

Supplementary Materials: Slow Magnetic Relaxation of Lanthanide(III) Complexes with a Helical Ligand

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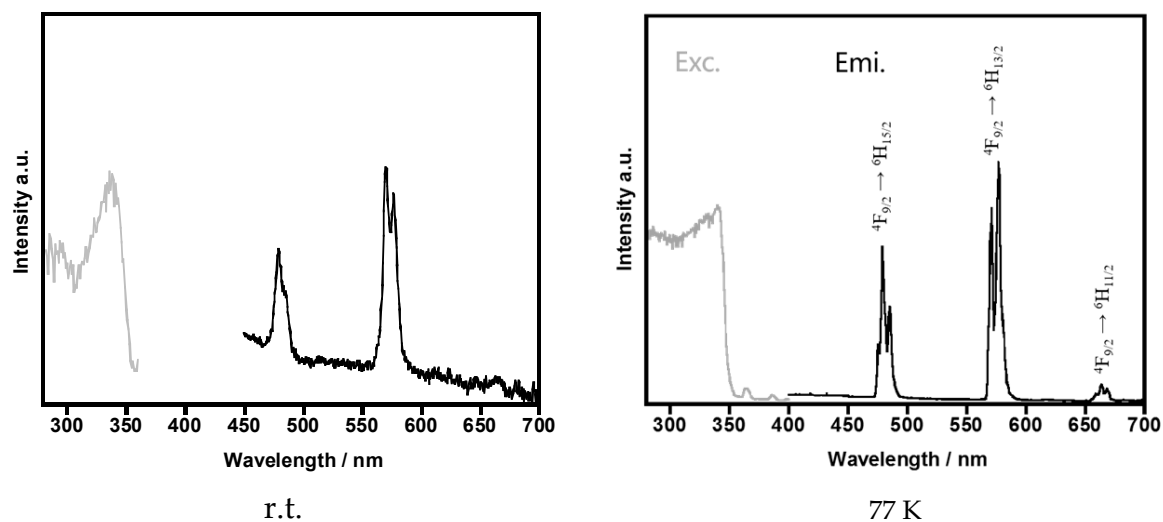


Figure S1. Excitation (gray) and emission (black) spectra of **3** in the solid state at r.t. and 77 K ($\lambda_{\text{ex}} = 315$ nm, $\lambda_{\text{mon}} = 577$ nm). Apparatus: Horiba Jovin-Yvon Fluorolog 3-22.

Table S1. Crystallographic data for Complex 3.

Empirical Formula	C ₂₆ H ₂₃ DyF ₆ N ₉ O ₆ P
Formula weight	865.00
Temperature	153(2) K
Wavelength	0.71075 Å
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 9.0555(17) Å
	<i>b</i> = 12.222(3) Å
	<i>c</i> = 16.139(3) Å
	α = 112.067(3)°
	β = 104.5016(19)°
Volume	γ = 91.5203(11)°
	1588.0(5) Å ³
<i>Z</i>	2
Density (calculated)	1.809 g/m ³
Absorption coefficient	2.494 mm ⁻¹
<i>F</i> (000)	850
Crystal size	0.08 × 0.07 × 0.06 mm ³
θ range for data collection	1.81 to 30.00°.
Index ranges	−12 ≤ <i>h</i> ≤ 12, −17 ≤ <i>k</i> ≤ 17, −22 ≤ <i>l</i> ≤ 22
Reflections collected	20,352
Independent reflections	9081 [<i>R</i> (int) = 0.0516]
Completeness to θ = 30.00°	97.9%
Max. and min. transmission	0.8648 and 0.8254
Refinement method	Full-matrix least squares on <i>F</i> ²
Data/restraints/parameters	9081/0/459
Goodness-of-fit on <i>F</i> ²	1.057
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0399, <i>wR</i> 2 = 0.0995
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0443, <i>wR</i> 2 = 0.1029
Largest diff. peak and hole	1.710 and −1.119 e.Å ⁻³

Table S2. Coordination distances [Å] and angles [°] of Complex 3.

