 (m), 1570 (s), 1730 (w), 1780 (w), 1980 (w), 2050 (w), 2250 (m), 2290 (w), 2535 (w).

Synthesis of [Ln(Tpm)Cl_3]·2MeCN

[Tb(Tpm)Cl_3]·2MeCN(4): MeCN (20 mL) was added to a mixture of $TbCl_3$ (0.150 g, 0.565 mmol) and Tpm (0.180 g, 0.621 mmol) and the resulting suspension was heated at 80 °C for 10 min to give a clear solution. Cooling the reaction mixture to room temperature afforded **4** as colourless prismatic crystals. The mother liquid was decanted and the crystals were washed twice with MeCN (5 mL). Crystals of **4** were dried in vacuum for 10 min.

Complexes **[Dy(Tpm)Cl_3]·2MeCN** (**5**) and **[Dy(Tpm)Cl_3]·2MeCN**(**6**) were prepared following the similar procedure and were isolated as colorless (**5**) or pale pink (**6**) crystals. Complexes **4–6** were isolated in 69, 63 and 75% yields respectively.

Characterization of **[Tb(Tpm)Cl$_3$]·2MeCN** (**4**)**:** Complex **4** crystallizes as a solvate [Tb(Tpm)Cl$_3$]·2MeCN. Elemental analysis calcd. (%) for: $C_{20}H_{28}Cl_3TbN_8$: C, 37.20; H, 4.37; N, 17.35; Tb, 24.61; found: C, 36.85; H, 4.39; N, 16.98; Tb, 24.58. IR (Nujol, KBr) ν/cm^{-1}: 475 (m), 485 (m), 590 (w), 635 (m), 705 (s), 765 (s), 780 (w), 795 (w), 805 (w), 825 (s), 860 (s), 880 (s), 905 (s), 920 (w), 985 (m), 1005 (m), 1040 (s), 1110 (m), 1260 (s), 1300 (s), 1320 (w), 1390 (m), 1410 (s), 1490 (m), 1560 (s), 1615 (w), 1640 (m), 2250 (m), 2290 (w).

Characterization of **[Dy(Tpm)Cl$_3$]·2MeCN** (**5**)**:** Complex **5** crystallizes as a solvate [Dy(Tpm)Cl$_3$]·2MeCN. Elemental analysis calcd. (%) for: $C_{20}H_{28}Cl_3DyN_8$: C, 36.99; H, 4.35; Dy, 25.03; N, 17.26; found: C, 36.68; H, 4.18; Dy, 25.23; N, 16.98. IR (Nujol, KBr) ν/cm^{-1}: 475 (m), 485 (m), 590 (w), 635 (m), 705 (s), 765 (s), 780 (w), 795 (w), 805 (w), 825 (s), 860 (s), 880 (s), 905 (s), 920 (w), 985 (m), 1005 (m), 1040 (s), 1110 (m), 1260 (s), 1305 (s), 1320 (w), 1390 (m), 1410 (s), 1490 (m), 1565 (s), 1615 (w), 1640 (m), 2250 (m), 2290 (w).

Characterization of [Er(Tpm)Cl$_3$]·2MeCN (**6**)**:** Complex **6** crystallizes as a solvate (Tpm)ErCl$_3$·2MeCN. Elemental analysis calcd. (%) for: $C_{20}H_{28}Cl_3ErN_8$: C, 36.72; H, 4.31; Er, 25.57; N, 17.13; found: C, 36.64; H, 4.42; Er, 25.45; N, 17.11. IR: 475 (m), 485 (m), 590 (w), 635 (m), 705 (s), 765 (s), 780 (w), 790 (w), 805 (w), 830 (s), 860 (s), 880 (s), 905 (s), 920 (w), 985 (m), 1005 (m), 1040 (s), 1110 (m), 1260 (s), 1305 (s), 1320 (w), 1390 (m), 1410 (s), 1490 (m), 1565 (s), 1615 (w), 1640 (m), 2250 (m), 2290 (w).

X-Ray crystallography.

