Electronic Supplementary Material (ESI) for Dalton Transactions.

Ln^{III}/Mn^{II}-Ln^{III} complexes derived from salicylic azo dye ligand: synthesis, structures, magnetic and fluorescent properties

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Table S1 Crystallographic data and structure refinement parameters summary for complexes **1–4.**

Complex	**1 Dy**	**2 Tb**	**3 Dy**	**4 Tb**
Formula	$C_{60}H_{78}N_{30}O_{33}Ln_2$		$C_{54}H_{70}Mn_2N_{36}O_{34}Ln_2$	
Formula weight	2072.52	2065.38	2202.34	2195.20
T (K)	100.00(11)	150.00(10)	100.00(10)	100.00(10)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/C$	$P2_1/C$	$P\bar{1}$	$P\bar{1}$
a (Å)	18.5421(4)	18.5550(4)	11.6378(2)	11.6539(3)
b (Å)	24.3774(5)	24.2497(5)	13.8140(2)	13.7912(3)
c (Å)	20.5877(5)	20.6085(5)	15.5581(2)	15.5805(4)
α (deg)	90	90	112.2770(10)	112.238(2)
β (deg)	100.629(2)	100.863(2)	94.1640(10)	94.0138(19)
γ (deg)	90	90	108.0530(10)	108.238(2)
θ (deg)	2.179–25.010	2.158–30.928	3.144–77.05	4.594–61.866
V(Å^3)	9146.1(4)	9106.7(4)	2148.59(6)	2147.48(10)
Z	4	4	1	2
D_c (g·cm^{-3})	1.505	1.506	1.702	1.697
μ (mm^{-1})	1.714	1.634	12.383	2.017
Unique reflns,	16124	28828	9088	13599
R_{int}	0.0524	0.0543	0.0425	0.0692
GOF	1.015	1.016	1.031	1.012
R_1 (I > 2σ(I))	0.0648	0.0618	0.0506	0.0434
wR_2 (I > 2σ(I))	0.1534	0.1379	0.1437	0.1092
R_1 (all data)	0.0846	0.0964	0.0561	0.0553
wR_2 (all data)	0.1665	0.1506	0.1545	0.1142

$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°) for complex **1.**

Bond distances			
Dy(1)–O(1)	2.346(6)	Dy(1)–O(2)	2.395(6)
Dy(1)–O(4)	2.314(5)	Dy(1)–O(5)	2.405(5)
Dy(1)–O(7)	2.309(5)	Dy(1)–O(8)	2.463(5)

Dy(1)–O(10)	2.398(6)	Dy(1)–O(11)	2.418(6)
Dy(2)–O(16)	2.325(5)	Dy(2)–O(17)	2.411(6)
Dy(2)–O(19)	2.320(5)	Dy(2)–O(20)	2.424(5)
Dy(2)–O(22)	2.309(6)	Dy(2)–O(23)	2.472(6)
Dy(2)–O(25)	2.408(6)	Dy(2)–O(26)	2.385(5)
Angles			
O(1)-Dy(1)-O(2)	71.6(2)	O(1)-Dy(1)-O(4)	79.27(19)
O(1)-Dy(1)-O(5)	118.9(2)	O(1)-Dy(1)-O(7)	148.02(18)
O(1)-Dy(1)-O(8)	79.76(19)	O(1)-Dy(1)-O(10)	77.2(2)
O(1)-Dy(1)-O(11)	136.6(2)	O(2)-Dy(1)-O(4)	114.1(2)
O(2)-Dy(1)-O(5)	72.82(19)	O(2)-Dy(1)-O(7)	139.76(19)
O(2)-Dy(1)-O(8)	147.00(18)	O(2)-Dy(1)-O(10)	84.1(2)
O(2)-Dy(1)-O(11)	74.2(2)	O(4)-Dy(1)-O(5)	72.30(18)
O(4)-Dy(1)-O(7)	79.81(19)	O(4)-Dy(1)-O(8)	74.95(18)
O(4)-Dy(1)-O(10)	143.5(2)	O(4)-Dy(1)-O(11)	140.24(19)
O(5)-Dy(1)-O(7)	76.66(18)	O(5)-Dy(1)-O(8)	137.56(17)
O(5)-Dy(1)-O(10)	144.0(2)	O(5)-Dy(1)-O(11)	73.9(2)
O(7)-Dy(1)-O(8)	71.59(18)	O(7)-Dy(1)-O(10)	107.1(2)
O(7)-Dy(1)-O(11)	72.5(2)	O(8)-Dy(1)-O(10)	73.74(19)
O(8)-Dy(1)-O(11)	120.3(2)	O(10)-Dy(1)-O(11)	73.4(2)
O(16)-Dy(2)-O(17)	72.61(19)	O(16)-Dy(2)-O(19)	77.65(18)
O(16)-Dy(2)-O(20)	118.08(19)	O(16)-Dy(2)-O(22)	147.51(19)
O(16)-Dy(2)-O(23)	79.32(19)	O(16)-Dy(2)-O(25)	135.2(2)
O(16)-Dy(2)-O(26)	78.2(2)	O(17)-Dy(2)-O(19)	115.04(19)
O(17)-Dy(2)-O(20)	73.92(18)	O(17)-Dy(2)-O(22)	139.22(19)
O(17)-Dy(2)-O(23)	147.79(18)	O(17)-Dy(2)-O(25)	72.5(2)
O(17)-Dy(2)-O(26)	85.1(2)	O(19)-Dy(2)-O(20)	71.70(17)
O(19)-Dy(2)-O(22)	80.44(19)	O(19)-Dy(2)-O(23)	72.75(18)
O(19)-Dy(2)-O(25)	143.66(19)	O(19)-Dy(2)-O(26)	141.63(19)
O(20)-Dy(2)-O(22)	76.38(19)	O(20)-Dy(2)-O(23)	135.07(17)
O(20)-Dy(2)-O(25)	77.28(19)	O(20)-Dy(2)-O(26)	146.61(19)
O(22)-Dy(2)-O(23)	71.40(19)	O(22)-Dy(2)-O(25)	74.2(2)
O(22)-Dy(2)-O(26)	106.0(2)	O(23)-Dy(2)-O(25)	121.0(2)
O(23)-Dy(2)-O(26)	73.83(19)	O(25)-Dy(2)-O(26)	71.7(2)

Table S3 Selected bond lengths (Å) and angles (°) for complex **2.**

Bond distances			
Tb(1)–O(1)	2.336(4)	Tb(1)–O(2)	2.382(4)
Tb(1)–O(4)	2.295(4)	Tb(1)–O(5)	2.403(4)
Tb(1)–O(7)	2.291(4)	Tb(1)–O(8)	2.455(3)
Tb(1)–O(10)	2.369(4)	Tb(1)–O(11)	2.393(4)
Tb(2)–O(16)	2.320(4)	Tb(2)–O(17)	2.402(5)
Tb(2)–O(19)	2.302(4)	Tb(2)–O(20)	2.409(4)

