Supporting Information

The role of 3d-4f exchange interaction on SMM behaviour and magnetic refrigeration in carbonato bridged $Cu^{II}_2Ln^{III}_2$ (Ln = Dy, Tb and Gd) complexes of an unsymmetrical N_2O_4 donor ligand

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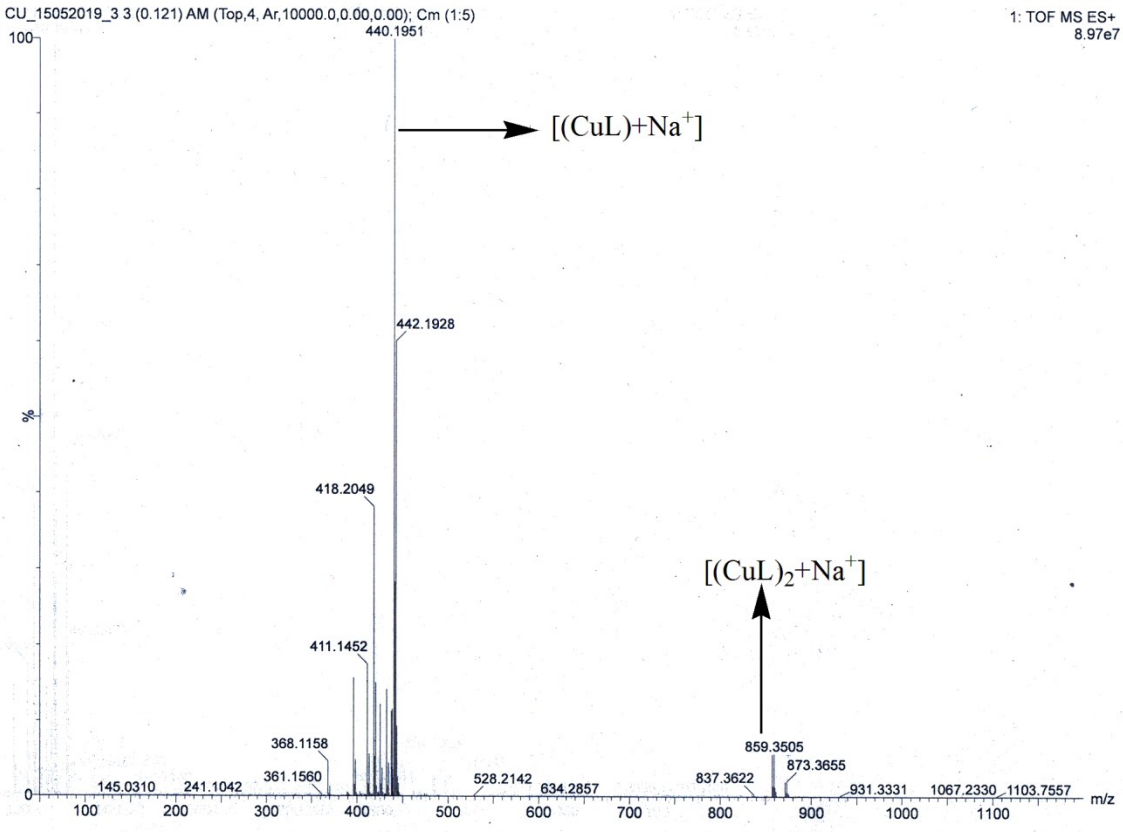


Fig.S1 ESI Mass spectrum of complex **1** (CuL).

