Supporting Information

Ln-nitronyl Nitroxide Chains Derived from Multidentate Nitronyl Nitroxides

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EXPERIMENTAL SECTION

Materials and Methods

All reagents were commercially available and used without further purification. The radical ligands Nit-Ph-3,5-bPy and Nit-Ph-3,5-btrz were prepared according to the literature methods.[1,2] Carbon, hydrogen, and nitrogen elemental analysis were carried out with a Perkin−Elmer 240 elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 Spectrophotometer in the 400−4000 cm^{-1} region using KBr pellets. Magnetic behaviors were measured on Quantum Design SQUID VSM/MPMS-5 magnetometers using crystalline powder samples embedded in eicosane, ac magnetic susceptibility under 4kOe dc field was measured on PPMS-9 magnetometer. Diamagnetic corrections were performed for both the sample holders and the constituent atoms based on Pascal's constants.[3]

Synthesis of $\{[Ln(hfac)_3]_2(Nit\text{-}Ph\text{-}3,5\text{-}btrz)\}_n$ (Ln^{III} = Gd, 1; Dy, 2)

$Gd(hfac)_3{\cdot}2H_2O$ or $Dy(hfac)_3{\cdot}2H_2O$ (0.01 mmol) was dissolved in dry boiling trichloromethane (15 ml). The solution was maintained to reflux for 3 hours, then cooled it to 35°C, followed by the addition of a CH_2Cl_2 solution (15 mL) of Nit-Ph-3,5-btrz radical (0.005 mmol, 0.0019g) and then filtered. Pink block-shaped crystals were obtained after three hours. Yield: 63% for **1**, 68% for **2**. **1:** Anal. calcd for $C_{47}H_{25}F_{36}Gd_2N_8O_{14}$ (%): C, 29.34; H, 1.31; N, 5.82. Found: C, 29.46; H, 1.61; N, 6.04. IR(KBr): 3236(m), 2874(w), 2447(m), 1795(m), 1617(s) 1358(m), 1159(s),

947(s), 860(s), 624(m), 549(s) cm^{-1}. **2:** Anal. calcd for $C_{47}H_{25}F_{36}Dy_2N_8O_{14}$ (%): C, 29.18; H, 1.30; N, 5.79. Found: C, 29.35; H, 1.54; N, 5.98. IR(KBr): 3236(m), 2872(w), 2450(m), 1795(m), 1617(s) 1358(m), 1161(s), 947(s), 861(s), 624(m), 549(s) cm^{-1}.

Synthesis of $\{[Dy(hfac)_3]_2(Nit\text{-}Ph\text{-}3,5\text{-}bPy)\}_n$, 3

$Dy(hfac)_3{\cdot}2H_2O$ (0.02 mmol) was dissolved in 15ml dry boiling heptane/trichloromethane (1:2, v/v), then the solution was kept to reflux for 3 hours, followed by the addition of a CH_2Cl_2 solution (10 mL) of Nit-Ph-3,5-bPy radical (0.01 mmol, 0.0039g). The resulted solution was stirred for 10 minutes to give a clear pink solution, then cooled it to ambient temperature. The filtrate was left undisturbed at room temperature, after one day, pink block-shaped crystals were obtained. Yield: 52% for **3**. **3:** Anal. calcd for $C_{53}H_{29}F_{36}Dy_2N_4O_{14}$ (%): C, 32.57; H, 1.50; N, 2.87. Found: C, 32.58; H, 1.64; N, 2.73. IR(KBr): 3133(m), 1640(s), 1617(s), 1360(w), 1260(s), 1140(s), 1066(s), 996(m), 950(s), 863(s), 621(m), 541(m), 514(m)cm^{-1}.

X-ray structure determination

For all complexes**,** crystallographic data were collected at 113 K on a Rigaku Saturn CCD diffractometer, employing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan absorption corrections were conducted using the SADABS program.[4] These structures were solved employing SHELXS-2014 by direct methods, and then refined using the program package SHELXL-2014 by full-matrix least-squares on F^2.[5] All non-H atoms were refined anisotropically and all the H atoms attached to C atoms were placed at calculated positions and refined using a riding model. To avoid some of the ADP problems, the command "isor'' was employed to restrain the F, C, O atoms. The crystallographic data of the complexes has been deposited with the CCDC (1835489, 1835490 and 1835491). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. Crystallographic data and structural refinement parameters are given in Table S1. Selected bond lengths and bond angles of the complexes are listed in Table S2-5.

Table S1.Crystallographic data and structure refinement summary for all compounds.

