Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A New Family of Fe_4Ln_4 (Ln = Dy^{III}, Gd^{III}, Y^{III}) Wheel type Complexes with Ferromagnetic Interaction, Magnetocaloric Effect and Zero-field SMM Behavior

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Table S1. Crystallographic parameters for complexes **1**-**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{156}H_{324}Dy_{12}Fe_{12}N_{40}O_{100}$	$C_{168}H_{360}Fe_{12}Gd_{12}N_{40}O_{112}$	$C_{168}H_{333}Fe_{12}N_{40}O_{109}Y_{12}$
Formula weight	6980.73	7290.14	6394.84
Temperature/K	296(2)	296(2)	296(2)
Crystal system	cubic	cubic	trigonal
Space group	I-43d	I-43d	R3c
a/Å	30.106(3)	30.282(2)	42.5407(3)
b/Å	30.106(3)	30.282(2)	42.5407(3)
c/Å	30.106(3)	30.282(2)	26.0507(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	120
Volume/$Å^3$	27287(7)	27769(7)	40828.1(7)
Z	4	4	6
$\rho_{calc}g/cm^3$	1.699	1.744	1.561
μ/mm^{-1}	3.939	3.515	3.232
F(000)	13776	14352	19638
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	9.952 to 49.374	3.294 to 50.636	5.066 to 52.788
Index ranges	$-17 \le h \le 32$, $-27 \le k \le 35$, $-13 \le l \le 35$	$-35 \le h \le 32$, $-24 \le k \le 32$, $-19 \le l \le 35$	$-53 \le h \le 34$, $-53 \le k \le 53$, $-32 \le l \le 22$
Reflections collected	20491	20784	81756
Independent reflections	3838 [R_{int} = 0.0751, R_{sigma} = 0.0585]	4135 [R_{int} = 0.0867, R_{sigma} = 0.0662]	16211 [R_{int} = 0.1182, R_{sigma} = 0.1102]
Data/restraints/parameters	3838/18/241	4135/0/260	16211/2701/1029
Goodness-of-fit on F^2	1.067	1.044	1.02
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1214	R_1 = 0.0425, wR_2 = 0.1055	R_1 = 0.0648, wR_2 = 0.1624
Final R indexes [all data]	R_1 = 0.0517, wR_2 = 0.1254	R_1 = 0.0494, wR_2 = 0.1101	R_1 = 0.1034, wR_2 = 0.1912
Largest diff. peak/hole / e $Å^{-3}$	1.73/-0.62	1.272/-0.569	1.85/-0.67
Flack parameter	-0.002(14)	-0.022(17)	-0.014(5)

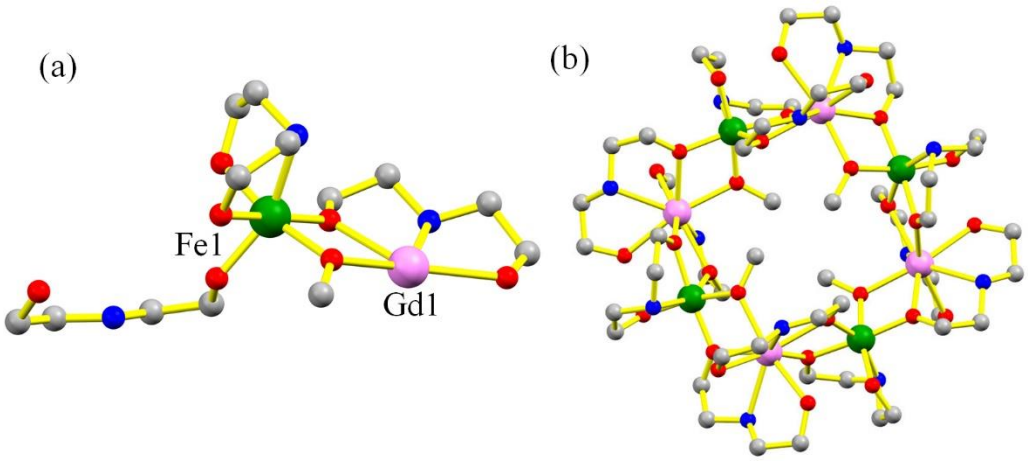

Fig. S1. Asymmetric unit (a) and molecular view (b) of complex **2**.