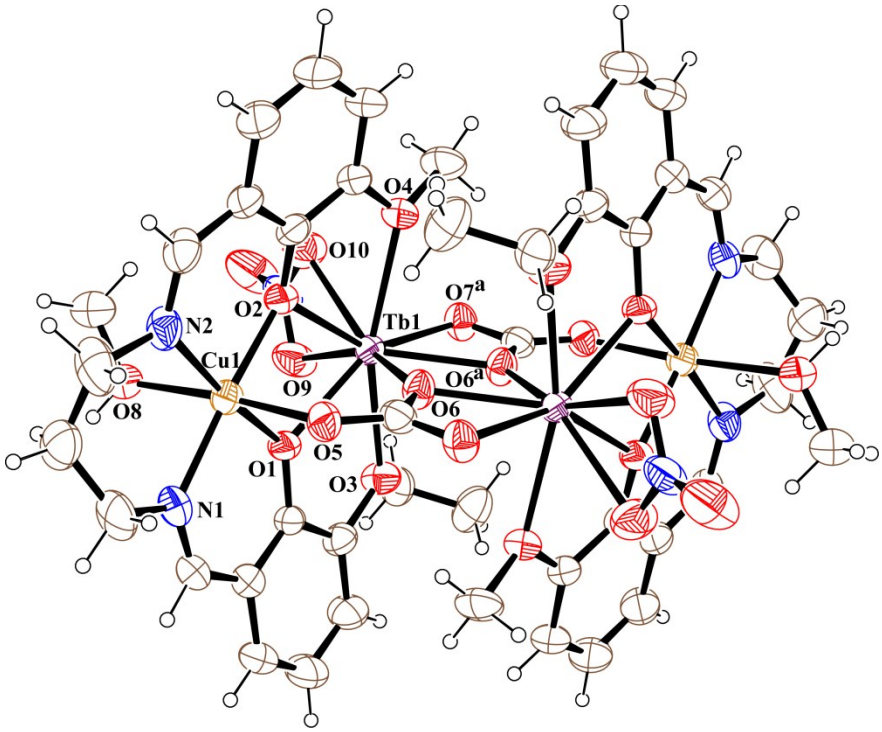


Fig. S2 ORTEP diagram of complex **3** with 30% ellipsoid probability. Disordered carbon atoms have been omitted for clarity.

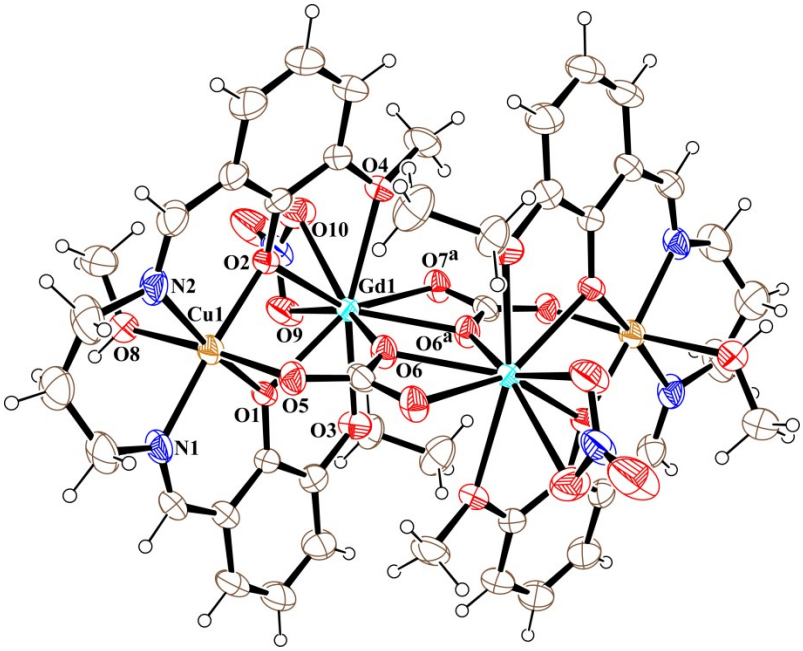


Fig. S3 ORTEP view of complex **4** with 30% ellipsoid probability. Disordered carbon atoms have been omitted for clarity.