Tb(2)–O(22)	2.278(5)	Tb(2)–O(23)	2.475(5)
Tb(2)–O(25)	2.405(5)	Tb(2)–O(26)	2.360(4)
Angles			
O(1)-Tb(1)-O(2)	71.77(15)	O(1)-Tb(1)-O(4)	79.84(15)
O(1)-Tb(1)-O(5)	120.41(15)	O(1)-Tb(1)-O(7)	148.05(13)
O(1)-Tb(1)-O(8)	78.95(14)	O(1)-Tb(1)-O(10)	76.72(18)
O(1)-Tb(1)-O(11)	134.99(16)	O(2)-Tb(1)-O(4)	113.80(18)
O(2)-Tb(1)-O(5)	72.90(14)	O(2)-Tb(1)-O(7)	139.76(14)
O(2)-Tb(1)-O(8)	146.99(13)	O(2)-Tb(1)-O(10)	85.12(18)
O(2)-Tb(1)-O(11)	73.87(19)	O(4)-Tb(1)-O(5)	72.70(13)
O(4)-Tb(1)-O(7)	80.47(13)	O(4)-Tb(1)-O(8)	74.54(12)
O(4)-Tb(1)-O(10)	143.21(14)	O(4)-Tb(1)-O(11)	141.68(14)
O(5)-Tb(1)-O(7)	76.60(13)	O(5)-Tb(1)-O(8)	137.35(12)
O(5)-Tb(1)-O(10)	144.03(14)	O(5)-Tb(1)-O(11)	74.48(15)
O(7)-Tb(1)-O(8)	71.67(12)	O(7)-Tb(1)-O(10)	105.82(17)
O(7)-Tb(1)-O(11)	73.13(16)	O(8)-Tb(1)-O(10)	73.43(14)
O(8)-Tb(1)-O(11)	120.58(16)	O(10)-Tb(1)-O(11)	72.19(16)
O(16)-Tb(2)-O(17)	72.74(16)	O(16)-Tb(2)-O(19)	78.28(13)
O(16)-Tb(2)-O(20)	118.55(15)	O(16)-Tb(2)-O(22)	147.23(18)
O(16)-Tb(2)-O(23)	78.84(16)	O(16)-Tb(2)-O(25)	135.60(18)
O(16)-Tb(2)-O(26)	77.98(16)	O(17)-Tb(2)-O(19)	114.76(15)
O(17)-Tb(2)-O(20)	73.26(15)	O(17)-Tb(2)-O(22)	139.43(18)
O(17)-Tb(2)-O(23)	147.79(15)	O(17)-Tb(2)-O(25)	72.8(2)
O(17)-Tb(2)-O(26)	85.13(19)	O(19)-Tb(2)-O(20)	71.86(13)
O(19)-Tb(2)-O(22)	80.20(16)	O(19)-Tb(2)-O(23)	72.79(15)
O(19)-Tb(2)-O(25)	142.60(15)	O(19)-Tb(2)-O(26)	142.37(16)
O(20)-Tb(2)-O(22)	76.88(16)	O(20)-Tb(2)-O(23)	135.57(14)
O(20)-Tb(2)-O(25)	76.25(15)	O(20)-Tb(2)-O(26)	145.71(16)
O(22)-Tb(2)-O(23)	71.33(17)	O(22)-Tb(2)-O(25)	73.9(2)
O(22)-Tb(2)-O(26)	105.84(18)	O(23)-Tb(2)-O(25)	121.6(2)
O(23)-Tb(2)-O(26)	74.27(19)	O(25)-Tb(2)-O(26)	70.8(2)

Table S4 Selected bond lengths (Å) and angles (°) for complex **3.**

Bond distances			
Dy(1)–O(1)	2.372(3)	Dy(1)–O(2)	2.270(3)
Dy(1)–O(4)	2.317(4)	Dy(1)–O(5)	2.270(4)
Dy(1)–O(7)	2.343(4)	Dy(1)–O(8)	2.274(4)
Dy(1)–O(10)	2.325(4)	Dy(1)–O(11)	2.326(4)
Mn(1)–O(17)	2.103(5)	Mn(1)–N(4)	2.224(5)
Mn(1)–N(6)	2.481(5)	Mn(1)–O(17a)	2.103(5)
Mn(1)–N(4a)	2.224(5)	Mn(1)–N(6a)	2.481(5)
Mn(2)–O(12)	2.140(4)	Mn(2)–O(13)	2.173(5)
Mn(2)–O(14)	2.206(4)	Mn(2)–O(12b)	2.140(4)

Mn(2)–O(13b)	2.173(5)	Mn(2)–O(14b)	2.206(4)
Angles			
O(1)-Dy(1)-O(2)	72.87(12)	O(1)-Dy(1)-O(4)	144.53(13)
O(1)-Dy(1)-O(5)	76.14(13)	O(1)-Dy(1)-O(7)	141.27(14)
O(1)-Dy(1)-O(8)	76.03(13)	O(1)-Dy(1)-O(10)	120.41(15)
O(1)-Dy(1)-O(11)	72.85(13)	O(2)-Dy(1)-O(4)	138.92(14)
O(2)-Dy(1)-O(5)	146.30(14)	O(2)-Dy(1)-O(7)	79.62(14)
O(2)-Dy(1)-O(8)	80.67(14)	O(2)-Dy(1)-O(10)	71.81(14)
O(2)-Dy(1)-O(11)	104.84(14)	O(4)-Dy(1)-O(5)	74.71(15)
O(4)-Dy(1)-O(7)	72.21(14)	O(4)-Dy(1)-O(8)	117.27(15)
O(4)-Dy(1)-O(10)	72.04(16)	O(4)-Dy(1)-O(11)	81.63(15)
O(5)-Dy(1)-O(7)	119.28(15)	O(5)-Dy(1)-O(8)	79.29(14)
O(5)-Dy(1)-O(10)	137.58(16)	O(5)-Dy(1)-O(11)	77.89(14)
O(7)-Dy(1)-O(8)	73.00(16)	O(7)-Dy(1)-O(10)	73.97(18)
O(7)-Dy(1)-O(11)	141.94(16)	O(8)-Dy(1)-O(10)	140.05(16)
O(8)-Dy(1)-O(11)	144.90(14)	O(10)-Dy(1)-O(11)	71.91(16)
N(4)-Mn(1)-N(6)	69.01(16)	N(4)-Mn(1)-O(17)	90.26(19)
N(6)-Mn(1)-O(17)	93.44(16)	O(12)-Mn(2)-O(13)	89.18(17)
O(12)-Mn(2)-O(14)	88.20(18)	O(13)-Mn(2)-O(14)	91.65(19)

a : 2–x,2–y,2–z; b : 2–x,2–y,1–z.