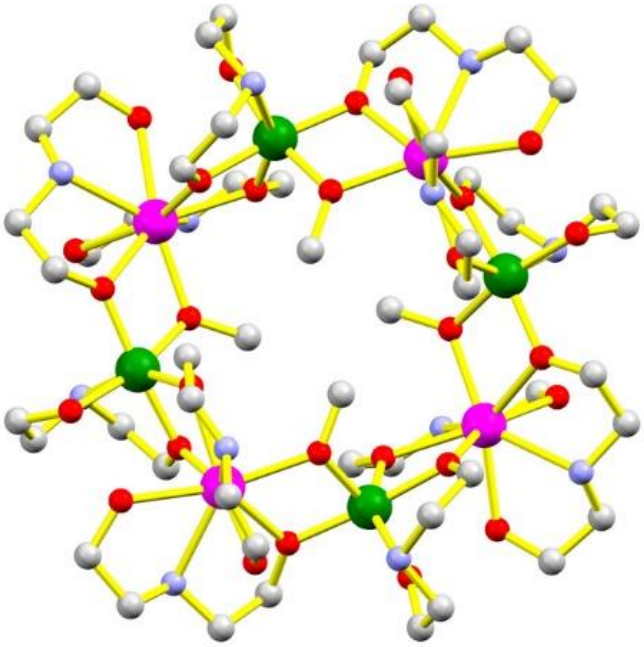

Fig. S2. Molecular view of complex **3**.

Table S2: Summary of Shape analysis of **1–3**

OP-8	**1**	D8h	Octagon
HPY-8	**2**	C7v	Heptagonal pyramid
HBPY-8	**3**	D6h	Hexagonal bipyramid
CU-8	**4**	Oh	Cube
SAPR-8	**5**	D4d	Square antiprism
TDD-8	**6**	D2d	Triangular dodecahedron
JGBF-8	**7**	D2d	Johnson gyrobifastigium J26

JETBPY-8 **8** D3h Johnson elongated triangular bipyramid J14

Complex	**[ML$_8$]**	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	**TDD-8**	JGBF-8	JETBPY-8
1	**Dy**	31.266	24.571	14.406	11.298	3.650	**2.230**	10.517	26.588
2	**Gd**	31.568	24.811	13.753	11.004	3.93936	**2.469**	10.130	26.112
3	**Y**	31.668	24.497	13.940	10.951	3.669	**2.285**	10.424	26.643

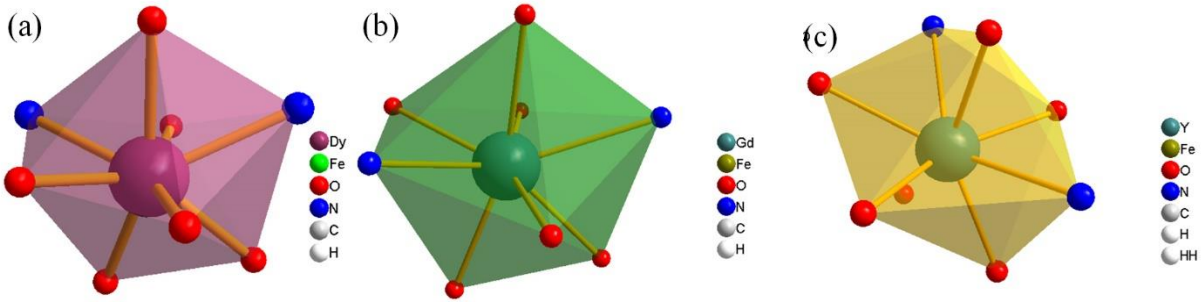

Figure S3. Dodecahedron geometry of Ln^{III} for complexes **1-3** (a-c).