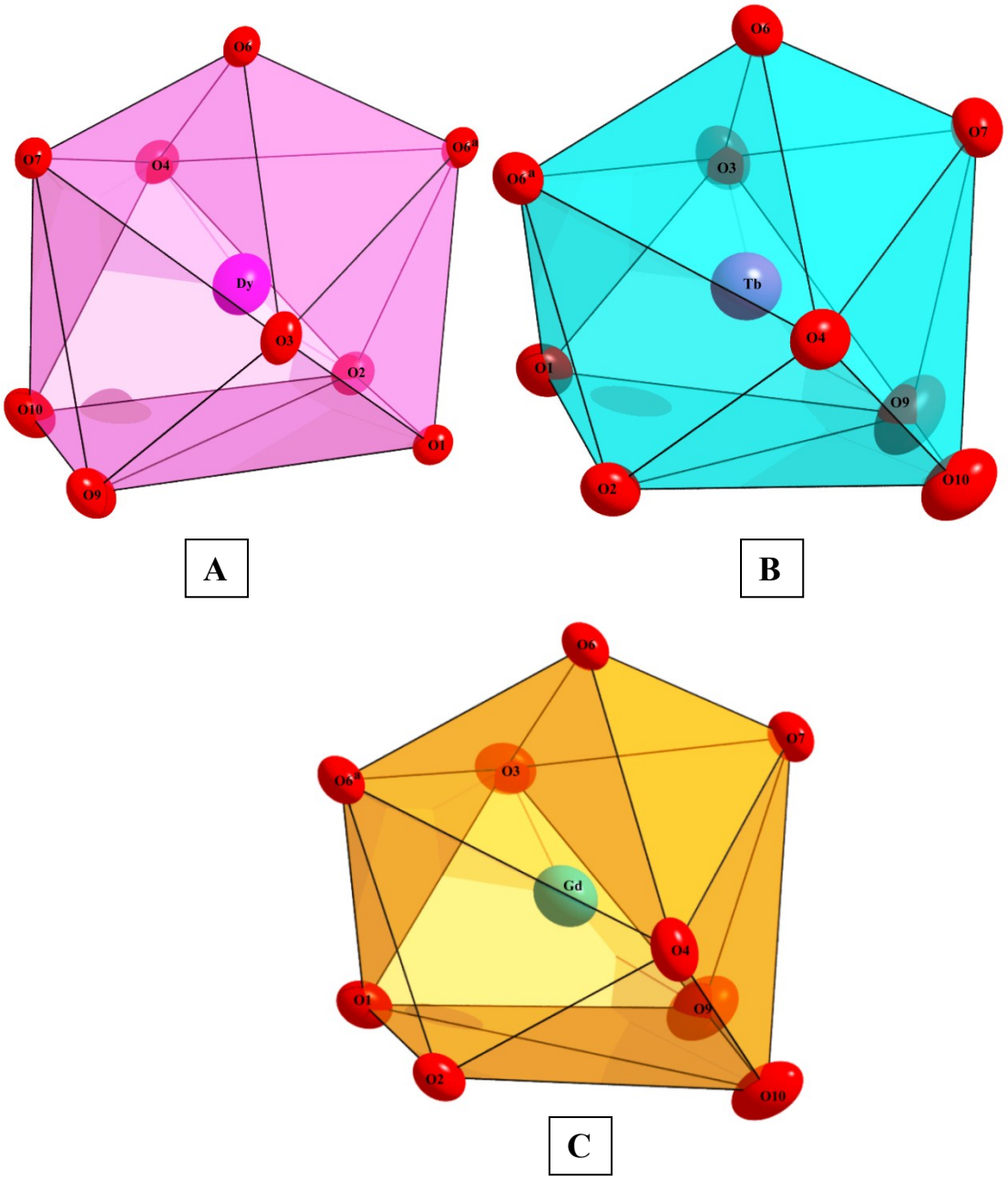


Fig. S4 Polyhedral view of the coordination sphere around the lanthanide centres for complexes **2(A), 3(B)** and **4(C)**.

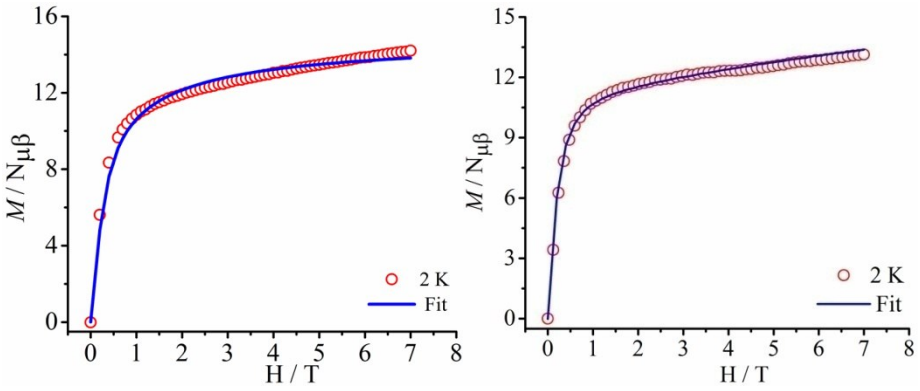


Fig. S5 $M/N\mu_B$ *vs*. H plot for complexes **2** (left) and **3** (right).