Dy–O1	2.451(3)	N3–Dy–N4	65.14(11)	N3–Dy–N1	124.16(9)
Dy–O4	2.465(3)	O1–Dy–N2	113.66(9)	N4–Dy–N1	146.42(10)
Dy–O2	2.481(3)	O4–Dy–N2	112.00(9)	N2–Dy–N1	61.95(9)
Dy–O5	2.488(3)	O2–Dy–N2	73.08(9)	N5–Dy–N1	111.15(9)
Dy–N3	2.495(3)	O5–Dy–N2	66.23(9)	N6–Dy–N1	68.93(9)
Dy–N4	2.496(3)	N3–Dy–N2	63.77(10)	O1–Dy–N7	25.90(8)
Dy–N2	2.555(3)	N4–Dy–N2	124.36(10)	O4–Dy–N7	147.56(8)
Dy–N5	2.576(3)	O1–Dy–N5	65.27(9)	O2–Dy–N7	25.93(8)
Dy–N6	2.586(3)	O4–Dy–N5	70.16(9)	O5–Dy–N7	158.94(9)
Dy–N1	2.596(3)	O2–Dy–N5	109.87(9)	N3–Dy–N7	99.03(10)
Dy–N7	2.891(3)	O5–Dy–N5	112.17(9)	N4–Dy–N7	74.62(10)
Dy–N8	2.893(3)	N3–Dy–N5	123.75(10)	N2–Dy–N7	93.00(9)
O1–Dy–O4	134.08(8)	N4–Dy–N5	63.34(10)	N5–Dy–N7	87.92(9)
O1–Dy–O2	51.80(9)	N2–Dy–N5	172.19(9)	N6–Dy–N7	114.71(9)
O4–Dy–O2	143.93(9)	O1–Dy–N6	91.77(9)	N1–Dy–N7	72.04(9)
O1–Dy–O5	161.94(9)	O4–Dy–N6	76.31(9)	O1–Dy–N8	155.01(8)
O4–Dy–O5	51.71(9)	O2–Dy–N6	137.16(9)	O4–Dy–N8	25.98(9)
O2–Dy–O5	137.31(8)	O5–Dy–N6	72.40(9)	O2–Dy–N8	150.71(8)
O1–Dy–N3	121.42(10)	N3–Dy–N6	146.23(10)	O5–Dy–N8	25.83(9)
O4–Dy–N3	75.70(9)	N4–Dy–N6	123.60(10)	N3–Dy–N8	75.69(9)
O2–Dy–N3	75.44(9)	N2–Dy–N6	111.00(9)	N4–Dy–N8	97.79(10)
O5–Dy–N3	75.54(10)	N5–Dy–N6	61.76(10)	N2–Dy–N8	89.81(9)
O1–Dy–N4	76.55(10)	O1–Dy–N1	71.78(9)	N5–Dy–N8	90.29(9)
O4–Dy–N4	74.22(10)	O4–Dy–N1	137.54(9)	N6–Dy–N8	70.86(9)
O2–Dy–N4	74.28(10)	O2–Dy–N1	77.53(9)	N1–Dy–N8	115.65(9)
O5–Dy–N4	119.24(10)	O5–Dy–N1	93.91(9)	N7–Dy–N8	172.18(8)