	1	**2**	**3**
Formula	$C_{47}H_{25}F_{36}Ln_2N_8O_{14}$		$C_{53}H_{29}F_{36}Dy_2N_4O_{14}$
Formula weight	1924.25	1934.75	1954.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*I*a	*I*a	*I*a
T, K	113	113	113
a/Å	15.832(4)	15.7905(17)	17.315(5)
b/Å	26.849(7)	27.074(2)	24.619(6)
c /Å	17.570(4)	17.5781(15)	17.483(4)
α, deg	90	90	90
β, deg	107.26(2)	106.941(7)	111.81(2)
γ, deg	90	90	90
V/Å^3	7132(3)	7188.7(12)	6919(3)
θ, deg	3.035/25.013	3.010/25.010	3.006/25.010
Z	4	4	4
D_{calcd} /g cm^{-3}	1.792	1.788	1.877
F(000)	3708	3724	3772
Reflections collected	30890	30751	31515
Unique reflns/ R_{int}	11941/0.1140	12664/0.0382	11612/0.0779
GOF (F^2)	1.063	1.033	1.029
R_1/wR_2 [I > 2σ(I)][a]	0.0726/0.1571	0.0386/0.0868	0.0396/0.0924
R_1/wR_2 (all data)[a]	0.1150/0.1974	0.0441/0.0891	0.0429/0.0933

[a] $R_1 = \Sigma(||Fo| - |Fc||)/\Sigma|Fo|$. w$R_2 = [\Sigma w(|Fo|^2 - |Fc|^2)^2/\Sigma w(|Fo|^2)^2]^{1/2}$

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

Bond distances			
Gd(1)-O(2)	2.333(15)	Gd(1)-O(3)	2.354(16)
Gd(1)-O(1)	2.364(16)	Gd(1)-O(7)	2.387(13)
Gd(1)-O(5)	2.387(15)	Gd(1)-O(6)	2.392(15)
Gd(1)-O(4)	2.396(15)	Gd(1)-N(3)	2.517(17)
Gd(2)-O(12)	2.359(18)	Gd(2)-O(14)	2.360(14)
Gd(2)-O(11)	2.366(17)	Gd(2)-O(10)	2.373(15)
Gd(2)-O(13)	2.381(16)	Gd(2)-O(9)	2.394(15)
Gd(2)-O(8)	2.488(15)	Gd(2)-N(6)#1	2.567(17)
O(7)-N(4)	1.29(2)	O(8)-N(5)	1.27(2)
Angles			
O(2)-Gd(1)-O(3)	83.5(6)	O(2)-Gd(1)-O(1)	70.9(5)
O(3)-Gd(1)-O(1)	74.7(6)	O(2)-Gd(1)-O(7)	143.9(5)
O(3)-Gd(1)-O(7)	97.6(5)	O(1)-Gd(1)-O(7)	144.3(5)
O(2)-Gd(1)-O(5)	142.9(5)	O(3)-Gd(1)-O(5)	81.4(6)
O(1)-Gd(1)-O(5)	72.5(5)	O(7)-Gd(1)-O(5)	71.9(5)
O(2)-Gd(1)-O(6)	102.2(5)	O(3)-Gd(1)-O(6)	143.8(5)
O(1)-Gd(1)-O(6)	73.7(5)	O(7)-Gd(1)-O(6)	97.8(5)
O(5)-Gd(1)-O(6)	72.7(5)	O(2)-Gd(1)-O(4)	75.0(5)
O(3)-Gd(1)-O(4)	72.0(5)	O(1)-Gd(1)-O(4)	134.3(5)
O(7)-Gd(1)-O(4)	71.3(5)	O(5)-Gd(1)-O(4)	130.5(5)
O(6)-Gd(1)-O(4)	144.1(5)	O(2)-Gd(1)-N(3)	78.8(5)
O(3)-Gd(1)-N(3)	144.6(6)	O(1)-Gd(1)-N(3)	126.1(6)
O(7)-Gd(1)-N(3)	80.0(5)	O(5)-Gd(1)-N(3)	129.5(5)
O(6)-Gd(1)-N(3)	70.6(5)	O(4)-Gd(1)-N(3)	73.8(5)
O(12)-Gd(2)-O(14)	109.9(6)	O(12)-Gd(2)-O(11)	70.6(6)
O(14)-Gd(2)-O(11)	74.5(6)	O(12)-Gd(2)-O(10)	77.2(6)
O(14)-Gd(2)-O(10)	146.9(5)	O(11)-Gd(2)-O(10)	78.0(5)
O(12)-Gd(2)-O(13)	86.5(6)	O(14)-Gd(2)-O(13)	71.0(6)
O(11)-Gd(2)-O(13)	128.4(6)	O(10)-Gd(2)-O(13)	142.1(5)
O(12)-Gd(2)-O(9)	134.8(6)	O(14)-Gd(2)-O(9)	82.7(6)
O(11)-Gd(2)-O(9)	71.7(6)	O(10)-Gd(2)-O(9)	71.3(5)
O(13)-Gd(2)-O(9)	137.4(6)	O(12)-Gd(2)-O(8)	146.4(6)
O(14)-Gd(2)-O(8)	88.9(5)	O(11)-Gd(2)-O(8)	142.8(5)
O(10)-Gd(2)-O(8)	102.4(5)	O(13)-Gd(2)-O(8)	73.3(5)
O(9)-Gd(2)-O(8)	73.3(5)	O(12)-Gd(2)-N(6)#1	73.7(6)
O(14)-Gd(2)-N(6)#1	142.5(5)	O(11)-Gd(2)-N(6)#1	136.6(6)
O(10)-Gd(2)-N(6)#1	70.6(5)	O(13)-Gd(2)-N(6)#1	72.0(5)
O(9)-Gd(2)-N(6)#1	122.4(5)	O(8)-Gd(2)-N(6)#1	74.7(5)
N(4)-O(7)-Gd(1)	140.7(13)	N(5)-O(8)-Gd(2)	131.8(12)