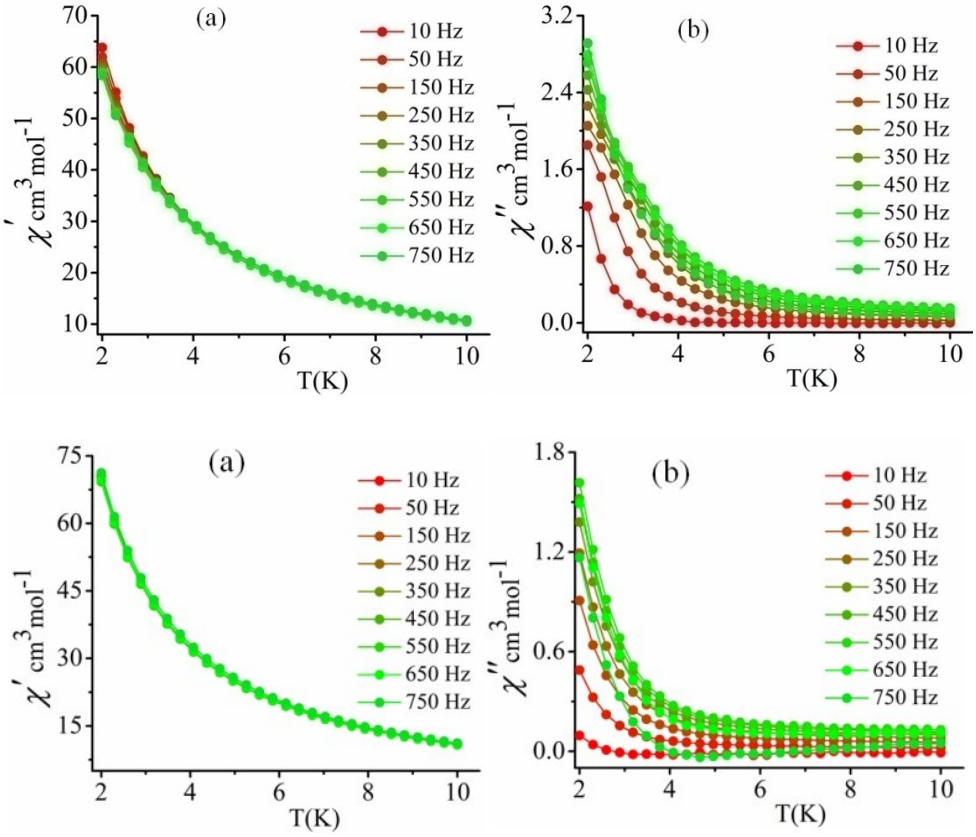


Fig. S6 Temperature dependence of in-phase (χ_M') (left) and out-of-phase (χ_M'') (right) under zero external dc field for complexes **2** (above) and **3** (below).

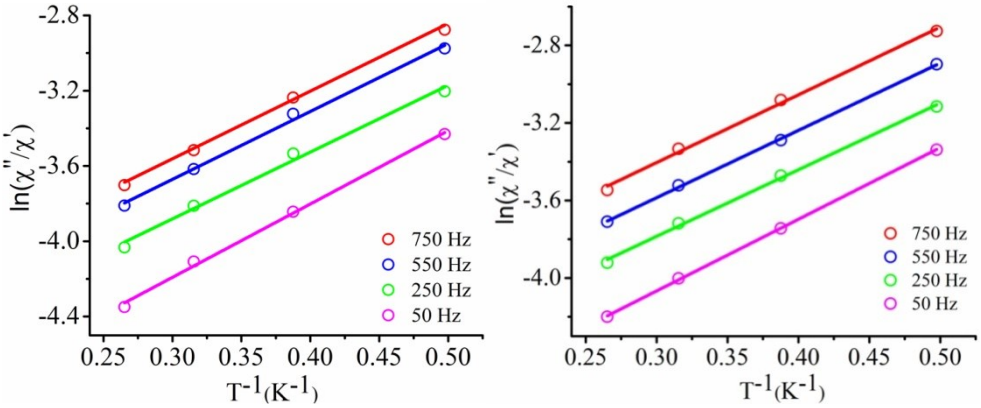


Fig. S7 ln(χ_M''/χ_M')*vs*1/T plot using Debye equation for complexes **2** (left) and **3** (right).

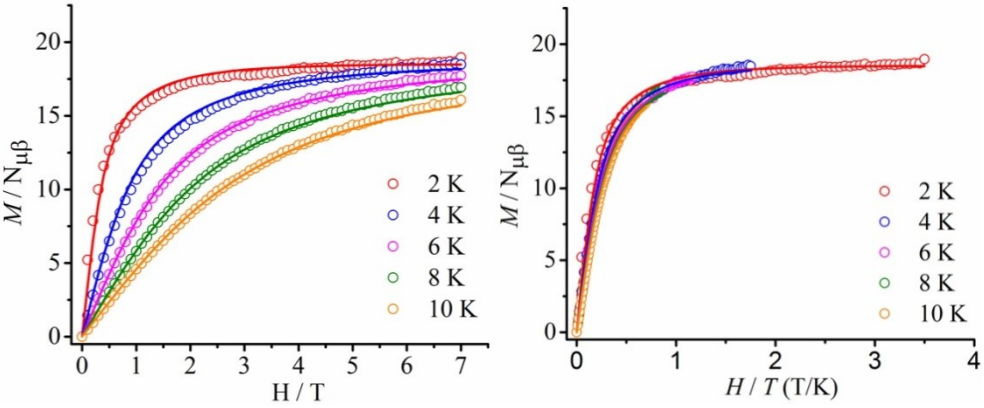
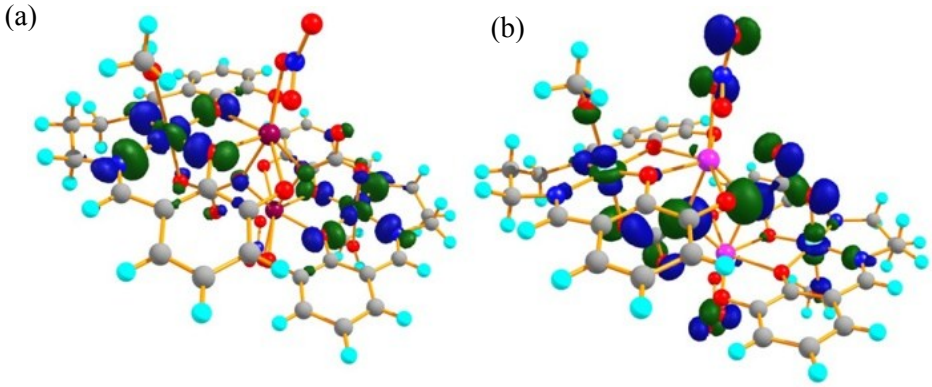