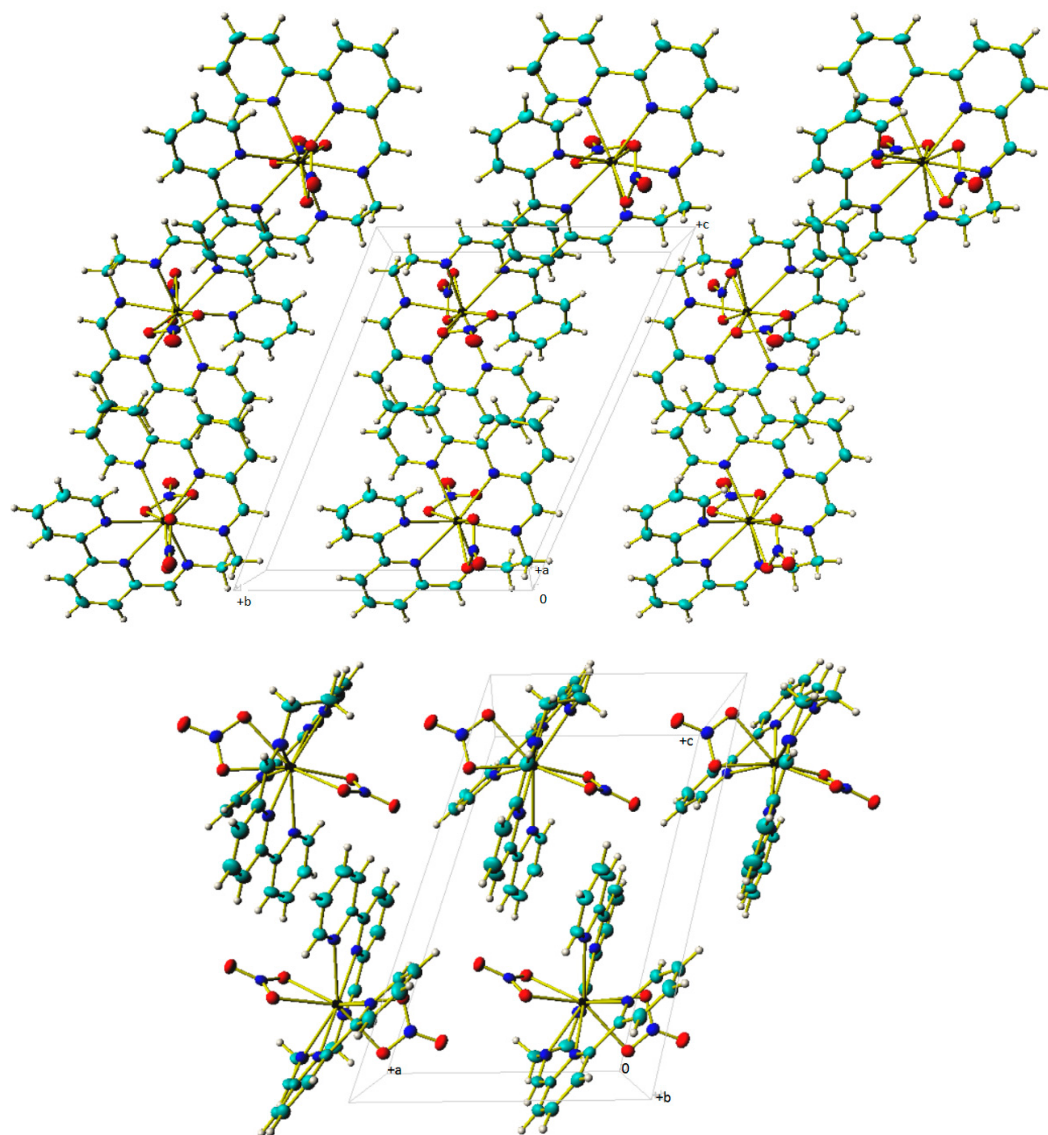


Figure S2. Crystal packing of 3.