Table S5 Selected bond lengths (Å) and angles (°) for complex **4.**

Bond distances			
Tb(1)–O(1)	2.387(3)	Tb(1)–O(2)	2.284(3)
Tb(1)–O(4)	2.343(3)	Tb(1)–O(5)	2.293(3)
Tb(1)–O(7)	2.360(3)	Tb(1)–O(8)	2.285(3)
Tb(1)–O(10)	2.351(3)	Tb(1)–O(11)	2.350(3)
Mn(1)–O(17)	2.102(4)	Mn(1)–N(4)	2.223(4)
Mn(1)–N(6)	2.486(3)	Mn(1)–O(17a)	2.102(4)
Mn(1)–N(4a)	2.223(4)	Mn(1)–N(6a)	2.486(3)
Mn(2)–O(12)	2.147(3)	Mn(2)–O(13)	2.176(3)
Mn(2)–O(14)	2.198(3)	Mn(2)–O(12b)	2.147(3)
Mn(2)–O(13b)	2.176(3)	Mn(2)–O(14b)	2.198(3)
Angles			
O(1)-Tb(1)-O(2)	72.56(9)	O(1)-Tb(1)-O(4)	144.71(9)

O(1)-Tb(1)-O(5)	75.97(10)	O(1)-Tb(1)-O(7)	141.71(10)
O(1)-Tb(1)-O(8)	76.51(10)	O(1)-Tb(1)-O(10)	119.60(11)
O(1)-Tb(1)-O(11)	72.66(10)	O(2)-Tb(1)-O(4)	139.28(10)
O(2)-Tb(1)-O(5)	145.96(11)	O(2)-Tb(1)-O(7)	79.15(10)
O(2)-Tb(1)-O(8)	80.84(10)	O(2)-Tb(1)-O(10)	71.88(10)
O(2)-Tb(1)-O(11)	104.83(10)	O(4)-Tb(1)-O(5)	74.70(11)
O(4)-Tb(1)-O(7)	72.60(10)	O(4)-Tb(1)-O(8)	116.39(11)
O(4)-Tb(1)-O(10)	72.74(11)	O(4)-Tb(1)-O(11)	82.10(10)
O(5)-Tb(1)-O(7)	120.21(11)	O(5)-Tb(1)-O(8)	79.51(10)
O(5)-Tb(1)-O(10)	137.25(11)	O(5)-Tb(1)-O(11)	77.35(10)
O(7)-Tb(1)-O(8)	72.49(12)	O(7)-Tb(1)-O(10)	73.64(13)
O(7)-Tb(1)-O(11)	142.36(12)	O(8)-Tb(1)-O(10)	140.46(11)
O(8)-Tb(1)-O(11)	145.01(10)	O(10)-Tb(1)-O(11)	71.44(12)
N(4)-Mn(1)-N(6)	69.05(12)	N(4)-Mn(1)-O(17)	90.25(15)
N(6)-Mn(1)-O(17)	94.21(13)	O(12)-Mn(2)-O(13)	89.58(13)
O(12)-Mn(2)-O(14)	89.30(13)	O(13)-Mn(2)-O(14)	91.90(13)

a : 2–x,2–y,2–z; b : 2–x,2–y,1–z.

Table S6 SHAPE analysis for complexes **1–4.**

Complex	Ln	SAPR-8	TDD-8	JBTPR-8	BTPR-8
1	**Dy1**	**0.452**	1.509	2.026	1.659
	Dy2	**0.572**	1.397	2.001	1.609
2	**Tb1**	**0.547**	1.320	1.961	1.563
	Tb2	**0.581**	1.391	1.862	1.554
3	**Dy1**	**0.392**	1.638	1.901	1.321
4	**Tb1**	**0.400**	1.632	1.896	1.324

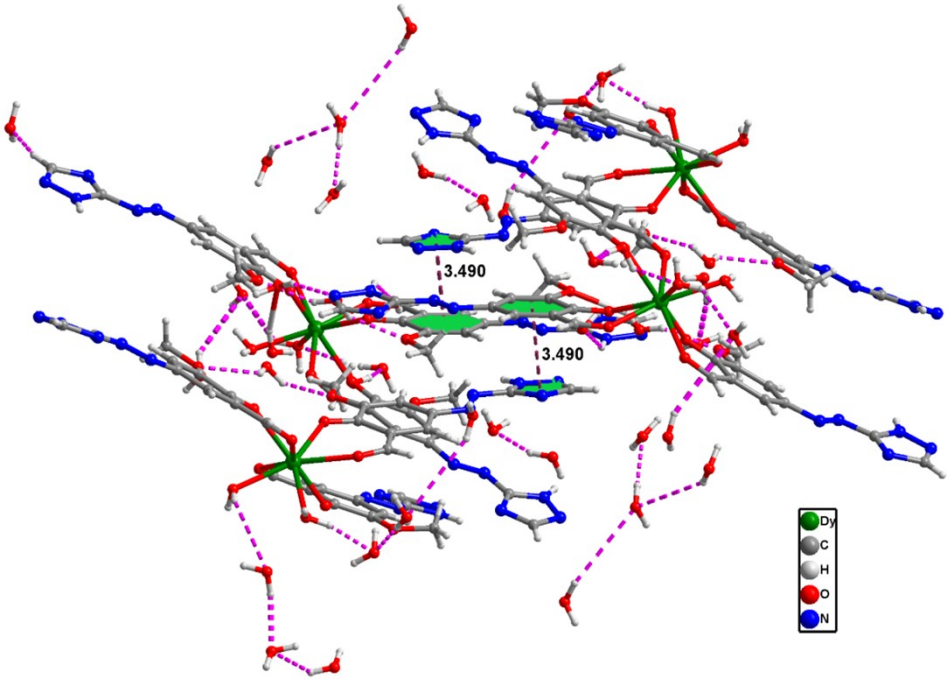


Figure S1 The hydrogen-bonds and the π–π stacking interaction in complex **1**.

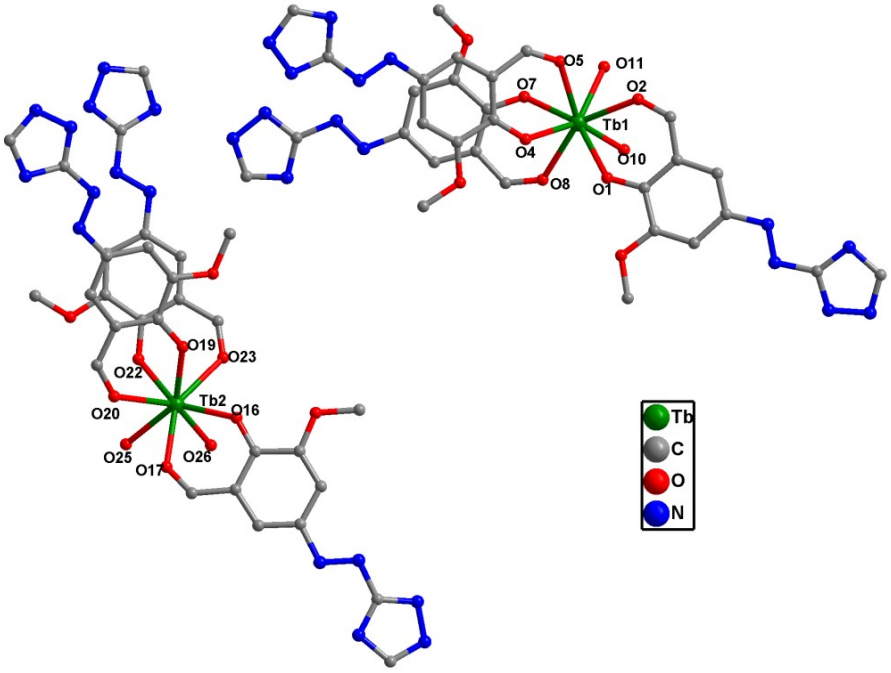


Figure S2 Crystal structure of complex **2**. Hydrogen atoms and uncoordinated solvent molecules were omitted for clarity reason.