#1 x+1,y,z

Table S3. Selected bond lengths [Å] and angles [°] for **2**.

Bond distances			
Dy(1)-O(3)	2.291(8)	Dy(1)-O(2)	2.300(8)
Dy(1)-O(1)	2.316(7)	Dy(1)-O(5)	2.331(6)
Dy(1)-O(4)	2.352(7)	Dy(1)-O(6)	2.357(8)
Dy(1)-O(7)	2.365(7)	Dy(1)-N(6)	2.505(8)
Dy(2)-O(11)	2.282(11)	Dy(2)-O(12)	2.319(8)
Dy(2)-O(10)	2.320(7)	Dy(2)-O(14)	2.342(7)
Dy(2)-O(13)	2.361(7)	Dy(2)-O(9)	2.391(9)
Dy(2)-O(8)#1	2.428(6)	Dy(2)-N(1)	2.495(9)
O(7)-N(7)	1.280(11)	O(8)-N(8)	1.289(11)
Angles			
O(3)-Dy(1)-O(2)	84.5(3)	O(3)-Dy(1)-O(1)	75.4(3)
O(2)-Dy(1)-O(1)	71.6(3)	O(3)-Dy(1)-O(5)	142.5(3)
O(2)-Dy(1)-O(5)	102.3(2)	O(1)-Dy(1)-O(5)	72.2(2)
O(3)-Dy(1)-O(4)	73.0(3)	O(2)-Dy(1)-O(4)	74.1(3)
O(1)-Dy(1)-O(4)	134.9(3)	O(5)-Dy(1)-O(4)	144.4(2)
O(3)-Dy(1)-O(6)	80.2(3)	O(2)-Dy(1)-O(6)	144.5(3)
O(1)-Dy(1)-O(6)	73.6(2)	O(5)-Dy(1)-O(6)	73.1(2)
O(4)-Dy(1)-O(6)	129.8(3)	O(3)-Dy(1)-O(7)	100.4(3)
O(2)-Dy(1)-O(7)	142.5(3)	O(1)-Dy(1)-O(7)	145.8(3)
O(5)-Dy(1)-O(7)	96.0(2)	O(4)-Dy(1)-O(7)	72.0(3)
O(6)-Dy(1)-O(7)	72.2(2)	O(3)-Dy(1)-N(6)	145.3(3)
O(2)-Dy(1)-N(6)	78.6(3)	O(1)-Dy(1)-N(6)	125.8(3)
O(5)-Dy(1)-N(6)	71.4(2)	O(4)-Dy(1)-N(6)	73.2(3)
O(6)-Dy(1)-N(6)	129.3(3)	O(7)-Dy(1)-N(6)	76.7(3)
O(11)-Dy(2)-O(12)	75.5(4)	O(11)-Dy(2)-O(10)	87.6(4)
O(12)-Dy(2)-O(10)	74.7(2)	O(11)-Dy(2)-O(14)	102.4(4)
O(12)-Dy(2)-O(14)	74.6(2)	O(10)-Dy(2)-O(14)	144.0(2)
O(11)-Dy(2)-O(13)	148.7(3)	O(12)-Dy(2)-O(13)	73.3(3)
O(10)-Dy(2)-O(13)	81.4(3)	O(14)-Dy(2)-O(13)	72.1(3)
O(11)-Dy(2)-O(9)	70.9(5)	O(12)-Dy(2)-O(9)	133.2(3)
O(10)-Dy(2)-O(9)	72.2(3)	O(14)-Dy(2)-O(9)	143.7(3)
O(13)-Dy(2)-O(9)	131.5(3)	O(11)-Dy(2)-O(8)#1	136.9(4)
O(12)-Dy(2)-O(8)#1	146.2(3)	O(10)-Dy(2)-O(8)#1	94.2(2)
O(14)-Dy(2)-O(8)#1	100.9(2)	O(13)-Dy(2)-O(8)#1	73.5(2)
O(9)-Dy(2)-O(8)#1	68.8(3)	O(11)-Dy(2)-N(1)	77.1(3)
O(12)-Dy(2)-N(1)	129.4(3)	O(10)-Dy(2)-N(1)	144.8(3)
O(14)-Dy(2)-N(1)	70.9(3)	O(13)-Dy(2)-N(1)	126.4(3)
O(9)-Dy(2)-N(1)	72.9(3)	O(8)#1-Dy(2)-N(1)	77.0(2)
N(7)-O(7)-Dy(1)	139.1(6)	N(8)-O(8)-Dy(2)#2	131.4(6)