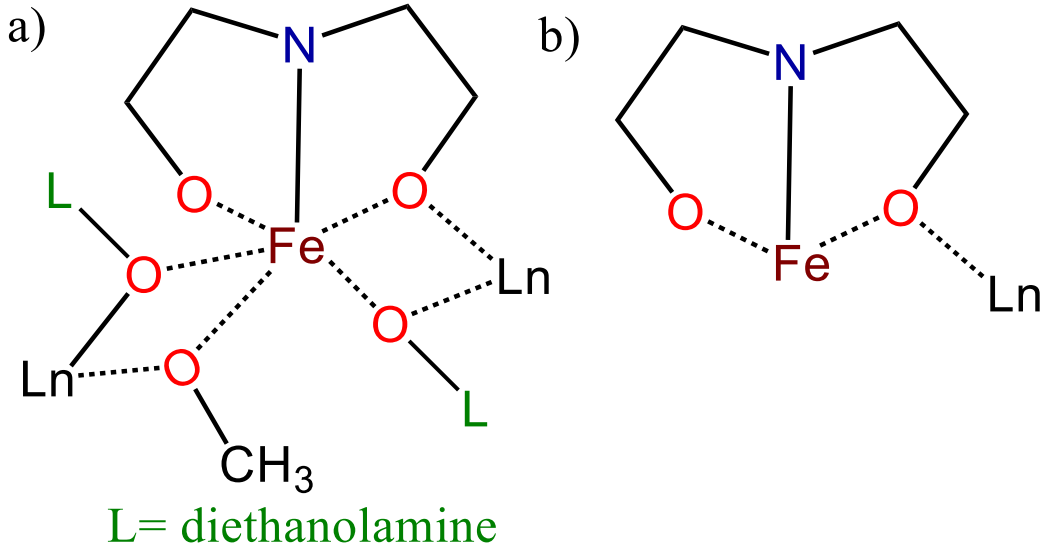

Fig. S4. Bridging coordination mode of the organic ligand (L) in Complexes **1-3.**
Ln = Dy (**1**), Gd (**2**), Y (**3**)

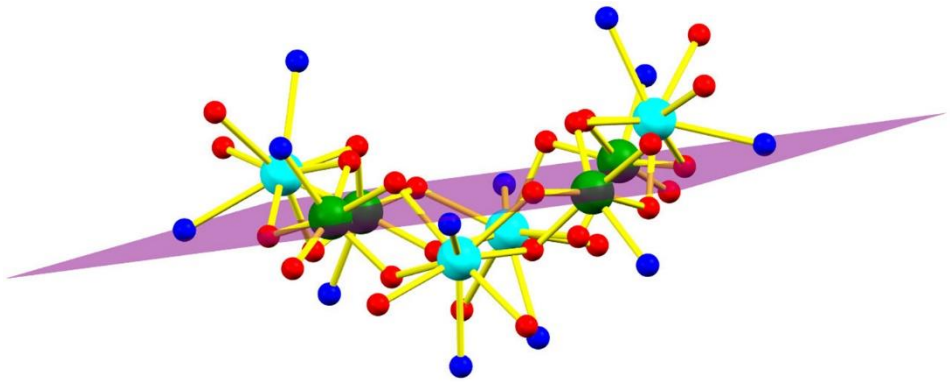

Fig. S5. An imaginary plane contains Fe^{III} centers.

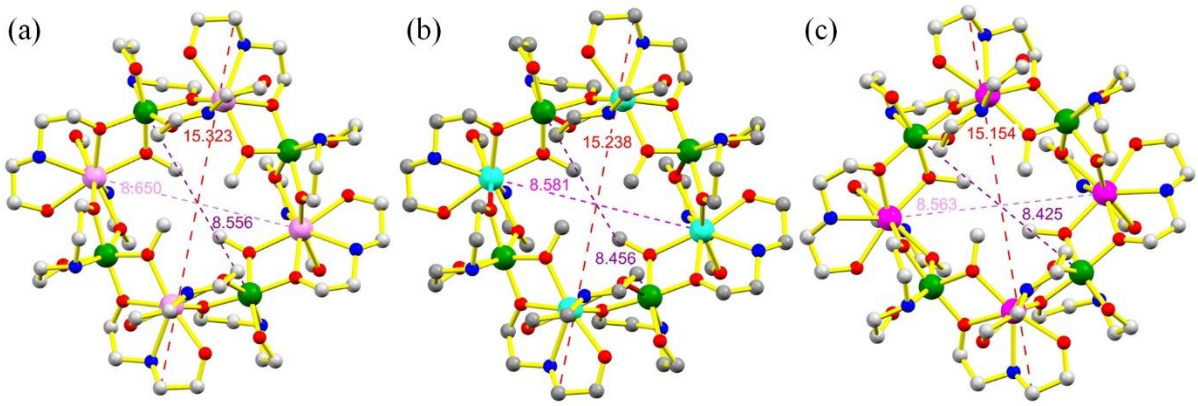

Fig. S6. The inner and outer distance for complexes **1-3** (a-c).