The X-ray data for **1-6** were collected on *Bruker D8 Quest* diffractometer (*MoK$_\alpha$*-radiation, ω-scans technique, λ = 0.71073 Å, T = 100(2) K) using *APEX3*[3] software package. The structures were solved by direct and dual-space methods[4] and were refined by full-matrix least squares on F^2 for all data using *SHELX*.[5] *SADA*BS[6] was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined in the “riding” model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms ($U(H)_{iso} = 1.5U_{eq}$ for methyl groups). CCDC–1817048 (**1**), 1817049 (**2**), 1817050 (**3**), 1817051 (**4**), 1817052 (**5**), and 1817053 (**6**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/structures. The crystal data and structure refinement details for **1-6** are given in Table S1.

Magnetic Measurements

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working in the range 1.8 – 350 K with the magnetic field up to 7 Tesla. The sample 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.

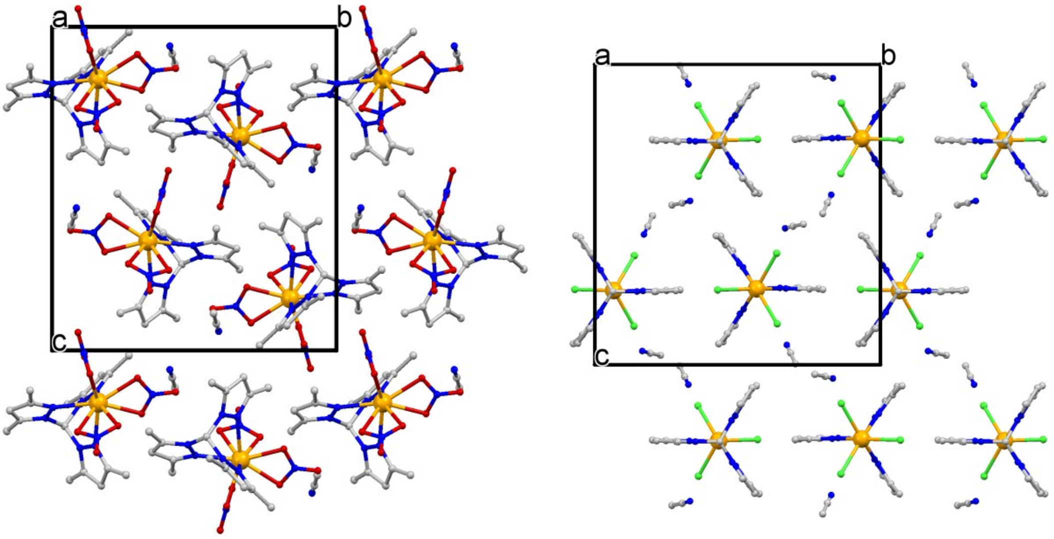


Figure S1: Perspective views of the crystal packing for **1** (left) and **4** (right). Hydrogen atoms have been omitted for clarity.