Fig. S8 *M*/Nμ_B *vs*. *H* (left) and *M*/Nμ_B *vs*. *H*/*T* (right) plot for complex **4**.



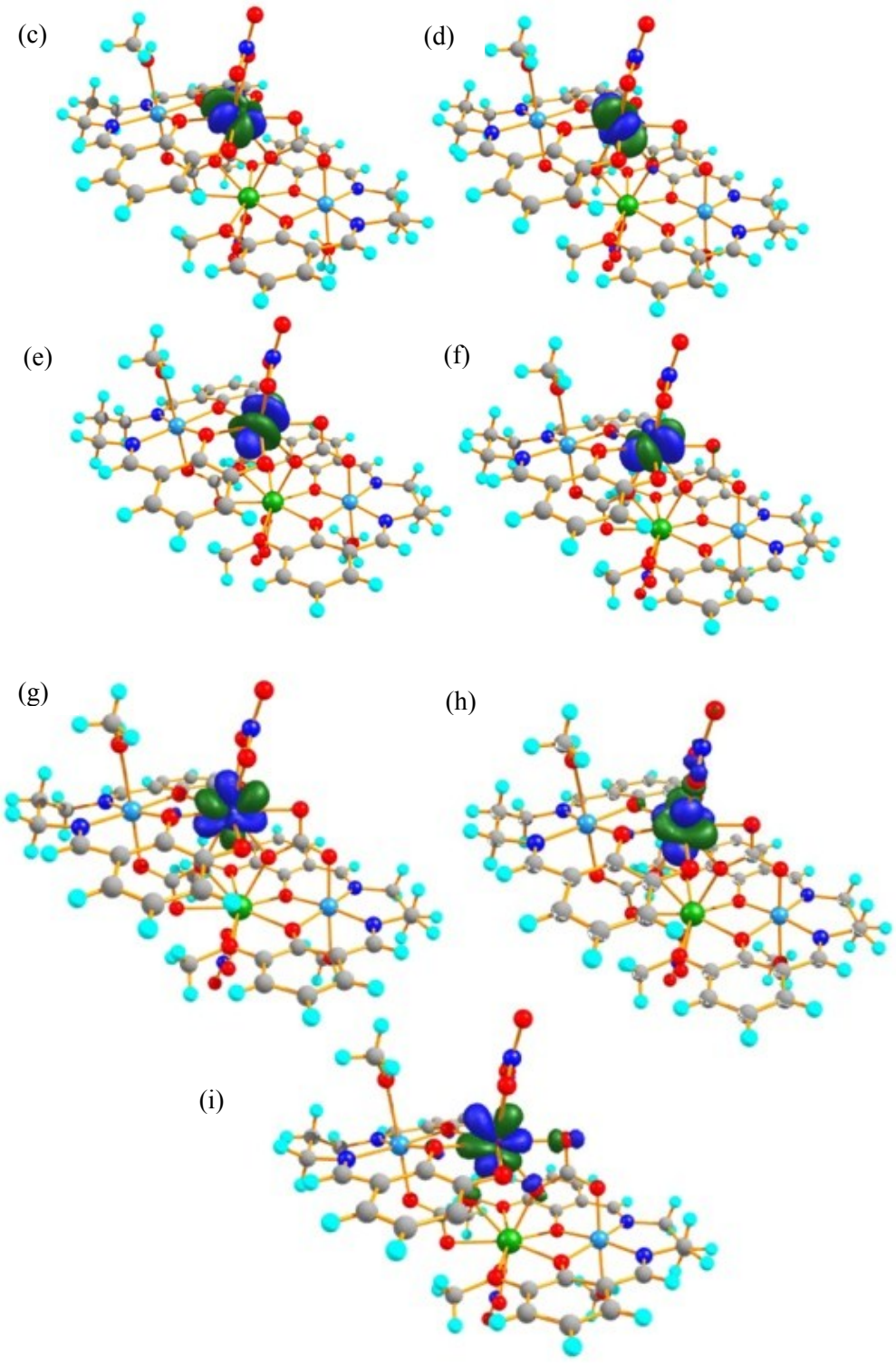


Fig. S9 Alpha molecular orbitals of Cu^{II} (a) dx^2-y^2, (b) dz^2 and the alpha MOs of the $4f^7$ of Gd^{III} (c-i) for complex **4**.