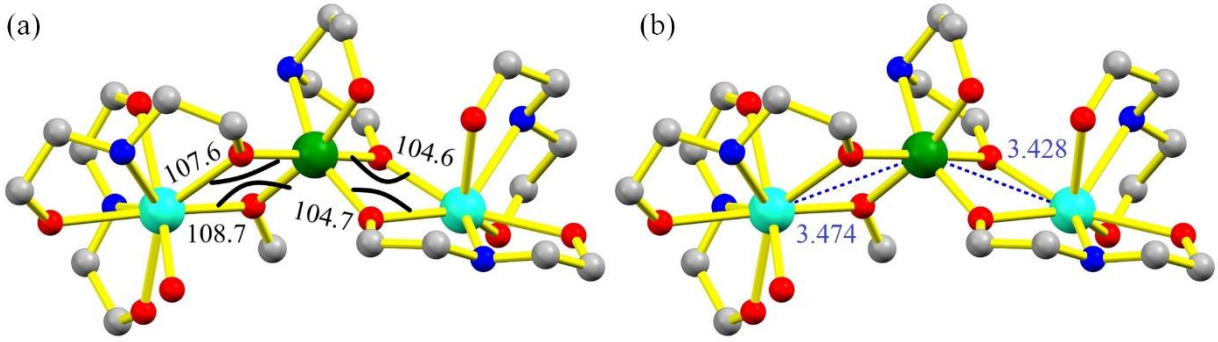

Fig. S7. Selected bond angles (a) and bond lengths (b) for complex **1**.

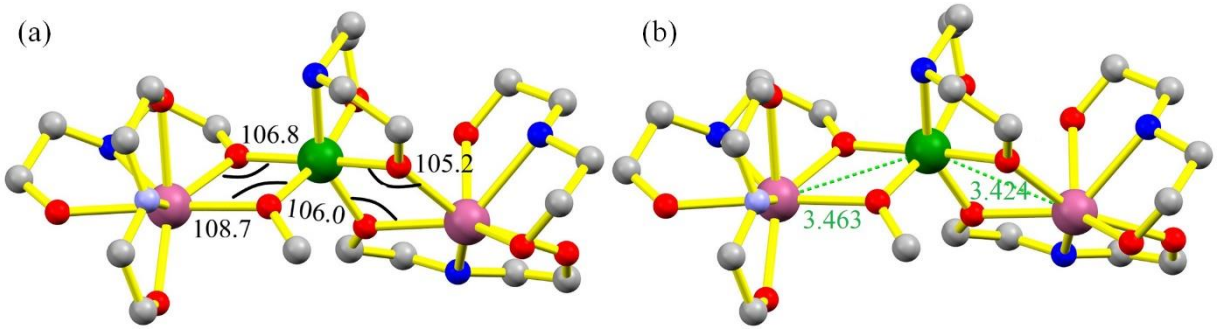

Figure S8. Selected bond angles (a) and bond lengths (b) for complex **3**.