#1 x+1,y,z; #2 x-1,y,z

Table S4. Selected bond lengths [Å] and angles [°] for **3**.

Bond distances			
Dy(2)-O(7)	2.294(8)	Dy(2)-O(6)	2.323(7)
Dy(2)-O(4)	2.325(7)	Dy(2)-O(8)	2.344(8)
Dy(2)-O(5)	2.345(7)	Dy(2)-O(1)	2.349(7)
Dy(2)-O(3)	2.396(8)	Dy(2)-N(3)	2.586(9)
Dy(1)-O(13)	2.312(8)	Dy(1)-O(11)	2.317(8)
Dy(1)-O(9)	2.327(7)	Dy(1)-O(14)	2.337(7)
Dy(1)-O(10)	2.343(8)	Dy(1)-O(12)	2.384(9)
Dy(1)-O(2)	2.398(7)	Dy(1)-N(4)#1	2.597(9)
O(1)-N(1)	1.305(10)	O(2)-N(2)	1.289(10)
Angles			
O(7)-Dy(2)-O(6)	90.4(3)	O(7)-Dy(2)-O(4)	94.1(3)
O(6)-Dy(2)-O(4)	143.2(3)	O(7)-Dy(2)-O(8)	71.9(3)
O(6)-Dy(2)-O(8)	73.3(3)	O(4)-Dy(2)-O(8)	73.5(3)
O(7)-Dy(2)-O(5)	77.6(3)	O(6)-Dy(2)-O(5)	72.0(3)
O(4)-Dy(2)-O(5)	144.5(3)	O(8)-Dy(2)-O(5)	132.9(3)
O(7)-Dy(2)-O(1)	144.5(3)	O(6)-Dy(2)-O(1)	98.3(3)
O(4)-Dy(2)-O(1)	98.9(3)	O(8)-Dy(2)-O(1)	143.5(3)
O(5)-Dy(2)-O(1)	72.7(2)	O(7)-Dy(2)-O(3)	142.8(3)
O(6)-Dy(2)-O(3)	82.7(2)	O(4)-Dy(2)-O(3)	71.8(2)
O(8)-Dy(2)-O(3)	71.1(3)	O(5)-Dy(2)-O(3)	133.0(3)
O(1)-Dy(2)-O(3)	72.6(2)	O(7)-Dy(2)-N(3)	73.0(3)
O(6)-Dy(2)-N(3)	143.3(3)	O(4)-Dy(2)-N(3)	72.1(3)
O(8)-Dy(2)-N(3)	128.0(3)	O(5)-Dy(2)-N(3)	72.5(3)
O(1)-Dy(2)-N(3)	79.8(3)	O(3)-Dy(2)-N(3)	129.8(3)
O(13)-Dy(1)-O(11)	81.0(3)	O(13)-Dy(1)-O(9)	141.0(3)
O(11)-Dy(1)-O(9)	79.5(3)	O(13)-Dy(1)-O(14)	70.8(3)
O(11)-Dy(1)-O(14)	103.8(3)	O(9)-Dy(1)-O(14)	147.1(3)
O(13)-Dy(1)-O(10)	139.6(3)	O(11)-Dy(1)-O(10)	136.7(3)
O(9)-Dy(1)-O(10)	73.1(2)	O(14)-Dy(1)-O(10)	83.6(3)
O(13)-Dy(1)-O(12)	126.1(3)	O(11)-Dy(1)-O(12)	71.2(3)
O(9)-Dy(1)-O(12)	78.1(3)	O(14)-Dy(1)-O(12)	72.4(3)
O(10)-Dy(1)-O(12)	70.8(3)	O(13)-Dy(1)-O(2)	78.0(3)
O(11)-Dy(1)-O(2)	148.4(3)	O(9)-Dy(1)-O(2)	102.8(3)
O(14)-Dy(1)-O(2)	91.2(3)	O(10)-Dy(1)-O(2)	71.7(3)
O(12)-Dy(1)-O(2)	140.3(3)	O(13)-Dy(1)-N(4)#1	70.0(3)
O(11)-Dy(1)-N(4)#1	76.3(3)	O(9)-Dy(1)-N(4)#1	72.7(3)
O(14)-Dy(1)-N(4)#1	140.3(3)	O(10)-Dy(1)-N(4)#1	124.1(3)
O(12)-Dy(1)-N(4)#1	139.4(3)	O(2)-Dy(1)-N(4)#1	74.5(3)
N(1)-O(1)-Dy(2)	135.4(6)	N(2)-O(2)-Dy(1)	133.4(6)