Table S1.Selected bond lengths (Å) and bond angles (º) of complexes **1**.

	1A	**1B**	**1C**
Cu–O(1)	1.924(6)	1.921(5)	1.911(6)
Cu–O(2)	1.921(5)	1.925(5)	1.925(5)
Cu–N(1)	1.971(8)	1.983(7)	1.967(7)
Cu–N(2)	1.984(6)	1.968(7)	1.971(6)
O(1)–Cu–O(2)	85.7(2)	87.2(2)	86.1(2)
O(1)–Cu–N(1)	91.0(3)	92.3(3)	93.4(2)
O(1)–Cu–N(2)	166.7(2)	155.4(2)	160.6(3)
O(2)–Cu–N(1)	164.6(3)	158.9(2)	155.4(2)
O(2)–Cu–N(2)	92.7(2)	92.2(2)	93.9(2)
N(1)–Cu–N(2)	93.9(3)	96.9(3)	94.5(3)

Table S2 Geometrical features of hydrogen bonding interactions (distances (Å) and angles(°)) of Complex **1A**.

D−H···A	**D−H**	**H···A**	**D···A**	**∠D−H···A**
O1W –H1WA···O1A	0.87	2.42	3.068(10)	132
O1W –H1WA···O3A	0.87	2.01	2.811(10)	152
O1W –H1WB···O2A	0.87	2.25	3.033(8)	149
O1W –H1WB···O4A	0.87	2.33	2.899(10)	123

Table S3 Geometrical features of hydrogen bonding interactions (distances (Å) and angles(°)) of Complexes **2-4**.

Complex	**D−H···A**	**D−H**	**H···A**	**D···A**	**∠D−H···A**
2	O8 –H8···O5	0.86	2.17	2.990(12)	160
3	O8 –H8···O5	0.86	2.19	3.017(8)	161
4	O8 –H8···O5	0.86	2.21	3.042(8)	164

Table S4 Summary of SHAPE analysis for nine coordinated Ln(III) centres in complexes **2-4.**

Geometry	Symmetry	Geometry (in words)	Complex **2**	Complex **3**	Complex **4**
OPY-9	C_8v	Octagonal	22.448	22.216	22.276

		pyramid			
HBPY-9	D_7h	Heptagonal bipyramid	17.842	17.788	17.724
JTC-9	C_3v	Johnson triangular cupola J3	15.849	16.107	16.000
JCCU-9	C_4v	Capped cube J8	9.930	9.785	9.844
CCU-9	C_4v	Spherical-relaxed capped cube	8.048	7.947	8.022
JCSAPR-9	C_4v	Capped square antiprism J10	4.380	4.467	4.499
CSAPR-9	C_4v	Spherical capped square antiprism	**3.083**	**3.196**	**3.218**
JTCTPR-9	D_3h	Tricappedtrigonal prism J51	5.428	5.618	5.561
TCTPR-9	D_3h	Spherical tricappedtrigonal prism	3.499	3.587	3.570
JTDIC-9	C_3v	Tridiminished icosahedron J63	8.763	8.519	8.464
HH-9	C_2v	Hula-hoop	9.650	9.591	9.585
MFF-9	Cs	Muffin	3.334	3.430	3.480

Table S5 Selected bond lengths (Å) and bond angles (º) of complexes **2–4**.

	2	**3**	**4**
M(1)–O(1)	2.329(6)	2.332(4)	2.339(4)
M(1)–O(2)	2.324(7)	2.336(4)	2.342(4)
M(1)–O(3)	2.516(7)	2.518(6)	2.529(6)