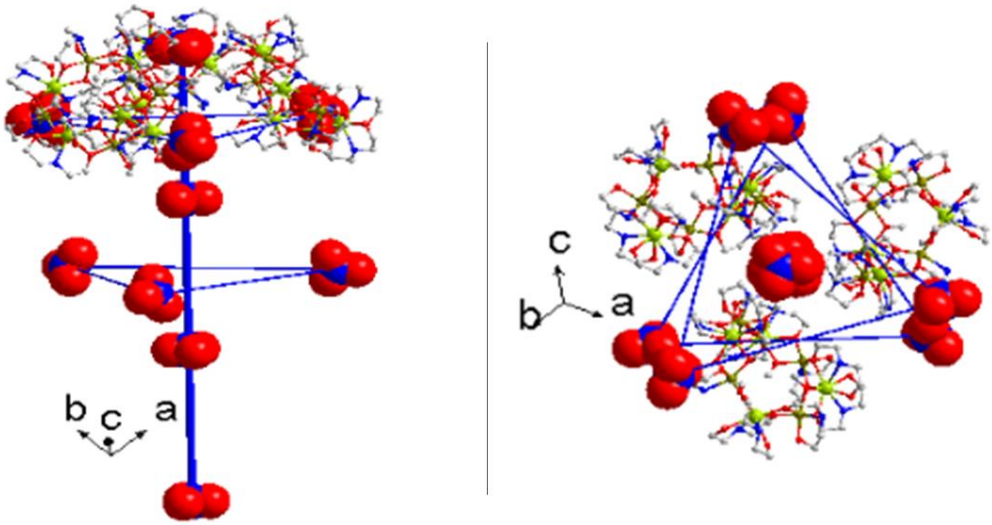

Fig. S9. NO_3^- with C_3 on (1 1 1) plane (above) showing assembly of three cyclic cluster. Another view from (0 1 1) plane (down) give a umbrella-stand geometry.

Table S3. List of selected bond length (Å) in complexes **1-3**

Complex 1				**Complex 2**			
Dy1–O6	2.266(10)	O3–Fe11	1.936(10)	Gd1–O41	2.287(8)	O6–C10	1.405(15)
Dy1–O1	2.277(9)	O6–C9	1.386(19)	Gd1–O1	2.312(9)	O6–Gd12	2.374(8)
Dy1–O4	2.317(10)	O6–Fe11	2.063(10)	Gd1–O3	2.364(8)	O2–C2	1.439(18)
Dy1–O3	2.377(10)	O7–C6	1.41(2)	Gd1–O61	2.374(8)	O10–N4	1.228(12)
Dy1–O5	2.417(11)	O2–C14	1.50(3)	Gd1–O2	2.449(9)	N1–C3	1.472(18)
Dy1–O2	2.476(12)	O8–N5	1.256(14)	Gd1–O71	2.517(10)	N1–C4	1.478(18)
Dy1–N1	2.549(13)	N3–C12	1.38(3)	Gd1–N1	2.587(11)	C6–C7	1.49(3)
Dy1–N3	2.575(17)	N3–C11	1.41(3)	Gd1–N31	2.605(14)	O7–C13	1.44(2)

Dy1–Fe11	3.428(2)	N1–C2	1.45(2)	Gd1–Fe11	3.4560(18)	O7–Gd12	2.517(10)
Dy1–Fe1	3.474(2)	N1–C4	1.50(2)	Gd1–Fe1	3.5107(18)	N4–O103	1.228(12)
Fe1–O32	1.936(10)	N5–O83	1.256(14)	Fe1–O6	1.962(8)	N4–O104	1.228(12)
Fe1–O4	1.981(10)	N5–O84	1.256(14)	Fe1–O3	2.004(8)	N2–C7	1.40(2)
Fe1–O1	1.992(10)	C13–C12	1.52(3)	Fe1–O5	2.004(9)	N2–C8	1.49(2)
Fe1–O7	2.015(11)	N2–C8	1.46(3)	Fe1–O1	2.011(9)	C10–C11	1.47(2)
Fe1–O62	2.063(10)	N2–C7	1.53(3)	Fe1–O4	2.064(8)	N3–C11	1.34(2)
Fe1–N2	2.207(15)	C6–C7	1.44(4)	Fe1–N2	2.199(12)	N3–C12	1.42(2)
Fe1–Dy12	3.428(2)	C4–C5	1.52(2)	Fe1–Gd12	3.4562(18)	N3–Gd12	2.605(13)
O1–C1	1.40(2)	C8–C92	1.48(3)	O1–C1	1.416(17)	C4–C5	1.50(2)
O5–C54	1.43(2)	C11–C14	1.40(4)	O3–C5	1.397(15)	C9–C8	1.43(3)
O4–C5	1.426(18)	C9–C81	1.48(3)	O5–C9	1.395(18)	C12–C13	1.41(3)
O3–C13	1.374(19)	C2–C54	1.54(3)	O4–C6	1.387(16)	C3–C2	1.53(2)
				O4–d12	2.287(8)	C14–O8	1.32(4)