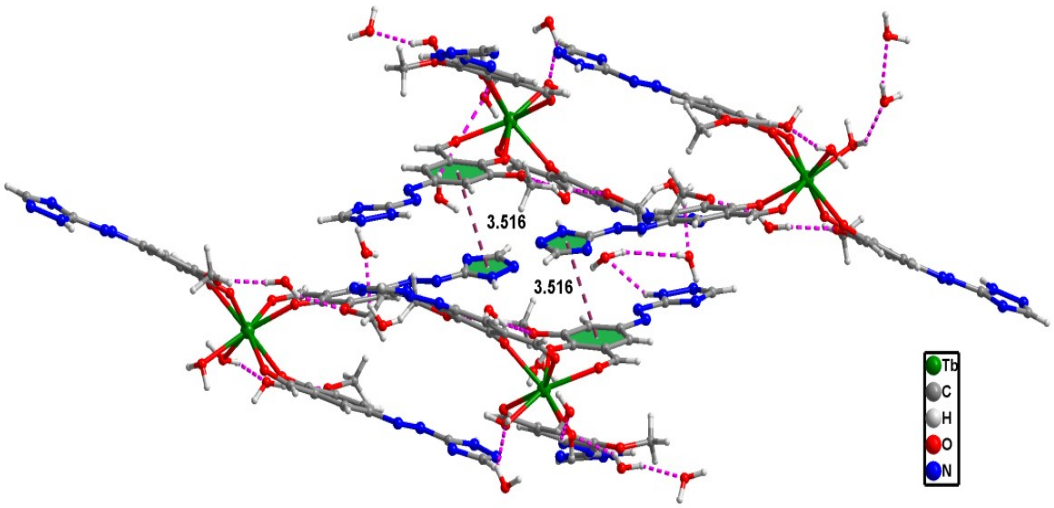


Figure S3 The hydrogen-bonds and the π–π stacking interaction in complex **2**.

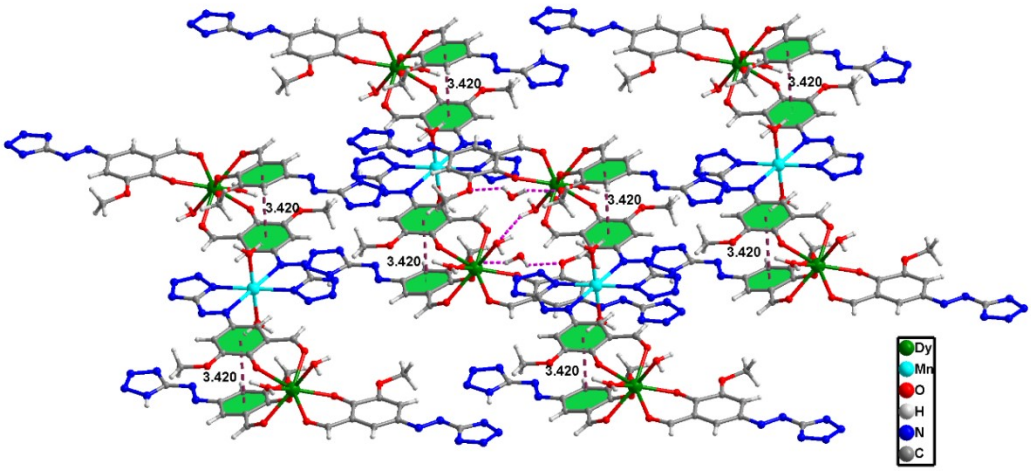


Figure S4 The hydrogen-bonds and the π–π stacking interaction in complex **3**.

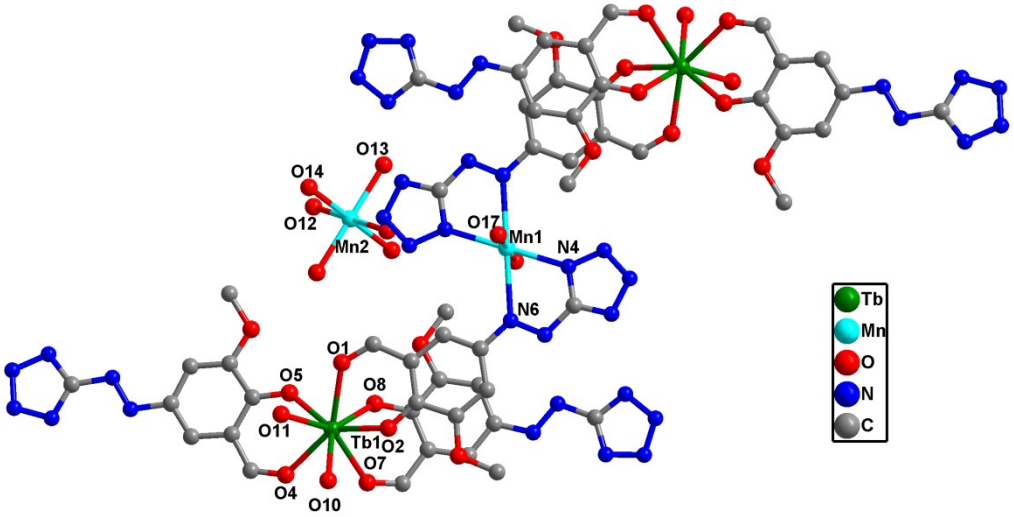


Figure S5 Crystal structure of complex **4**. Hydrogen atoms and uncoordinated solvent molecules

were omitted for clarity reason.

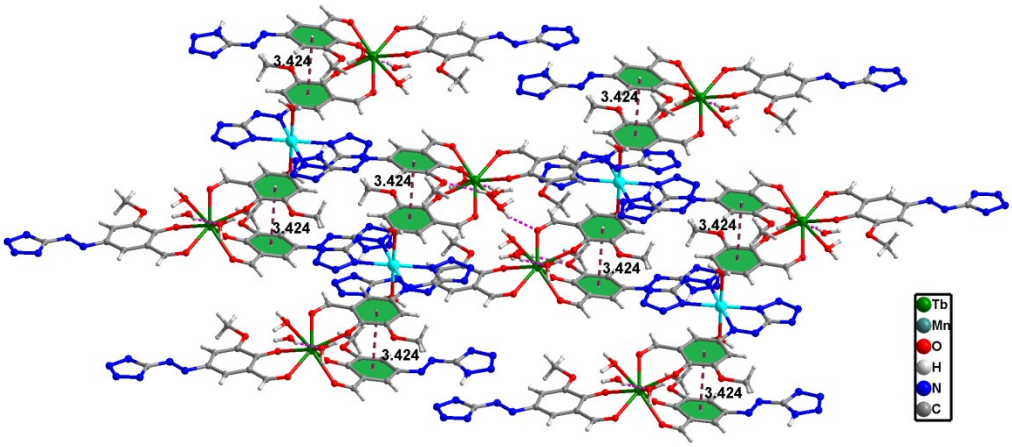


Figure S6 The hydrogen-bonds and the π–π stacking interaction in complex **4**.