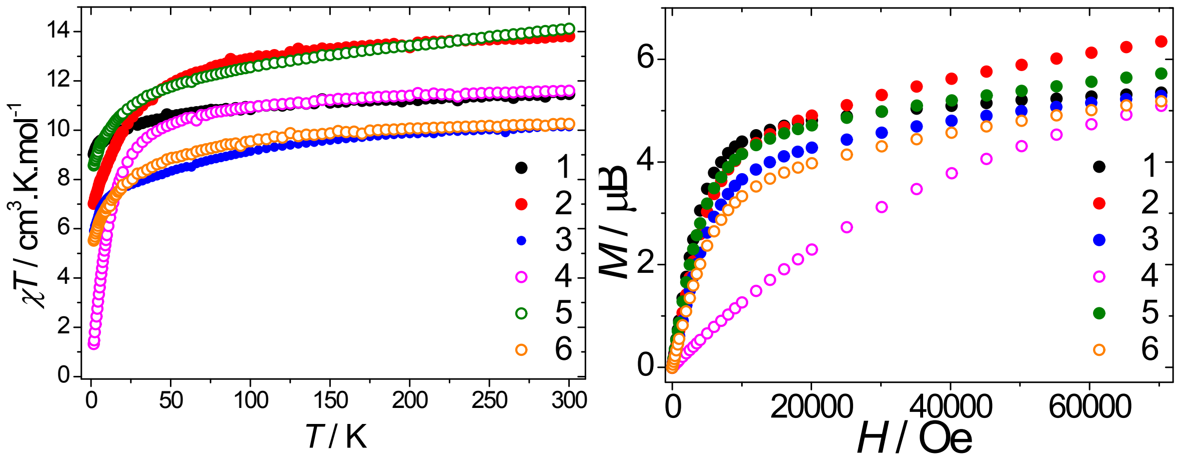


Figure S2: Left: temperature dependence of χT under an applied magnetic field of 1000 Oe for **1** - **6**. Right: field dependence of the magnetization at 1.8 K for **1** - **6**.

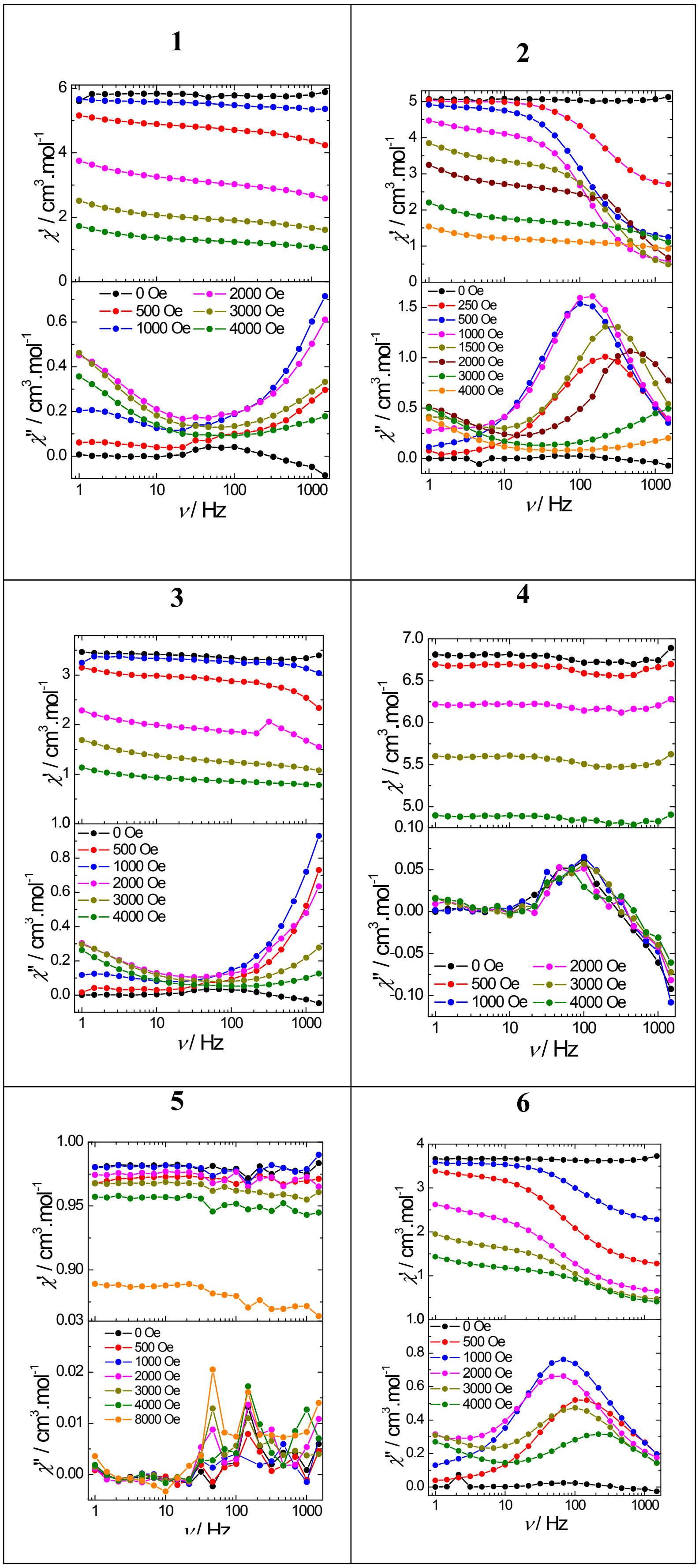


Figure S3. Frequency dependence of χ' and χ'' at 2 K and for various dc fields for compounds **1-6.**