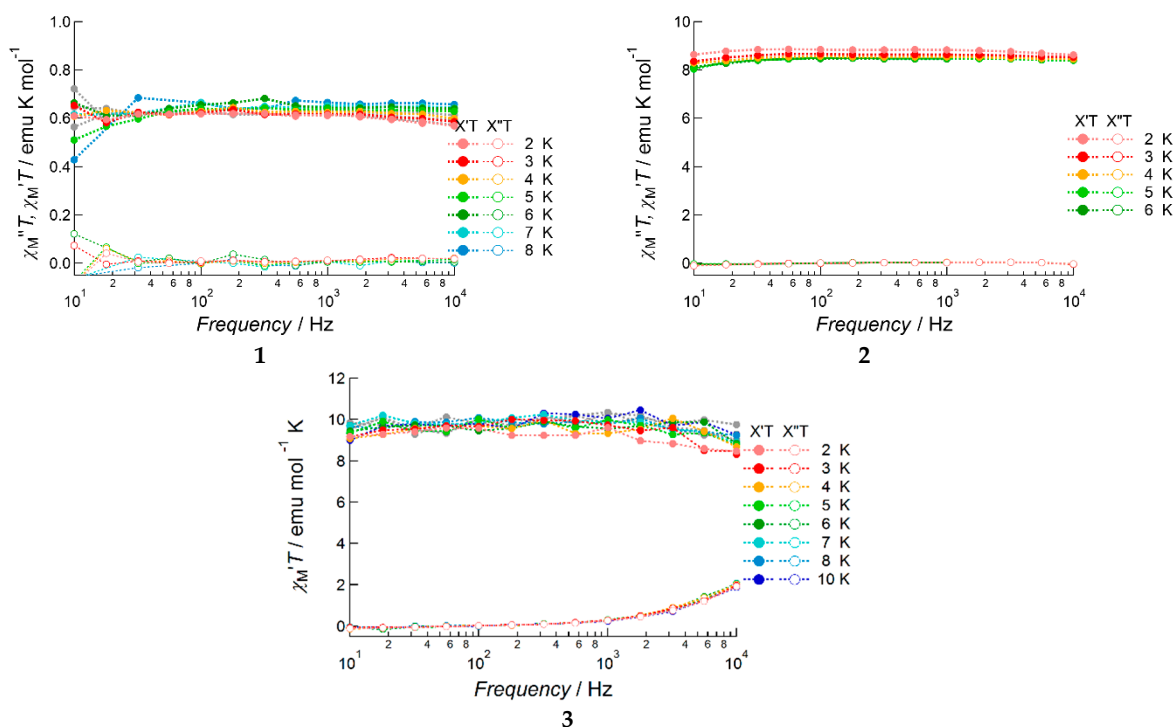


Figure S3. Frequency dependence of $\chi_M' T$ (closed circles) and $\chi_M'' T$ (open circles) of 1–3, measured under an oscillating field of 3 Oe and zero DC field.

Table S3. Best fitted parameters of extended Debye fitting for **1** measured under 1000 Oe DC field.

T/K	$\chi_T/\text{emu}\cdot\text{mol}^{-1}$	$\chi_s/\text{emu}\cdot\text{mol}^{-1}$	τ/s	α
2.0	0.465(8)	0.029(3)	0.0112	0.11(2)
2.2	0.491(3)	0.027(2)	0.0067	0.109(8)
2.4	0.407(5)	0.027(2)	0.00294(7)	0.04(2)
2.6	0.387(4)	0.025(2)	0.00155(5)	0.01(1)
2.8	0.367(3)	0.021(2)	0.00088(2)	0.03(1)
3.0	0.330(2)	0.022(2)	0.000508(7)	0.00(9)
3.2	0.305(2)	0.021(3)	0.000308(7)	0.01(2)
3.4	0.281(2)	0.021(3)	0.000186(5)	0.00(2)
3.6	0.265(2)	0.022(4)	0.000119(4)	0.00(2)
3.8	0.249(2)	0.023(5)	0.000076(3)	0.00(2)
4.0	0.234(1)	0.026(6)	0.000049(2)	0.00(2)
4.2	0.213(2)	0.02(2)	0.000030(4)	0.00(5)
4.4	0.203(2)	0.03(4)	0.000020(4)	0.00(5)