M(1)–O(4)	2.500(7)	2.504(6)	2.510(5)
M(1)–O(6)	2.360(7)	2.361(5)	2.374(5)
M(1)–O(9)	2.461(10)	2.474(7)	2.479(6)
M(1)–O(10)	2.524(10)	2.536(7)	2.538(7)
M(1)–O(6^{a})	2.308(7)	2.318(5)	2.343(5)
M(1)–O(7^{a})	2.399(7)	2.426(6)	2.438(5)
Cu(1)–O(1)	2.018(6)	2.019(5)	2.025(5)
Cu(1)–O(2)	2.033(7)	2.031(4)	2.040(4)
Cu(1)–O(5)	2.142(8)	2.128(6)	2.105(5)
Cu(1)–O(8)	2.347(10)	2.303(6)	2.287(6)
Cu(1)–N(1)	2.021(9)	2.025(7)	2.023(6)
Cu(1)–N(2)	2.027(9)	2.022(6)	2.031(6)
O(1)–M(1)–O(2)	68.5(2)	68.42(15)	68.67(15)
O(1)–M(1)–O(3)	64.0(2)	63.73(17)	63.49(17)
O(1)–M(1)–O(4)	133.7(2)	133.49(17)	133.20(16)
O(1)–M(1)–O(6)	74.0(2)	73.57(18)	73.03(16)
O(1)–M(1)–O(9)	82.3(3)	83.7(2)	83.93(18)
O(1)–M(1)–O(10)	112.1(3)	113.1(2)	113.3(2)
O(1)–M(1)–O(6^{a})	120.7(2)	120.11(18)	119.68(15)
O(1)–M(1)–O(7^{a})	144.2(2)	144.30(18)	144.17(16)
O(2)–M(1)–O(3)	132.4(2)	132.03(17)	132.06(17)
O(2)–M(1)–O(4)	66.0(2)	65.85(17)	65.40(16)
O(2)–M(1)–O(6)	74.0(3)	73.63(16)	73.46(16)
O(2)–M(1)–O(9)	103.0(3)	103.7(2)	103.8(2)
O(2)–M(1)–O(10)	78.6(3)	79.2(2)	78.67(19)
O(2)–M(1)–O(6^{a})	128.3(3)	128.10(17)	127.62(17)
O(2)–M(1)–O(7^{a})	145.8(2)	146.05(17)	146.15(16)
O(3)–M(1)–O(4)	161.2(2)	161.70(18)	162.02(18)

O(3)–M(1)–O(6)	95.2(3)	95.49(18)	95.14(17)
O(3)–M(1)–O(9)	68.6(3)	68.5(2)	68.8(2)
O(3)–M(1)–O(10)	116.8(3)	116.7(2)	117.4(2)
O(3)–M(1)–O(6^a)	80.8(3)	81.04(18)	81.17(17)
O(3)–M(1)–O(7^a)	80.7(2)	80.91(19)	80.93(17)
O(4)–M(1)–O(6)	86.1(3)	85.90(19)	85.77(15)
O(4)–M(1)–O(9)	115.3(3)	114.8(2)	115.01(18)
O(4)–M(1)–O(10)	66.2(3)	66.0(2)	65.86(19)
O(4)–M(1)–O(6^a)	83.2(2)	83.40(19)	83.32(16)
O(4)–M(1)–O(7^a)	82.1(2)	82.21(19)	82.63(16)
O(6)–M(1)–O(9)	155.6(3)	156.5(2)	156.25(17)
O(6)–M(1)–O(10)	147.1(3)	147.1(2)	146.61(18)
O(6)–M(1)–O(6^a)	63.1(3)	62.95(17)	62.85(15)
O(6)–M(1)–O(7^a)	117.3(2)	116.94(19)	116.72(16)
O(9)–M(1)–O(10)	49.4(3)	49.2(2)	49.5(2)
O(6^a)–M(1)–O(9)	128.0(3)	127.5(2)	127.9(2)
O(7^a)–M(1)–O(9)	79.3(3)	78.7(2)	79.11(19)
O(6^a)–M(1)–O(10)	126.3(3)	126.0(2)	126.35(19)
O(7^a)–M(1)–O(10)	77.6(3)	77.4(2)	78.3(2)
O(6^a)–M(1)–O(7^a)	54.4(3)	54.25(19)	54.09(17)
O(1)–Cu(1)–O(2)	80.5(3)	80.77(18)	81.01(18)
O(1)–Cu(1)–O(5)	93.8(3)	93.7(2)	93.95(19)
O(1)–Cu(1)–O(8)	85.3(3)	85.5(2)	85.6(2)
O(1)–Cu(1)–N(1)	90.9(3)	91.0(2)	90.5(2)
O(1)–Cu(1)–N(2)	170.2(3)	170.7(2)	170.3(2)
O(2)–Cu(1)–O(5)	92.6(3)	93.0(2)	93.20(18)
O(2)–Cu(1)–O(8)	91.4(3)	91.0(2)	90.3(2)
O(2)–Cu(1)–N(1)	171.2(4)	171.5(2)	171.3(2)

O(2)–Cu(1)–N(2)	91.1(3)	91.1(2)	90.5(2)
O(5)–Cu(1)–O(8)	175.7(3)	175.8(2)	176.41(19)
O(5)–Cu(1)–N(1)	90.0(3)	89.6(3)	89.3(2)
O(5)–Cu(1)–N(2)	91.5(3)	91.2(3)	91.2(2)
O(8)–Cu(1)–N(1)	85.9(4)	86.3(2)	87.1(3)
O(8)–Cu(1)–N(2)	90.0(4)	90.2(3)	89.9(3)
N(1)–Cu(1)–N(2)	97.3(4)	97.0(3)	97.8(3)
M(1)–O(1)–Cu(1)	104.5(2)	104.52(19)	104.23(19)
M(1)–O(2)–Cu(1)	104.2(3)	103.97(18)	103.67(18)
M(1)–O(6)–M(1[a])	117.0(3)	117.1(2)	117.15(18)

Symmetry element: [a] = 1-x, 1-y, 1-z for Gd, Tb and Dy, respectively.