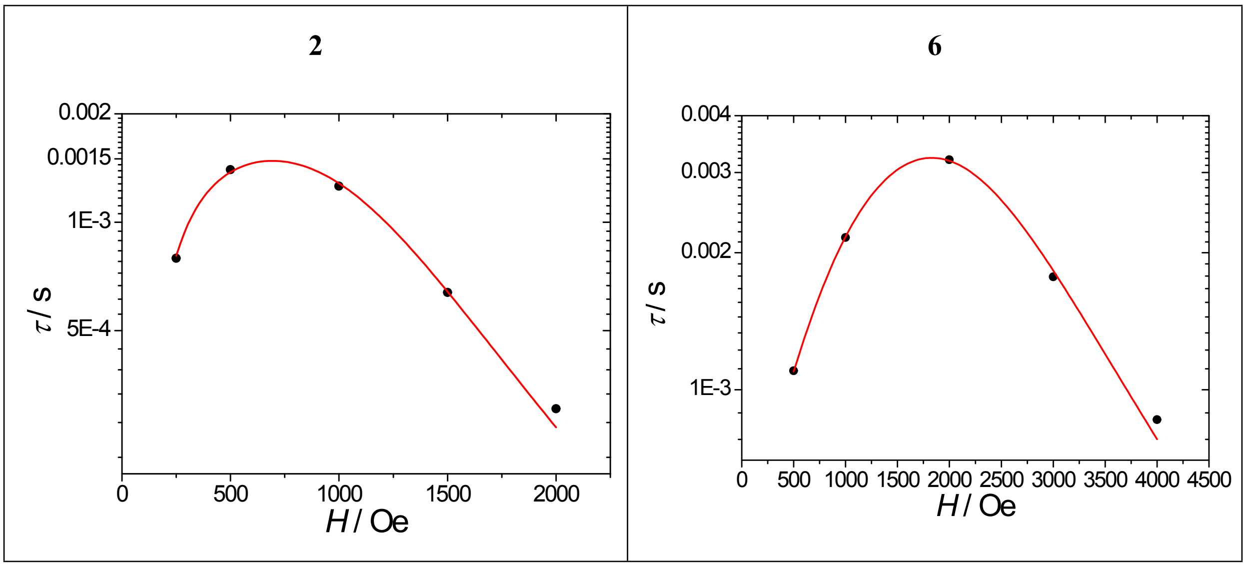


Figure S4. Field dependence of the relaxation time for **2** and **6** at 2 K. The red solid line represent the fit with Equation 1.