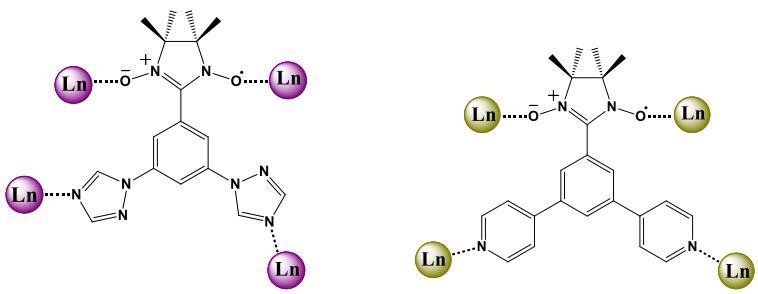
#1 x+0,-y+3/2,z+1/2

Table S5. Important bond lengths [Å] and angles [°] for all complexes.

	1 Gd	**2** Dy	**3** Dy
Ln-O(rad)	2.387(13),2.488(15)	2.365(7),2.428(6)	2.349(7),2.398(7)
Ln-O(hfac)	2.333(15)-2.394(15)	2.291(8)-2.391(9)	2.294(8)-2.396(8)
Ln-N	2.517(17),2.567(17)	2.505(8),2.495(9)	2.586(9),2.597(9)
Ln-O-N	140.7(13),131.8(12)	139.1(6),131.4(6)	135.4(6),133.4(6)

Table S6. SHAPE analysis for the Ln coordination spheres for **2** and **3**.

Compound	SAPR-8	TDD-8	JBTPR-8	BTPR-8	JSD-8
2 Dy1	1.926	**0.449**	2.653	2.018	2.699
2 Dy2	2.907	**0.393**	2.816	2.023	2.764
3 Dy1	**1.381**	**1.320**	2.301	1.873	3.054
3 Dy2	2.962	**0.438**	2.775	2.199	2.320



Scheme S1. Coordination mode of Nit-Ph-3,5-btrz in 1 and 2 (left) and Nit-Ph-3,5-bPy in 3 (right) radical ligands.