Table S6 SINGLE_ANISO computed crystal-field parameters for complexes **2** and **3**.

k	Q	Complex **2**	Complex **3**
2	-2	0.1890E+01	-0.155E+02
	-1	0.3466E+01	0.479E+01
	0	-0.432E+01	-0.134E+02
	1	0.309E+01	0.966E+01
	2	0.675E+01	-0.131E+02
4	-4	-0.116E-01	0.607E+00
	-3	0.180E+00	0.275E+01
	-2	0.404E-01	0.701E+00
	-1	-0.559E-02	0.237E+00
	0	0.580E-02	-0.355E-01
	1	0.539E-02	0.523E+00
	2	0.497E-01	0.356E+00
	3	-0.225E+00	0.220E+00
	4	-0.468E-01	0.262E+00
	-6	0.833E-03	0.370E-01
	-5	-0.729E-02	0.220E+00
	-4	-0.463E-02	0.462E+00
	-3	-0.190E-02	0.848E-01
	-2	-0.194E-02	-0.186E+00
	-1	-0.373E-03	-0.164E+00

6	0	-0.695E-03	0.287E-01
	1	-0.514E-03	-0.132E+00
	2	-0.406E-02	-0.117E+00
	3	0.278E-02	0.227E+00
	4	-0.968E-02	-0.558E-01
	5	-0.642E-05	0.680E+00
	6	0.175E-02	-0.505E-01

Table S7 Fitting and BS-DFT calculated parameters for complex **2-4**.

Complex	Fitting Parameters			BS-DFT Calculated	
	J_1 (Cu-Ln) (cm^{-1})	J_2 (Ln-Ln) (cm^{-1})	$J_{dipolar}$	J_1 (Cu-Ln)	J_2 (Ln-Ln)
2	+3.20	+0.408	+0.004	+3.12	+0.25
3	+5.29	+0.080	+0.0009	+3.75	+0.36
4	+2.48	+0.09		+1.25	+0.04

Table S8 The *ab initio* computed energy of the KDs and principle values of the ground state g tensor resulting from single-ion anisotropy calculation for complex **2**.

Kramers doublets	Energy (cm^{-1})	g_x	g_y	g_z	Wavefunctions
1	0.000	0.14	0.53	17.77	75%|±15/2>+13%|±11/2>+9%|±7/2>
2	52.586	0.50	0.54	13.05	42%|±13/2>+30%|±9/2>+15%|±5/2>+4%|±3/2>
3	109.23	0.41	0.84	13.61	34%|±11/2>+20%|±15/2>+18%|±7/2>13%|±3/2>10%|±1/2>
4	226.09	1.52	2.23	13.69	38%|±13/2>+26%|±9/2>+18%|±11/2>+5%|±5/2>
5	288.83	1.79	5.58	9.68	37%|±7/2>+33%|±11/2>+18%|±9/2>+8%|±1/2>
6	333.22	3.59	4.43	13.08	33%|±5/2>+21%|±1/2>+20%|±9/2>+14%|±3/2>+7%|±7/2>
7	397.52	0.33	0.78	16.30	29%|±3/2>+24%|±5/2>+20%|±7/2>+12%|±9/2>+4%|±11/2>
8	509.92	0.04	0.15	19.37	46%|±1/2>+30%|±3/2>+16%|±5/2>+5%|±7/2>

Table S9 The *ab initio* computed energy of the KDs and principle values of the ground state g tensor resulting from single-ion anisotropy calculation for complex **3**.

Energy levels	Energy (cm^{-1})	Tunnel Splitting (Δ_{tun})	g_z	Wavefunctions
1	0.000	0.113	17.80	98%|±6>+1%|±4>
2	0.113			98%|±6>+1%|±4>
3	88.469	5.115	13.84	84%|±5>+6%|±3>+4%|±2>5%|0>
4	93.584			96%|±5>+3%|±3>
5	135.897			46%|±4>+28%|±1>+14%|±2>+8%|±3>3%|0>
6	161.326			42%|±4>+25%|±2>+13%|0>10%|±3>7%|±1>

7	200.981	4.504	14.54	47%|±4>+41%|0>+9%|±3>
8	205.485			40%|±4>+30%|±3>+26%|±1>+4%|0>
9	238.232			47%|±3>+21%|0>+18%|±2>+16/%|±1>
10	327.896	2.87	13.57	38%|±2>+30%|±3>+18%|±4>+15%|±1>
11	330.766			40%|±2>+32%|±3>+18%|±1>+4%|±5>
12	488.769	0.336	17.67	50%|0>+30%|±1>+20%|±2>
13	489.105			46%|0>+38%|±1>+14%|±2>