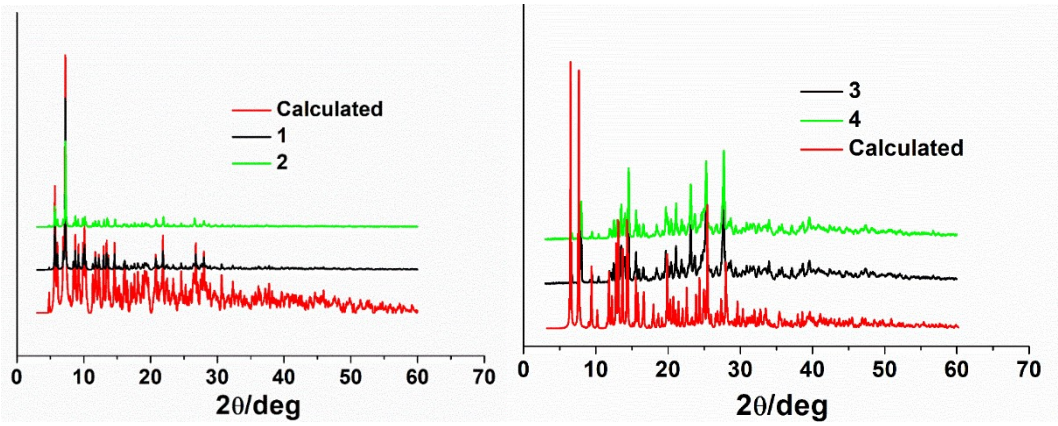
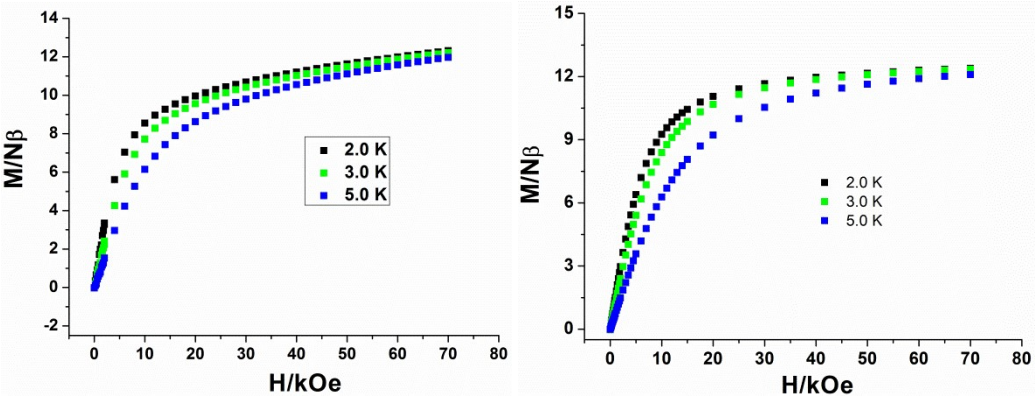


Figure S7 Powder X-ray diffraction (PXRD) patterns for complexes **1**–**4**.



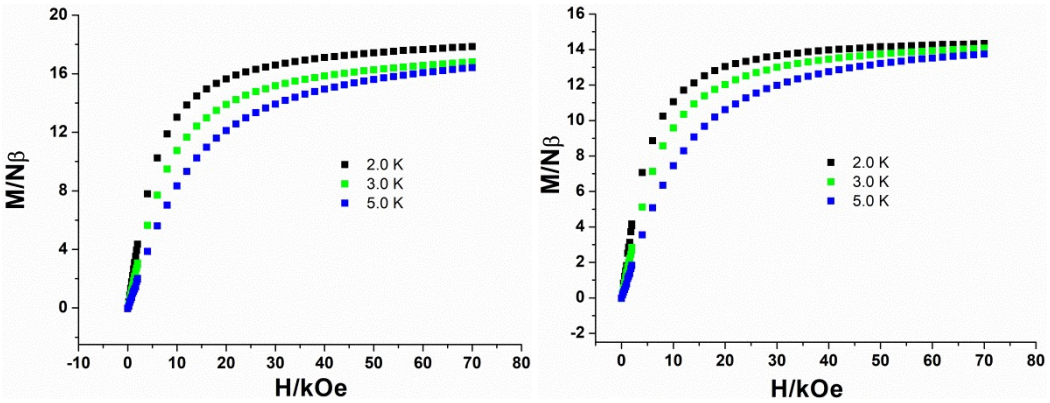


Figure S8 *M* versus *H* plot at 2, 3, 5 K for complexes **1–4.**

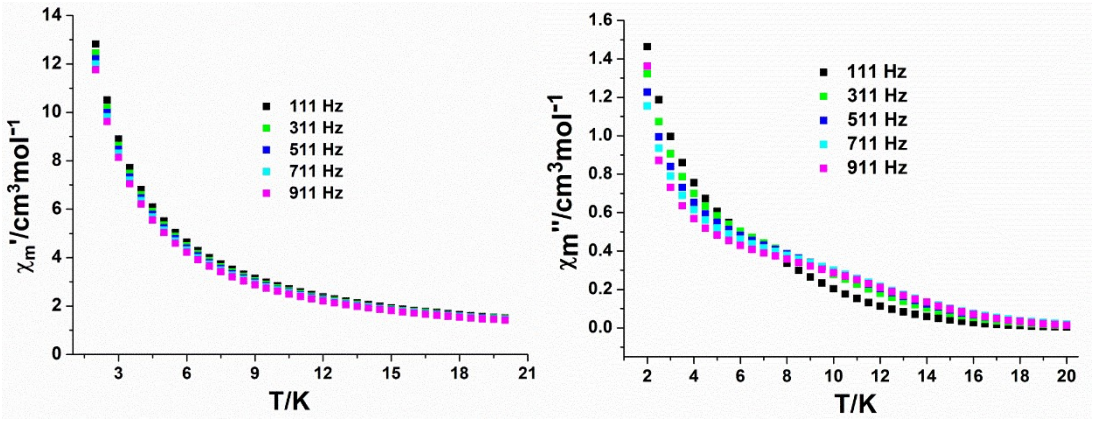


Figure S9 Temperature dependence of the in-phase and out-phase in zero field for complex **1**.