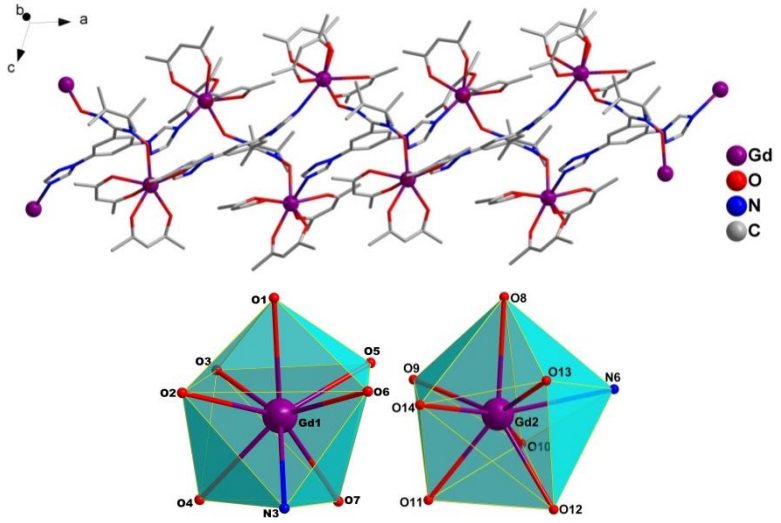


Figure S1. One-dimension structure and local coordination geometry of Gd(III) ions for complex **1** (Hydrogen, Fluorine atoms are not shown for the sake of clarity).

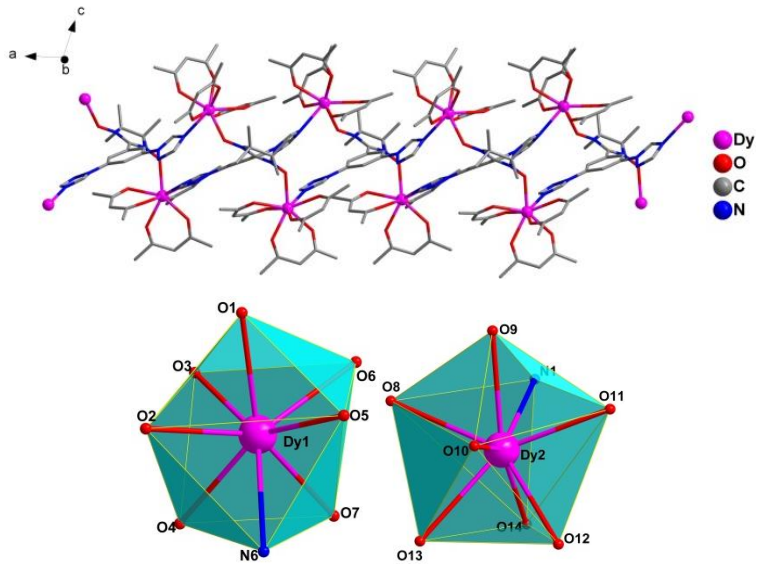


Figure S2. One-dimension structure and local coordination geometry of Dy(III) ions for complex **2** (Hydrogen, Fluorine atoms are not shown for the sake of clarity).

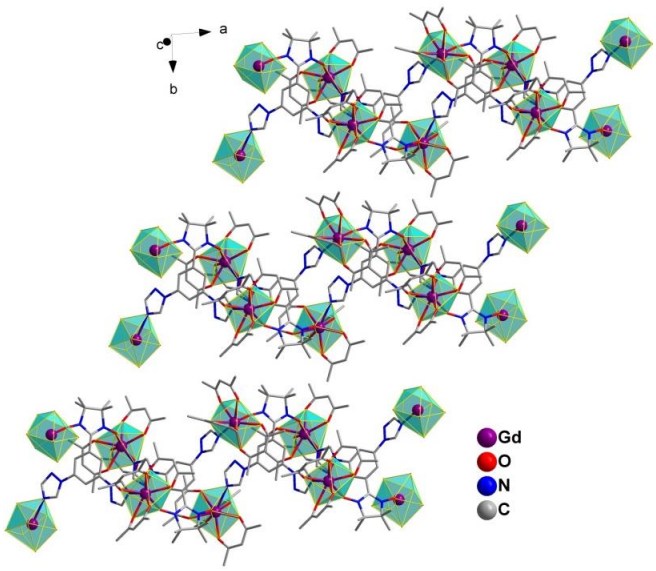


Figure S3. Packing arrangement of the chains in **1** (H and F atoms are omitted for clarity).

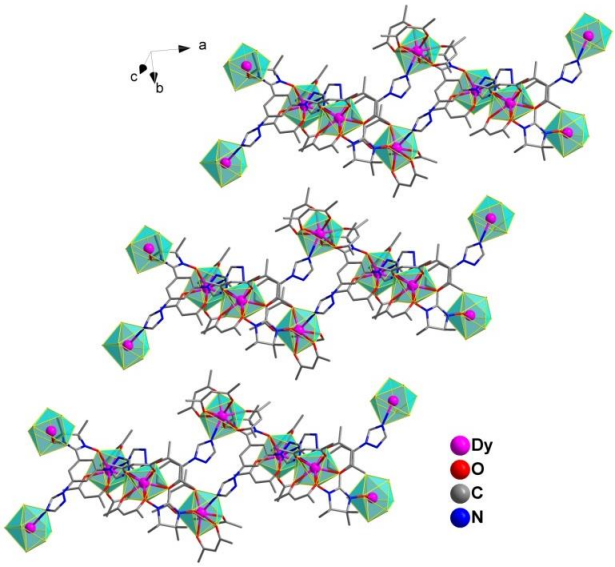


Figure S4. Packing arrangement of the chains in **2** (H and F atoms are omitted for clarity).