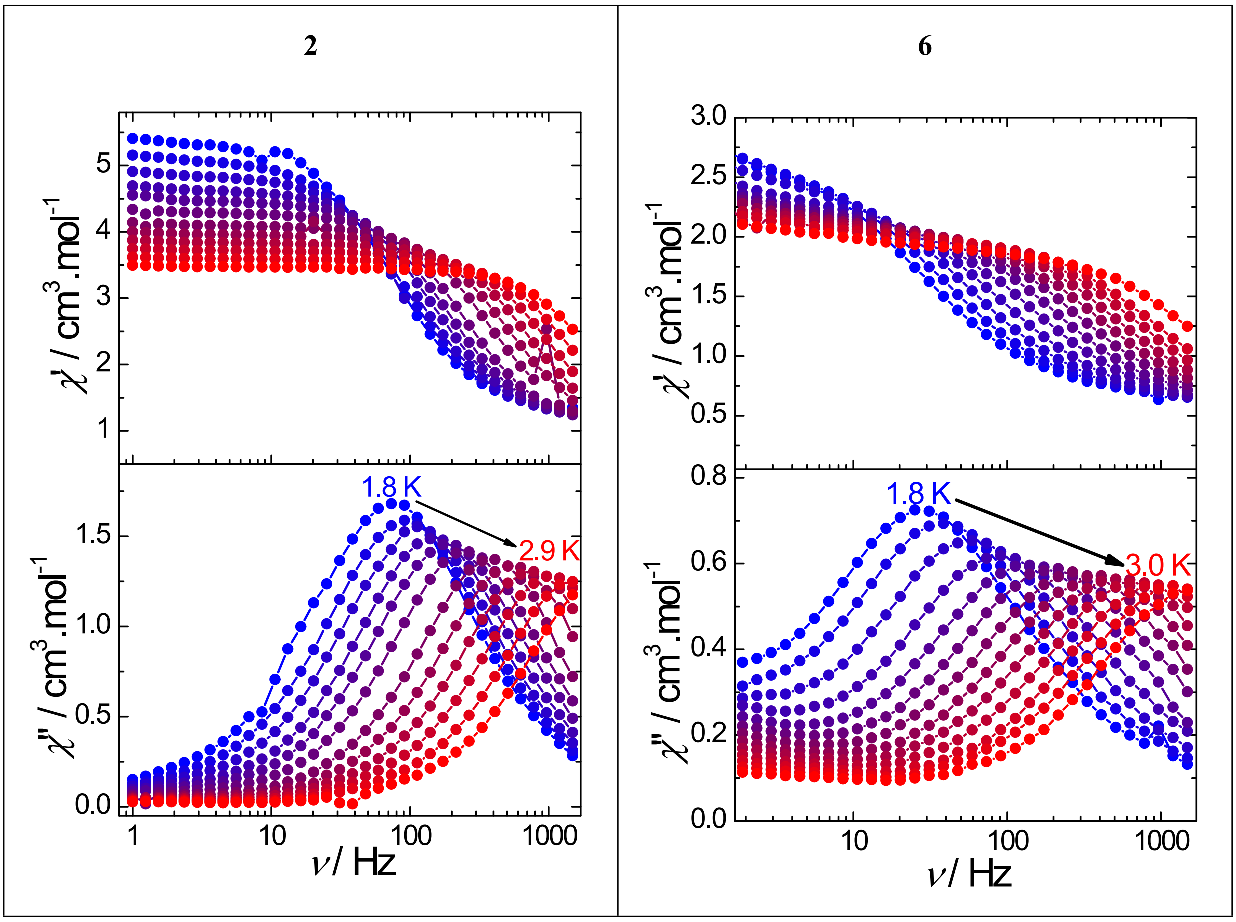
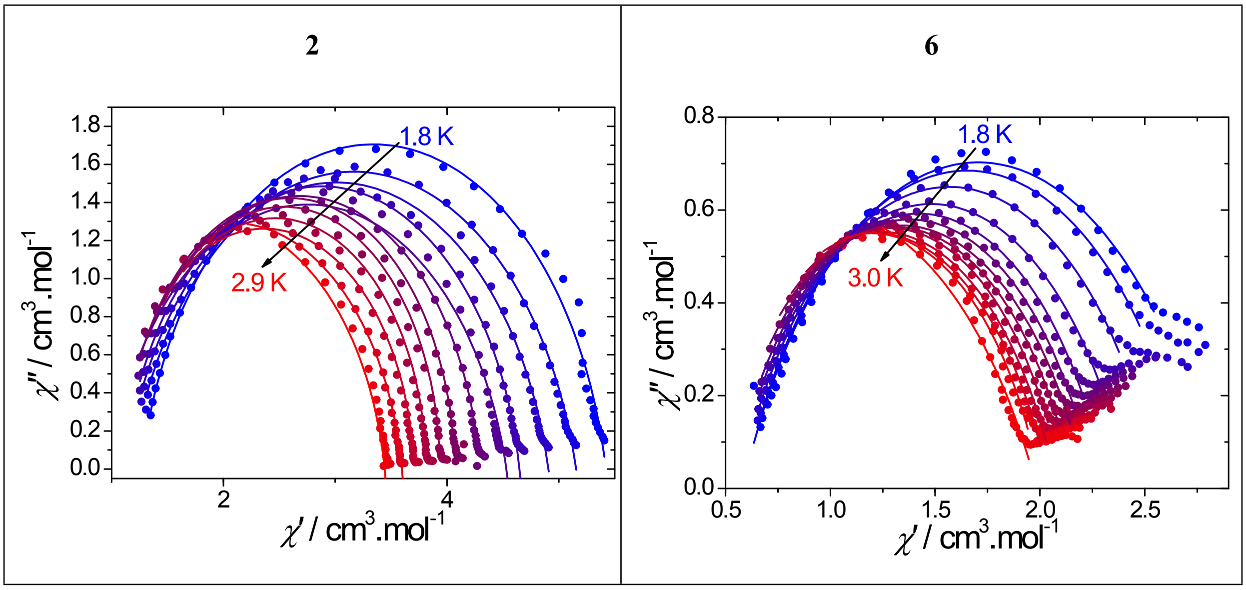