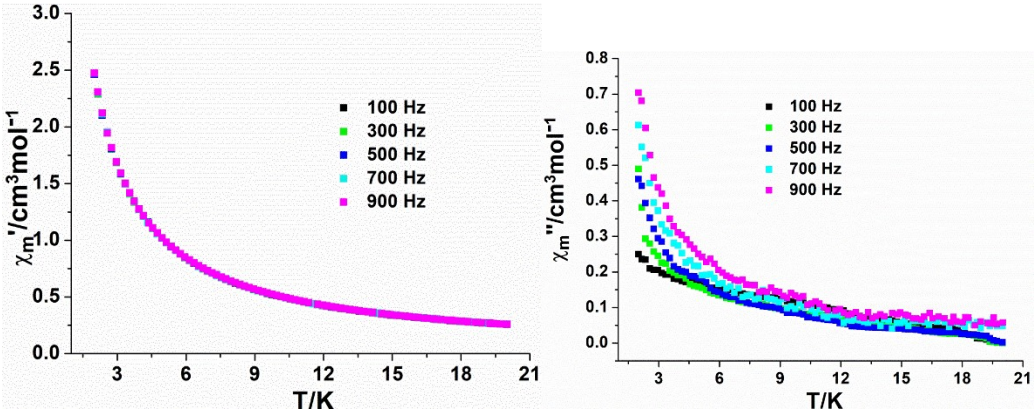


Figure S10 Temperature-dependence of in-phase and out-phase in zero field for complex **2.**

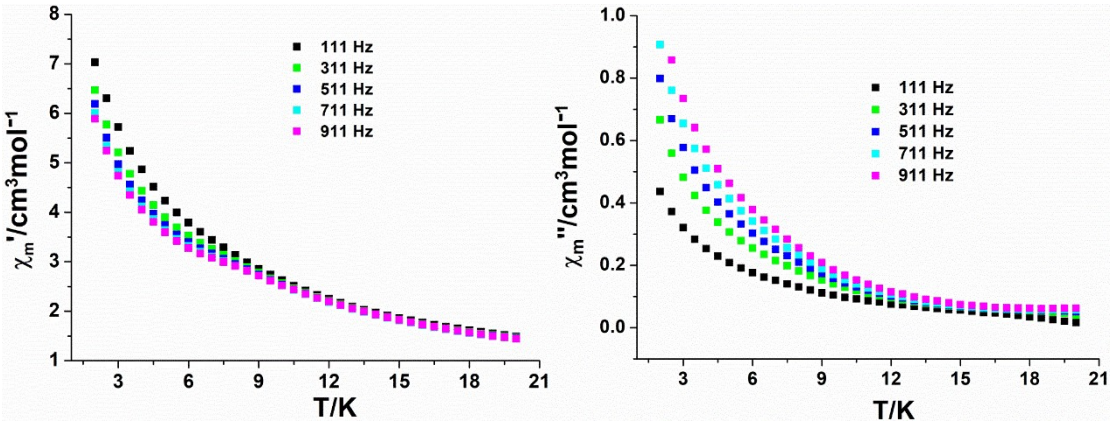


Figure S11 Temperature dependence of the in-phase and out-phase in zero field for complex **3**.

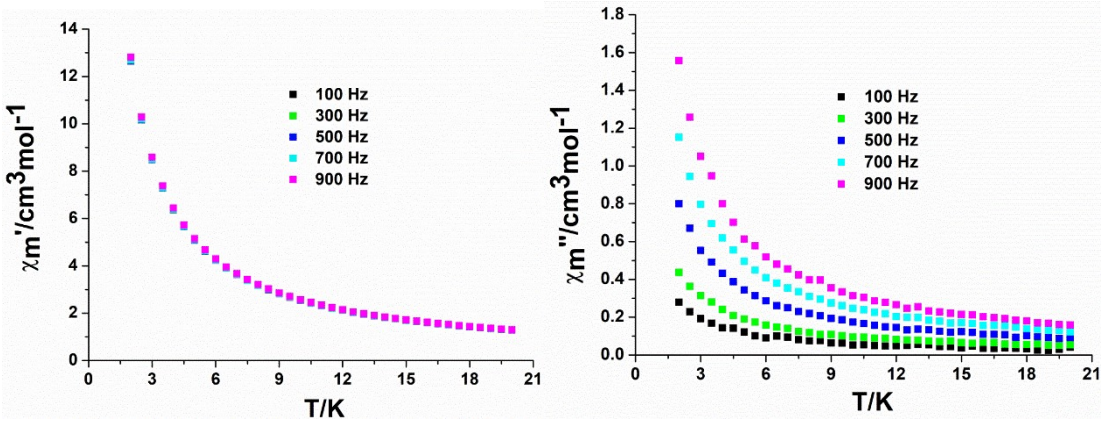
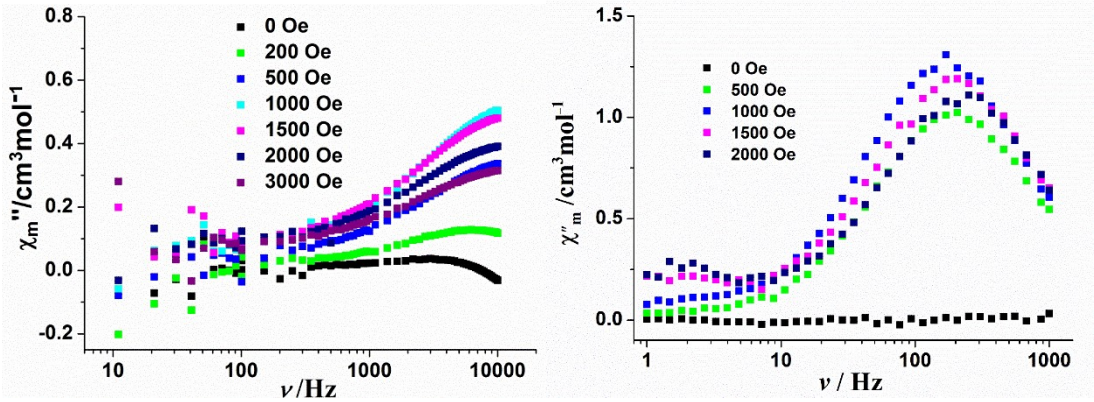


Figure S12 Temperature-dependence of in-phase and out-phase in zero field for complex **4.**



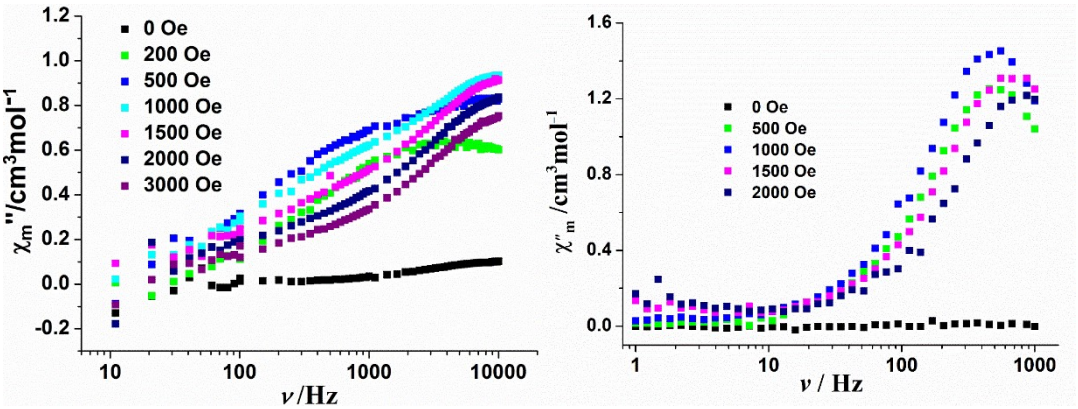


Figure S13 AC susceptibility data for complexes **1–4** at 2 K under dc applied fields in the range 1-1000/10000 Hz.