Complex 3			
Y3–O15	2.257(9)	O10–C21	1.385(17)
Y3–O21	2.266(9)	O29–C52	1.411(17)
Y3–O18	2.323(9)	O23–C0AA	1.413(17)
Y3–O17	2.349(9)	O15–C23	1.397(18)
Y3–O19	2.411(9)	O8–C13	1.420(18)
Y3–O20	2.468(9)	O22–C36	1.405(18)
Y3–N7	2.548(12)	O13–C14	1.441(19)
Y3–N8	2.569(14)	O16–C26	1.407(18)
Y3–Fe2	3.423(2)	O30–C49	1.401(18)
Y3–Fe3	3.462(2)	O9–C10	1.391(19)
Y2–O14	2.245(9)	O19–C31	1.411(19)
Y2–O8	2.257(10)	O31–C5	1.434(18)
Y2–O12	2.297(9)	N14–O371	1.236(12)
Y2–O10	2.341(9)	N14–O372	1.236(12)
Y2–O13	2.399(10)	N14–O37	1.236(12)
Y2–O11	2.458(10)	O25–C40	1.452(18)
Y2–N10	2.533(12)	O20–C30	1.44(2)
Y2–N11	2.560(13)	O34–C4	1.45(2)
Y2–Fe1	3.424(2)	O28–C47	1.43(2)
Y2–Fe2	3.466(2)	N13–O42	1.212(19)
Y1–O29	2.252(9)	N13–O40	1.228(17)
Y1–O7	2.256(9)	N13–O41	1.23(2)
Y1–O32	2.302(9)	N1–C6	1.43(2)
Y1–O33	2.347(9)	N1–C7	1.495(18)
Y1–O31	2.412(9)	O11–C18	1.49(2)
Y1–O34	2.459(10)	N7–C32	1.456(18)

Y1–N1	2.535(12)	N7–C33	1.508(19)
Y1–N2	2.576(13)	N5–C41	1.46(2)
Y1–Fe4	3.422(2)	N5–C43	1.49(2)
Y1–Fe1	3.467(2)	N6–C1AA	1.41(2)
Y4–O27	2.261(9)	N6–C37	1.52(2)
Y4–O23	2.261(9)	N10–C15	1.453(19)
Y4–O26	2.317(10)	N10–C16	1.484(19)
Y4–O24	2.336(9)	N12–C12	1.43(2)
Y4–O25	2.412(10)	N12–C11	1.50(2)
Y4– O28	2.470(10)	C7– C8	1.52(2)
Y4– N5	2.548(12)	C33– C34	1.52(2)
Y4– N4	2.573(13)	C16– C17	1.50(2)
Y4– Fe3	3.424(2)	N9– C24	1.43(2)
Y4– Fe4	3.467(2)	N9– C25	1.53(2)
Fe2– O17	1.940(9)	N3– C51	1.45(2)
Fe2– O12	1.999(9)	N3– C50	1.52(2)
Fe2– O14	2.004(9)	C43– C42	1.52(2)
Fe2– O16	2.016(9)	C0AA– C1AA	1.48(2)
Fe2– O15	2.042(10)	C52– C51	1.49(2)
Fe2– N9	2.186(13)	C13– C12	1.50(2)
Fe1– O10	1.939(10)	N2– C54	1.37(2)
Fe1– O7	1.995(9)	N2– C3	1.40(2)
Fe1– O32	1.996(9)	C53– C54	1.49(2)
Fe1– O9	2.005(10)	N11– C20	1.38(2)
Fe1– O8	2.041(9)	N11– C19	1.42(2)
Fe1– N12	2.180(13)	C23– C24	1.49(2)
Fe3– O24	1.939(9)	C44– C45	1.45(2)
Fe3– O18	1.979(9)	C40– C41	1.48(2)
Fe3– O21	1.990(9)	N4– C45	1.36(2)
Fe3– O22	2.013(11)	N4– C46	1.42(2)
Fe3– O23	2.047(9)	N8– C28	1.37(2)
Fe3– N6	2.178(12)	N8– C29	1.44(2)
Fe4– O33	1.956(9)	C29– C30	1.38(3)
Fe4– O26	1.991(9)	C27– C28	1.48(2)
Fe4– O27	1.993(10)	C49– C50	1.50(3)
Fe4– O30	2.022(10)	C36– C37	1.48(3)
Fe4– O29	2.045(9)	C3– C4	1.44(3)
Fe4– N3	2.177(12)	C21– C20	1.49(2)
O18– C34	1.390(17)	C14– C15	1.50(2)
O12– C17	1.381(16)	C19– C18	1.45(3)
O14– C22	1.425(18)	C32– C31	1.47(2)