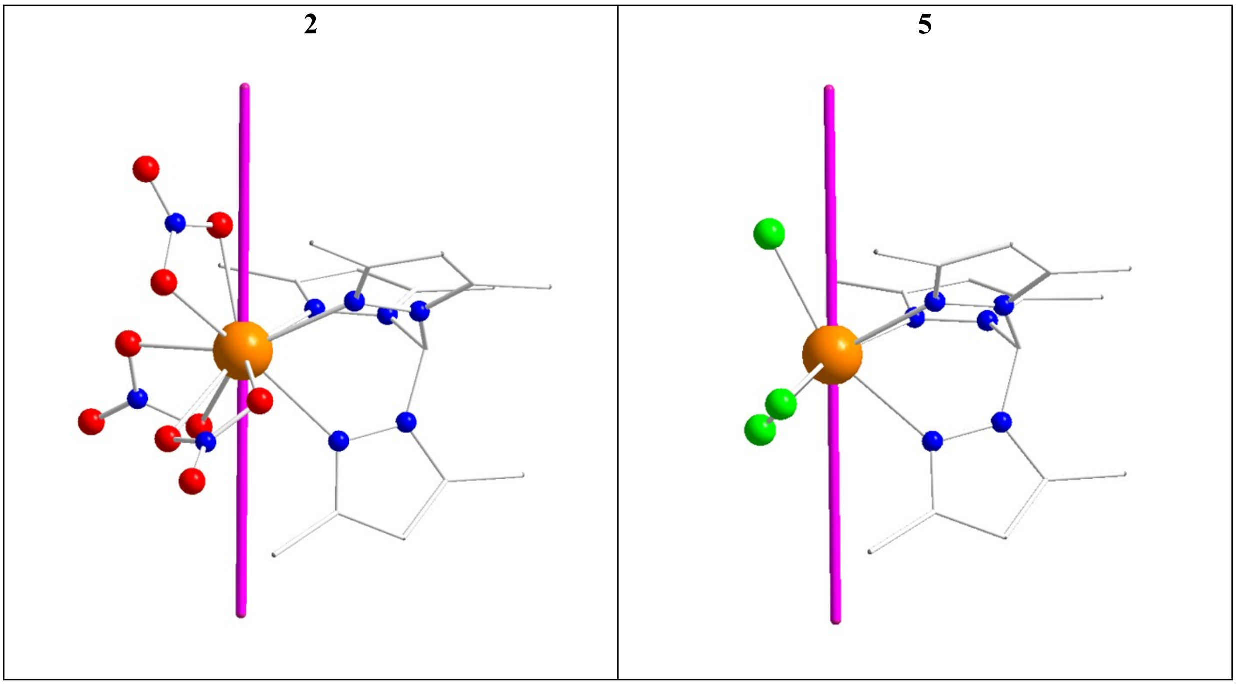