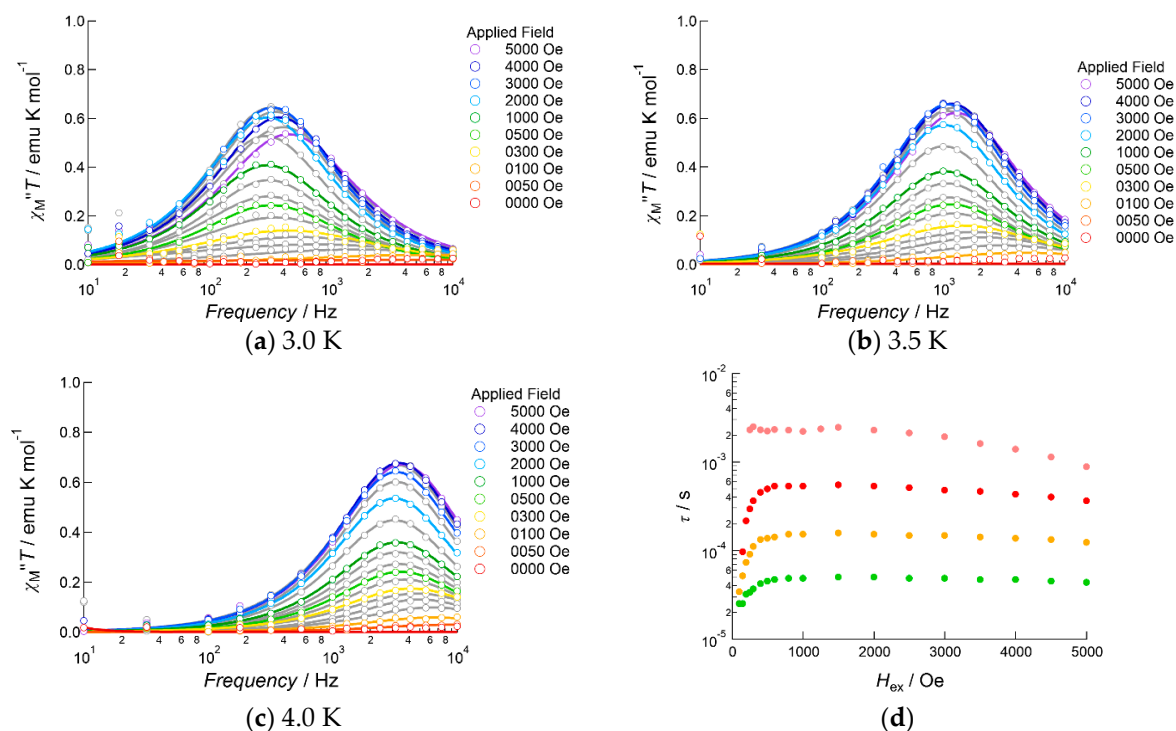


Figure S4. (a–c) DC bias field dependence of the products $\chi_M''T$ of **1**, measured at several temperatures. Solid curves represent the fits to the generalized Debye model; (d) DC field dependence of the relaxation time τ measured in the temperature range from 2.5 K (pink) to 4.0 K (green).

Table S4. Best fitted parameters of the extended Debye fitting for **3**, measured under 1000 Oe DC field.

T/K	$\chi_T/\text{emu}\cdot\text{mol}^{-1}$	$\chi_S/\text{emu}\cdot\text{mol}^{-1}$	τ/s	α
3.0	7.2(2)	0 *	0.0078(6)	0.30(1)
4.0	6.38(7)	0 *	0.00323(9)	0.255(6)
5.0	5.14(3)	0 *	0.00130(2)	0.196(6)
6.0	4.31(2)	0 *	0.000621(9)	0.151(7)
7.0	3.68(2)	0 *	0.000324(5)	0.113(7)
8.0	3.220(12)	0 *	0.000181(2)	0.084(7)
9.0	2.865(9)	0 *	0.000106(2)	0.063(6)
10.0	2.574(8)	0 *	0.0000628(7)	0.044(7)
11.0	2.340(6)	0 *	0.0000373(4)	0.029(7)
12.0	2.144(5)	0 *	0.0000213(2)	0.015(8)
13.0	1.980(4)	0 *	0.0000117(3)	0.01(1)
14.0	1.839(3)	0 *	0.0000064(4)	0.00(2)

* fixed at 0 $\text{emu}\cdot\text{mol}^{-1}$.