O32– C8	1.400(16)	C26– C25	1.47(3)
O7– C9	1.430(18)	C10– C11	1.47(3)
O26– C42	1.401(16)	C47– C46	1.31(3)
O21– C35	1.405(18)	C6– C5	1.50(2)
O33– C53	1.353(16)	C99A– O36	1.25(6)
O17– C27	1.372(18)	C99B– O36	1.65(6)
O27– C48	1.412(17)	O38– C2	1.39(4)
O24– C44	1.376(17)	O39– C1A	1.48(6)

Table S4. List of selected bond angle (º) in complexes **1-3**

Complex 1			
O6–Dy1–O1	107.4(4)	O4–Fe1–N2	96.9(5)
O6–Dy1–O4	90.9(4)	O1–Fe1–N2	91.4(5)
O1–Dy1–O4	65.8(3)	O7–Fe1–N2	81.0(6)
O6–Dy1–O3	67.1(3)	O62–Fe1–N2	78.4(5)
O1–Dy1–O3	88.4(3)	O32–Fe1–Dy12	42.1(3)
O4–Dy1–O3	139.8(4)	O4–Fe1–Dy12	148.2(3)
O6–Dy1–O5	84.9(4)	O1–Fe1–Dy12	109.0(3)
O1–Dy1–O5	157.4(4)	O7–Fe1–Dy12	83.5(3)
O4–Dy1–O5	134.4(4)	O62–Fe1–Dy12	39.8(3)
O3–Dy1–O5	78.9(4)	N2–Fe1–Dy12	113.6(4)
O6–Dy1–O2	158.9(4)	O32–Fe1–Dy1	108.7(3)
O1–Dy1–O2	86.4(4)	O4–Fe1–Dy1	39.5(3)
O4–Dy1–O2	80.1(4)	O1–Fe1–Dy1	38.4(3)
O3–Dy1–O2	130.7(4)	O7–Fe1–Dy1	131.6(3)
O5–Dy1–O2	87.8(4)	O62–Fe1–Dy1	130.9(3)
O6–Dy1–N1	81.7(4)	N2–Fe1–Dy1	94.7(4)
O1–Dy1–N1	133.0(4)	Dy12–Fe1–Dy1	139.13(7)
O4–Dy1–N1	68.1(4)	C1–O1–Fe1	120.7(11)
O3–Dy1–N1	135.0(4)	C1–O1–Dy1	126.4(10)
O5–Dy1–N1	66.4(4)	Fe1–O1–Dy1	108.8(4)
O2–Dy1–N1	77.2(5)	C54–O5–Dy1	121.4(10)
O6–Dy1–N3	132.4(4)	C5–O4–Fe1	130.4(9)
O1–Dy1–N3	81.3(5)	C5–O4–Dy1	122.0(9)
O4–Dy1–N3	132.7(5)	Fe1–O4–Dy1	107.6(4)
O3–Dy1–N3	66.5(5)	C13–O3–Fe11	125.3(10)
O5–Dy1–N3	76.5(5)	C13–O3–Dy1	123.8(9)