Figure S5. Frequency dependence of χ' and χ'' under a 500 Oe (**2**) (left) and 2000 Oe (**6**) (right) dc fields.


2

6

Figure S6: Cole-Cole (Argand) plot obtained using the ac susceptibility data for **2** (500 Oe) and **6** (2000 Oe). The solid lines correspond to the best fit obtained with a generalized Debye model.


2

5

Figure S7. Orientation of the anisotropic axes (purple) obtained with the MAGELLAN[7] software in **2** and **5**.

Table S1. The Crystal Data and Structures Refinement Details for Complexes **1-6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{16}H_{22}N_9O_9Tb$, C_2H_3N	$C_{16}H_{22}N_9O_9Dy$, C_2H_3N	$C_{16}H_{22}N_9O_9Er$, C_2H_3N	$C_{16}H_{22}Cl_3N_6Tb$, $2(C_2H_3N)$	$C_{16}H_{22}Cl_3N_6Dy$, $2(C_2H_3N)$	$C_{16}H_{22}Cl_3N_6Er$, $2(C_2H_3N)$
Formula Weight	684.40	687.98	692.74	645.77	649.35	654.11
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	10.8271(5)	10.8339(3)	10.8169(3)	9.5146(6)	9.4983(3)	9.4683(3)
b, Å	14.8273(7)	14.8275(4)	14.8226(5)	16.2693(10)	16.2661(4)	16.2801(5)
c, Å	16.3000(8)	16.3088(5)	16.2864(5)	17.1333(11)	17.1262(5)	17.1285(5)
α, °	90	90	90	90	90	90
β, °	95.757(2)	95.8810(10)	96.0506(11)	94.245(3)	94.3140(10)	94.4690(10)
γ, °	90	90	90	90	90	90
V, Å^3	2603.6(2)	2606.05(13)	2596.73(14)	2644.9(3)	2638.51(13)	2632.24(14)
Z	4	4	4	4	4	4
d_{calc}, Mg/m^3	1.746	1.753	1.772	1.622	1.635	1.651
μ, mm^{-1}	2.783	2.933	3.298	3.000	3.159	3.516
$F(000)$	1360	1364	1372	1280	1284	1292
Crystal Size, mm	0.43×0.19×0.14	0.20×0.11×0.11	0.35×0.16×0.15	0.37×0.18×0.09	0.47×0.36×0.30	0.18×0.08×0.06
θ Range for Data Collection, °	2.34–30.00	2.34–29.96	2.34–28.00	2.38–30.00	2.38–35.77	2.49–28.00
Index Ranges	$-15 \leq h \leq 15$ $-20 \leq k \leq 20$ $-22 \leq l \leq 22$	$-15 \leq h \leq 15$ $-20 \leq k \leq 20$ $-22 \leq l \leq 22$	$-14 \leq h \leq 14$ $-19 \leq k \leq 19$ $-21 \leq l \leq 21$	$-13 \leq h \leq 13$ $-22 \leq k \leq 22$ $-24 \leq l \leq 24$	$-15 \leq h \leq 15$ $-26 \leq k \leq 26$ $-28 \leq l \leq 28$	$-12 \leq h \leq 12$ $-21 \leq k \leq 21$ $-22 \leq l \leq 22$
Reflns Collected	34395	37341	56351	35546	52459	57788
Independent Reflns (R_{int})	7590 (0.0444)	7574 (0.0233)	6275 (0.0238)	7698 (0.0338)	12269 (0.0299)	6292 (0.0550)
Completeness to θ, %	99.9	100.0	99.9	99.4	99.9	98.9
Data / Restraints / Parameters	7590 / 0 / 350	7574 / 0 / 350	6275 / 0 / 350	7698 / 0 / 295	12269 / 0 / 297	6292 / 0 / 297
S (F^2)	1.057	1.021	1.058	1.044	1.042	1.087
Final R Indices ($I > 2\sigma(I)$)	$R_1 = 0.0223$ $R_2 = 0.0537$	$R_1 = 0.0161$ $R_2 = 0.0374$	$R_1 = 0.0137$ $R_2 = 0.0346$	$R_1 = 0.0374$ $R_2 = 0.0922$	$R_1 = 0.0251$ $R_2 = 0.0587$	$R_1 = 0.0313$ $R_2 = 0.0822$
R Indices (all data)	$R_1 = 0.0292$ $R_2 = 0.0555$	$R_1 = 0.0195$ $R_2 = 0.0385$	$R_1 = 0.0148$ $R_2 = 0.0350$	$R_1 = 0.0405$ $R_2 = 0.0932$	$R_1 = 0.0290$ $R_2 = 0.0602$	$R_1 = 0.0350$ $R_2 = 0.0832$
Largest Diff. Peak and Hole, e/Å^3	1.16 / –1.19	0.42 / –0.84	0.39 / –0.67	2.61 / –4.22	0.73 / – 2.17	2.11 / –3.30

Table S2. SHAPE analysis for compounds **1-3**.