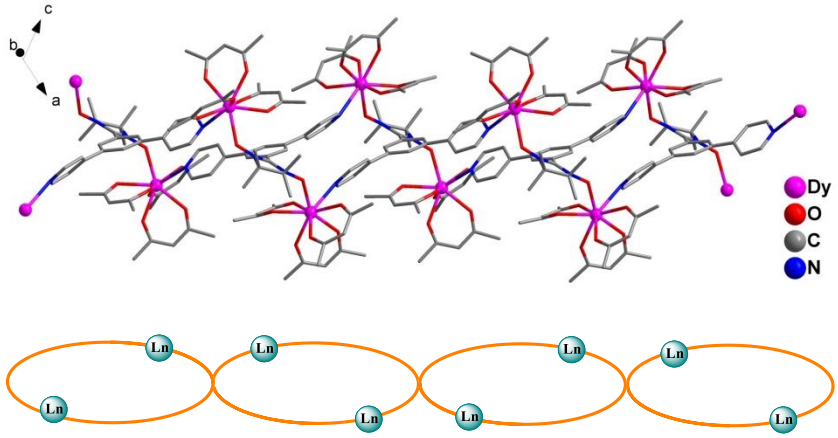


Figure S5. One-dimension structure of **3** and schematic view of the 1D loop chain for **3** (Hydrogen, Fluorine atoms are not shown for the sake of clarity).

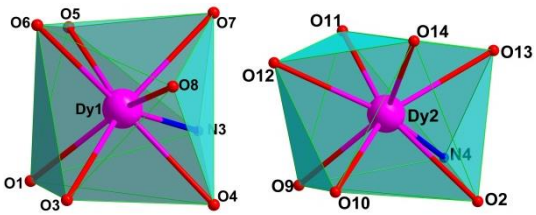


Figure S6. Local coordination geometry of Dy(III) ions for complex **3**.

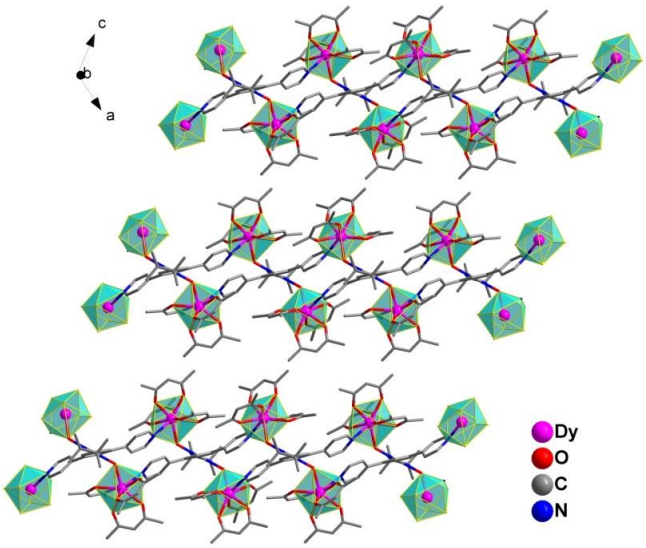


Figure S7. Packing arrangement of the chains in **3** (H and F atoms are omitted for clarity).

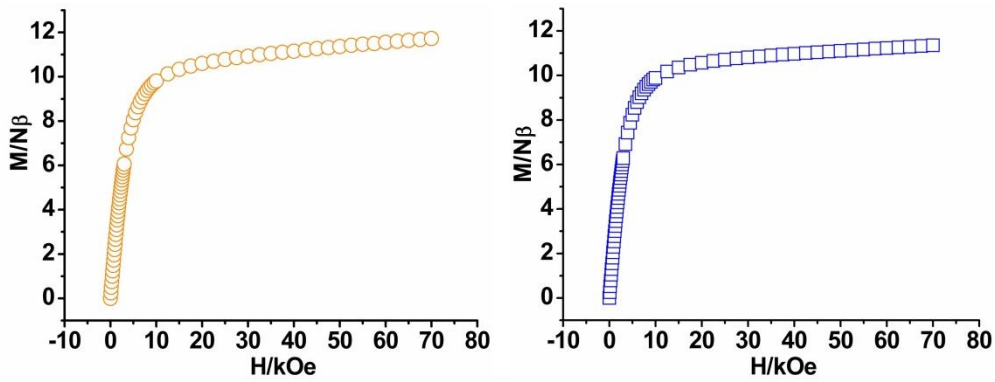


Figure S8. Field dependence of magnetization for **2** (left) and **3** (right) at 2.0 K.