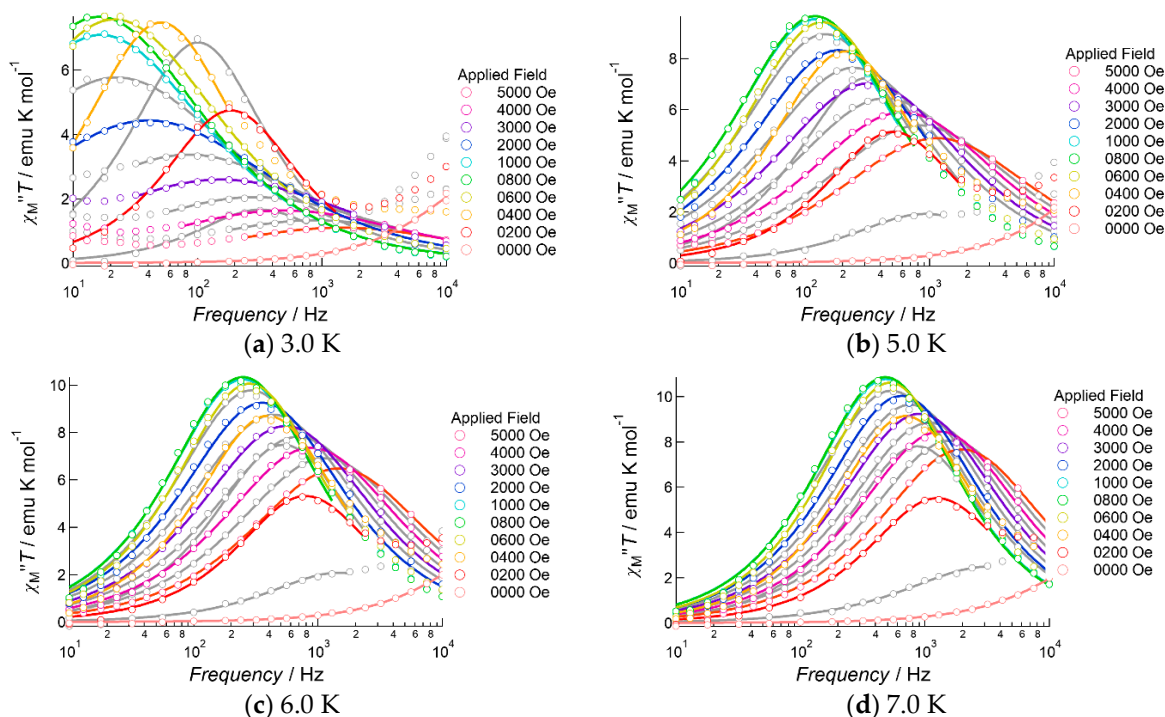


Figure S5. DC bias field dependence of the products $\chi_M''T$ of **3**, measured at several temperatures. Solid curves represent the fits to the generalized Debye model.

Table S5. Best fitted parameters of fitting for **3** using Equation (4).

T/K	$A/10^{-12} \text{ s}^{-1} \text{ Oe}^{-4} \text{ K}^{-1}$	B_1/s^{-1}	B_2/Oe^{-2}	$D/10^2 \text{ s}^{-1}$
3.0	4.60(9)	$2.8(5) \times 10^3$	$4(2) \times 10^{-5}$	0.0(7)
4.0	2.50(5)	$5.1(5) \times 10^3$	$6(1) \times 10^{-5}$	3.1(5)
5.0	2.11(8)	$9(1) \times 10^3$	$8(3) \times 10^{-5}$	9(1)
6.0	2.1(1)	$16(4) \times 10^3$	$11(5) \times 10^{-5}$	19(2)
7.0 *	2.3(2)	$3 \times 10^8 \pm 5 \times 10^{12}$	$1 \pm 4 \times 10^4$	36(3)

* least square fitting failed.

Table S6. Best fitted parameters of fitting for **3** using Equation (3).

Relaxation Process	$H_{\text{ex}} = 500 \text{ Oe}$	$H_{\text{ex}} = 1000 \text{ Oe}$
TA-QTM		
$\Delta E \text{ k}_B^{-1}/\text{K}$	81(5)	81(5)
τ_0/ns	20(9)	24(10)
Raman		
C	1.3(4)	0.29(7)
n	4.1(2)	4.8(1)
Raman + TA-QTM		
$\Delta E \text{ k}_B^{-1}/\text{K}$	7(2)	19(5)
τ_0/ms	0.6(3)	0.11(15)
$C/\text{s}^{-1} \text{ K}^{-5}$	0.191(10)	0.16(2)
n (fixed)	5	5
Raman + TA-QTM		
$\Delta E \text{ k}_B^{-1}/\text{K}$	16(1)	21.8(5)
τ_0/ms	0.30(8)	0.15(2)
$C/10^{-6} \text{ s}^{-1} \text{ K}^{-9}$	9(1)	7.2(5)
n (fixed)	9	9