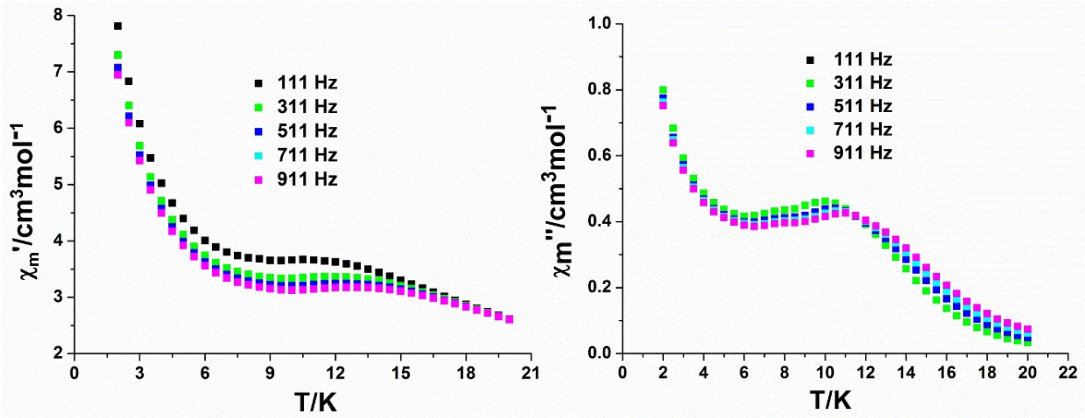


Figure S14 Temperature-dependence of in-phase and out-phase in 1000Oe dc field for complex **1.**

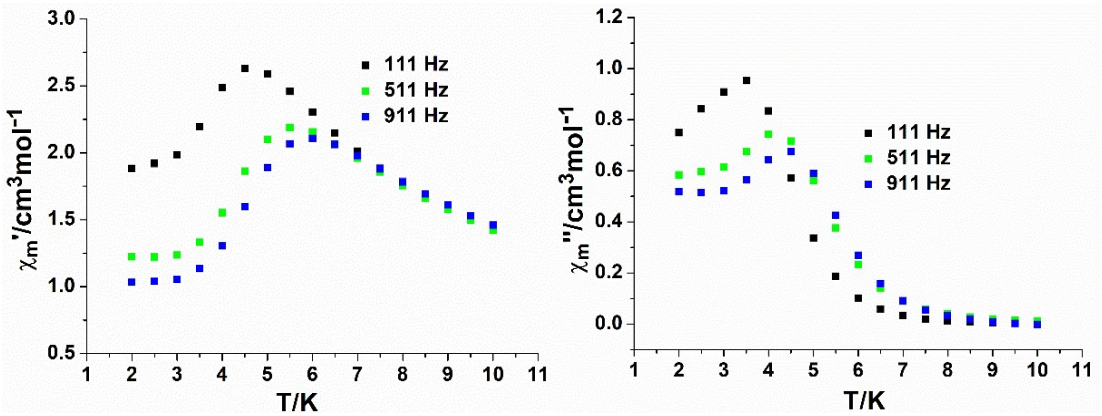


Figure S15 Temperature-dependence of in-phase and out-phase in 1000Oe dc field for complex **2.**

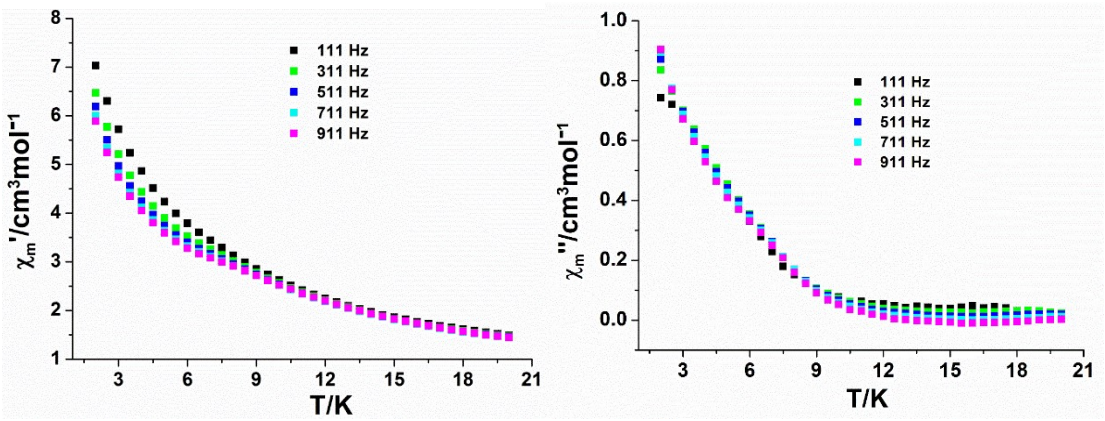


Figure S16 Temperature-dependence of in-phase and out-phase in 1000Oe dc field for complex **3.**

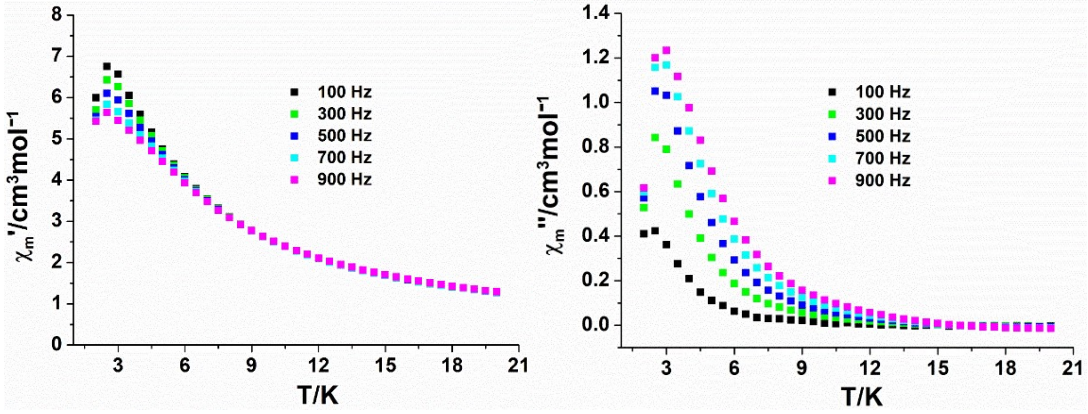
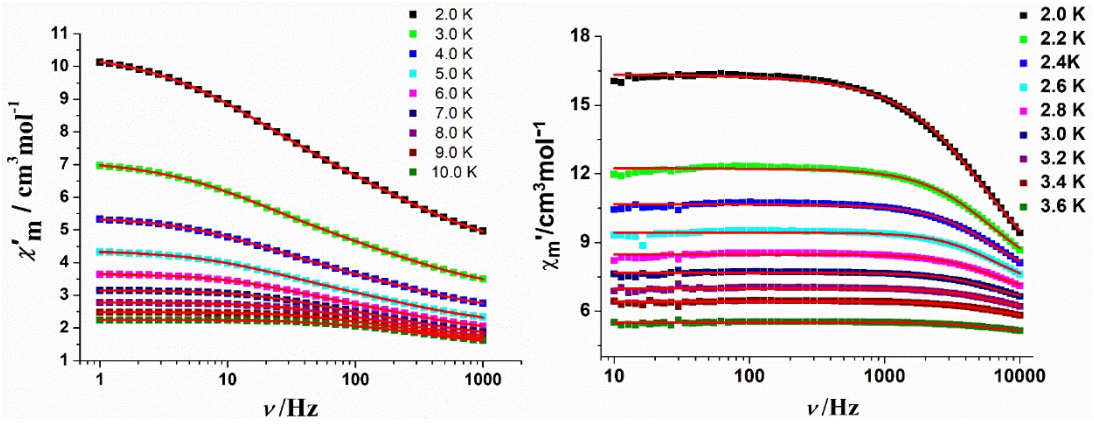