	JJCU	**CCU**	**JCSAPR**	**CSAPR**	**JTCTPR**	**TCTPR**
1	10.956	9.293	4.046	2.764	4.514	1.926
2	10.912	9.239	4.000	2.704	4.417	1.860
3	10.869	9.204	3.921	2.627	4.266	1.773

JJCU:Capped cube
CCU: Spherical-relaxed capped cube
JCSAPR: Capped square antiprism
CSAPR: Spherical capped square antiprism
JTCTPR: Tricapped trigonal prism
TCTPR: Spherical tricapped trigonal prism

Table S3. SHAPE analysis for compounds **4-6**.

	HP	**PPY**	**OC**	**TPR**	**JPPY**
4	33.175	27.515	1.709	16.934	32.328
5	33.176	27.555	1.650	16.918	32.360
6	33.320	27.553	1.540	18.856	32.333

HP: Hexagon
PPY: Pentagonal Pyramid
OC: Octahedron
TPR: Trigonal Prism
JPPY: Johnson Pentagonal Pyramid

Table S4. Some parameters from static magnetic properties for compounds **1-6**.

Compound	Ln(III) Ground state	Theoretical χT (cm^3.K.mol^{-1})	Experimental χT (cm^3.K.mol^{-1})	M at 70 kOe 1.8 K~~,~~ (μ_B)
1	$^7F_6$	11.82	11.46	5.35
2	$^6H_{15/2}$	14.17	13.81	6.34
3	$^4I_{15/2}$	11.48	10.13	5.28
4	$^7F_6$	11.82	11.59	5.09
5	$^6H_{15/2}$	14.17	14.11	5.72
6	$^4I_{15/2}$	11.48	10.25	5.18

Table S5. Fit parameters of the field dependence of the relaxation time obtained using the Eq. 1

Compound	D ($s^{-1}K^{-1}Oe^{-4}$)	B_1 (s^{-1})	B_2 (Oe^{-2})	K
2	9.9×10^{-11}	306630	0.00693	538.52
6	2.16×10^{-12}	1531	4.12×10^{-6}	157.56

Table S6. Fitting of the Cole-Cole plots with a generalized Debye model for temperature ranging from 2 to 24 K under a zero dc field for **2**.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
1.8	1.52615	5.15967	0.14271
1.9	1.48368	4.84521	0.17997
2	1.39896	4.6293	0.16853
2.1	1.30425	4.45066	0.12612
2.2	1.25982	4.25183	0.18241
2.3	1.18561	4.17217	0.08092
2.4	1.14907	4.03601	0.02615
2.5	1.15596	3.92503	0.00965
2.6	1.13711	3.79406	0.01571
2.7	1.07543	3.65401	0.03915
2.8	0.72698	3.44775	0.10978
2.9	0.51618	3.28039	0.11681

Table S7. Fitting of the Cole-Cole plots with a generalized Debye model under a 2000 Oe dc field for **6**.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
1.8	0.95992	2.45236	0.40362
1.9	0.91813	2.38648	0.37845
2	0.86796	2.26653	0.36507
2.1	0.82034	2.14219	0.35747

2.2	0.78257	2.06356	0.34388
2.3	0.75227	2.0047	0.34917
2.4	0.73113	1.94802	0.37316
2.5	0.6997	1.9175	0.34531
2.6	0.67341	1.89244	0.31489
2.7	0.64246	1.83831	0.34584
2.8	0.61555	1.80589	0.34773
2.9	0.5974	1.79303	0.31414
3	0.34682	1.55401	0.49363

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