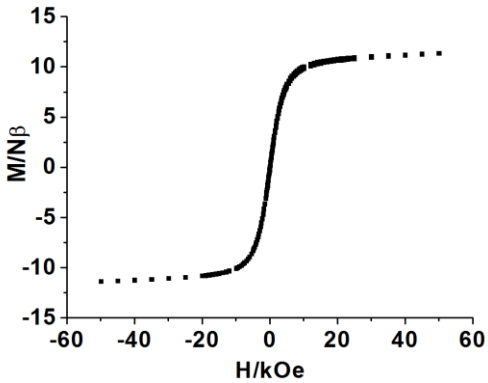


Figure S9. *M* vs *H* behavior for **3** at 2 K recorded from 50 kOe to -50 kOe and back.

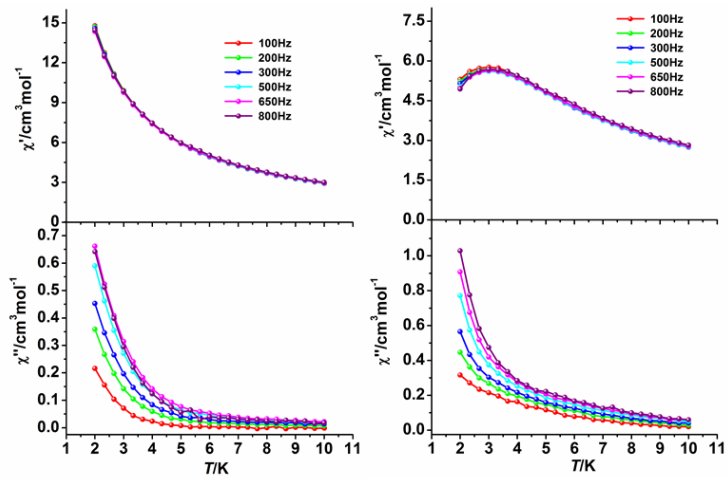


Figure S10. Temperature dependence of the χ′ (top) and χ″ (bottom) under zero dc field (left) and 3000 Oe dc field (right) for compound **2** at different frequencies.

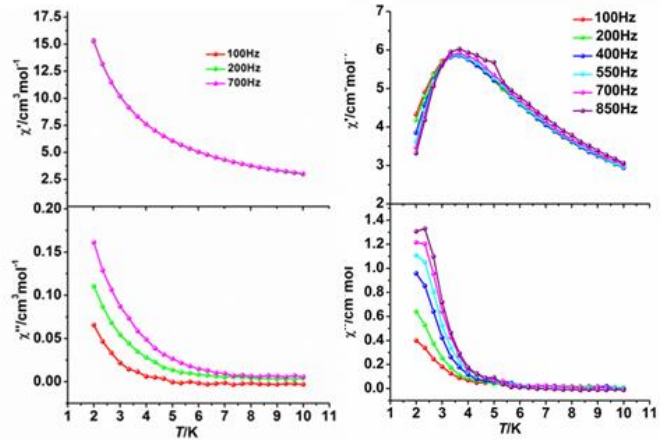


Figure S11. Temperature dependence of the χ′ (top) and χ″ (bottom) under zero dc field (left) and 3000 Oe dc field (right) for compound **3** at different frequencies.

Notes and references

(1) Maligaspe, E.; Kumpulainen, T.; Lemmetyinen, H.; Tkachenko, N, V.; Subbaiyan, N. K.; Zandler, M. E.; D'Souza, F. Ultrafast singlet-singlet energy transfer in self-assembled via metal-ligand axial coordination of free-base porphyrin-zinc phthalocyanine and free-base porphyrin-zinc naphthalocyanine dyads. *J. Phys. Chem. A*, **2009**, *114*, 268-277. (b) Alonso, F.; Beletskaya, I. P.; Yus, M. Non-conventional methodologies for transition-metal catalysed carbon-carbon coupling: A critical overview. Part 2: The Suzuki reaction. *Tetrahedron*, **2008**, *64*, 3047-3101.

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