Figure S17 Temperature-dependence of in-phase and out-phase in 1000 Oe dc field for complex **4.**



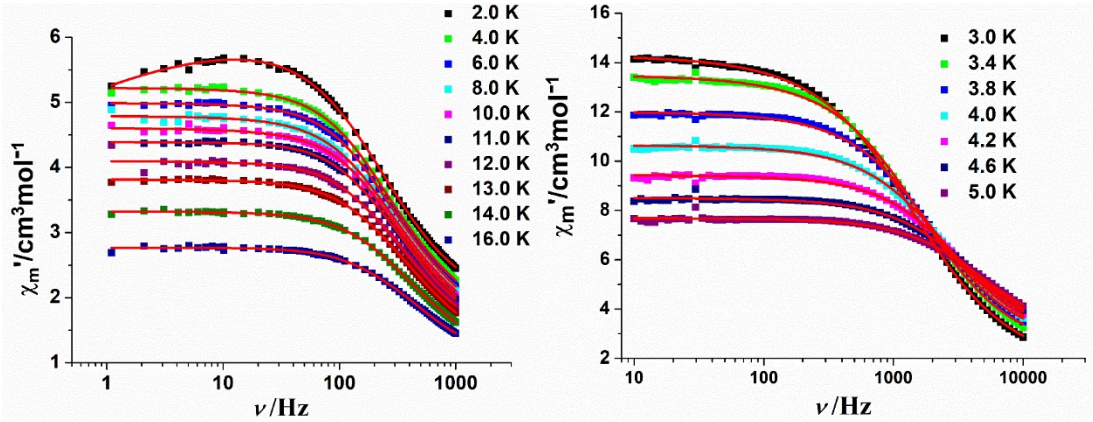


Figure S18 Frequency dependence of χ′ ac susceptibility components under 1000 Oe dc field for complexes of **1**–**4.**

Table S7 The energies and *g*-tensors (g_x, g_y, g_z) of the low-lying spin-orbit states for individual Dy^{III} fragments in complex **1**.

	Dy1			Dy2		
	E **/ cm^{-1}**	***g*-tensors**	m_J	***E*** **/ cm^{-1}**	***g*-tensors**	m_J
1	0	0.002 0.003 19.736	±15/2	0	0.001 0.002 19.715	±15/2
2	161.7	0.036 0.044 17.157	±13/2	160.8	0.049 0.053 17.008	±13/2
3	277.9	0.463 0.652 13.780	±11/2	275.6	1.914 3.250 12.086	±11/2
4	335.1	2.739 4.819 13.543	±5/2	312.9	0.124 4.234 13.300	±1/2
5	371.1	1.112 2.728 13.908	±7/2	358.9	0.264 2.996 13.539	±7/2
6	401.0	0.680 3.746 15.313	±1/2	375.9	10.006 7.124 2.662	±5/2
7	444.1	0.644 1.302 17.961	±3/2	418.8	1.298 1.896 17.882	±3/2
8	589.8	0.015 0.024 19.503	±9/2	564.0	0.020 0.037 19.588	±9/2

Table S8 The energies and *g*-tensors (g_x, g_y, g_z) of the low-lying spin-orbit states for individual

Tb^{III} fragments in complex **2**.

	Tb1 of 2			Tb2 of 2		
	E / cm^{-1}	***g***-tensors	m_J	E / cm^{-1}	***g***-tensors	m_J
1	0 0.089	0.000 0.000 17.762	±6	0 0.087	0.000 0.000 17.758	±6
2	151.1 152.0	0.000 0.000 14.820	±5	127.8 128.4	0.000 0.000 15.322	±5
3	211.8 213.8	0.000 0.000 14.256	±4	170.1 171.7	0.000 0.000 13.011	±4
4	293.7 304.1	0.000 0.000 9.122	±3	260.6 267.6	0.000 0.000 9.222	±3
5	372.8 406.2	0.000 0.000 5.665	±2	336.6 366.2	0.000 0.000 5.573	±2
6	436.7 540.3	0.000 0.000 2.801	±1	396.6 509.2	0.000 0.000 2.879	±1
7	545.0			513.2		0

Table S9 Wave functions with definite projection of the total moment | m_J > for the lowest two doublets of Dy1, Dy2, Tb1, Tb2 fragments**.**

	E **/ cm^{-1}**	**Wave functions**
Dy1	0	97.8%|±15/2>
	161.7	84.8%|±13/2> + 9.4%|±11/2>
Dy2	0	97.4%|±15/2>
	160.8	85.9%|±13/2> + 7.6%|±11/2> + 5.5%|±9/2>
Tb1	0	98%|±6>
	0.089	
	151.1	85%|±5> + 8%|±4>
	152.0	
Tb2	0	97%|±6>
	0.106	
	116.2	70%|±5> + 16%|±4> + 6%|±3>
	116.6	

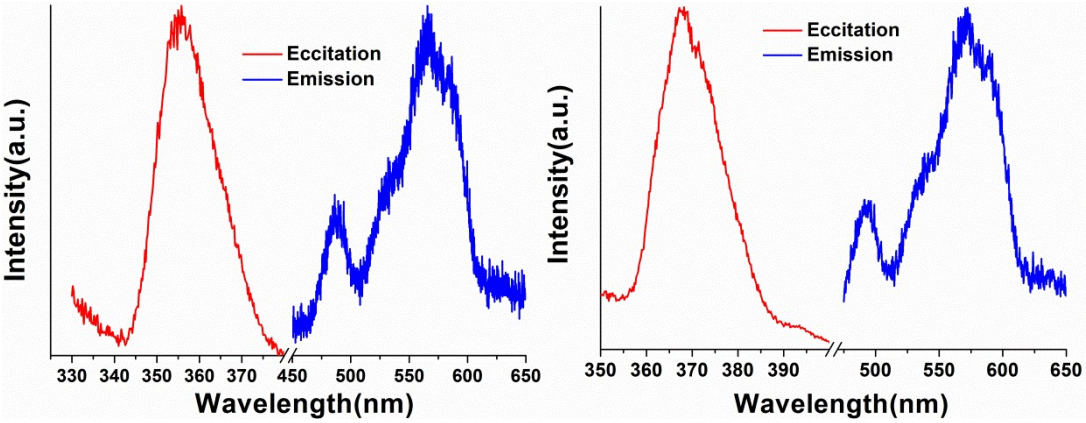


Figure S19 Room-temperature luminescence spectra of complexes **1** and **3**.