O2–Dy1–N3	64.2(5)	Fe11–O3–Dy1	104.8(4)
N1–Dy1–N3	126.8(5)	C9–O6–Fe11	116.1(10)
O6–Dy1–Fe11	35.6(3)	C9–O6–Dy1	138.4(10)
O1–Dy1–Fe11	106.4(3)	Fe11–O6–Dy1	104.6(4)
O4–Dy1–Fe11	123.7(3)	C6–O7–Fe1	114.8(11)
O3–Dy1–Fe11	33.1(2)	C14–O2–Dy1	120.5(13)
O5–Dy1–Fe11	72.4(3)	C12–N3–C11	116.9(19)
O2–Dy1–Fe11	155.8(3)	C12–N3–Dy1	112.2(13)
N1–Dy1–Fe11	106.2(3)	C11–N3–Dy1	115.8(13)
N3–Dy1–Fe11	96.8(4)	C2–N1–C4	114.7(13)
O6–Dy1–Fe1	101.2(3)	C2–N1–Dy1	110.1(10)
O1–Dy1–Fe1	32.9(2)	C4–N1–Dy1	109.6(9)
O4–Dy1–Fe1	32.9(3)	O8–N5–O83	119.998(10)
O3–Dy1–Fe1	116.2(2)	O8–N5–O84	120.000(12)
O5–Dy1–Fe1	164.8(3)	O83–N5–O84	119.999(11)
O2–Dy1–Fe1	81.6(3)	O3–C13–C12	112.1(14)
N1–Dy1–Fe1	100.5(3)	C8–N2–C7	112(2)
N3–Dy1–Fe1	108.0(4)	C8–N2–Fe1	104.6(13)
Fe11–Dy1–Fe1	120.31(6)	C7–N2–Fe1	104.0(13)
O32–Fe1–O4	106.5(5)	O7–C6–C7	109.7(16)
O32–Fe1–O1	101.7(4)	N1–C4–C5	107.7(12)
O4–Fe1–O1	77.8(4)	C6–C7–N2	113(2)
O32–Fe1–O7	89.2(5)	O4–C5–C4	108.3(13)
O4–Fe1–O7	92.8(4)	N2–C8–C92	114.8(17)
O1–Fe1–O7	167.3(4)	C14–C11–N3	114(2)
O32–Fe1–O62	79.9(4)	N3–C12–C13	114.2(17)
4–Fe1–O62	169.5(4)	C11–C14–O2	111(2)
O1–Fe1–O62	92.8(4)	O6–C9–C81	113.8(15)
O7–Fe1–O62	95.7(4)	N1–C2–C54	107.7(15)
O32–Fe1–N2	155.1(5)	O5–C54–C2	109.8(15)

Complex 2			
O41–Gd1–O1	106.9(3)	O3–Fe1–N2	97.2(4)
O41–Gd1–O3	90.9(3)	O5–Fe1–N2	79.8(4)
O1–Gd1–O3	66.0(3)	O1–Fe1–N2	92.6(4)
O41–Gd1–O61	66.7(3)	O4–Fe1–N2	79.0(4)
O1–Gd1–O61	88.1(3)	O6–Fe1–Gd12	41.5(2)
O3–Gd1–O61	139.8(3)	O3–Fe1–Gd12	147.5(3)
O41–Gd1–O2	84.6(3)	O5–Fe1–Gd12	84.0(3)
O1–Gd1–O2	158.5(3)	O1–Fe1–Gd12	107.9(3)
O3–Gd1–O2	133.3(3)	O4–Fe1–Gd12	39.7(2)

O61–Gd1–O2	79.7(3)	N2–Fe1–Gd12	113.9(3)
O41–Gd1–O71	159.3(3)	O6–Fe1–Gd1	108.6(3)
O1–Gd1–O71	87.6(3)	O3–Fe1–Gd1	40.2(2)
O3–Gd1–O71	81.3(3)	O5–Fe1–Gd1	131.9(3)
O61–Gd1–O71	130.0(3)	O1–Fe1–Gd1	38.7(2)
O2–Gd1–O71	86.8(3)	O4–Fe1–Gd1	130.3(3)
O41–Gd1–N1	81.5(3)	N2–Fe1–Gd1	95.0(3)
O1–Gd1–N1	132.0(3)	Gd12–Fe1–Gd1	138.63(6)
O3–Gd1–N1	66.7(3)	C1–O1–Fe1	122.3(8)
O61–Gd1–N1	135.5(3)	C1–O1–Gd1	126.0(8)
O2–Gd1–N1	66.6(3)	Fe1–O1–Gd1	108.4(4)
O71–Gd1–N1	77.8(4)	C5–O3–Fe1	131.7(7)
O41–Gd1–N31	130.7(4)	C5–O3–Gd1	121.6(7)
O1–Gd1–N31	82.5(5)	Fe1–O3–Gd1	106.7(3)
O3–Gd1–N31	134.5(4)	C9–O5–Fe1	115.4(9)
O61–Gd1–N31	65.3(4)	C6–O4–Fe1	115.8(8)
O2–Gd1–N31	76.3(5)	C6–O4–Gd12	137.9(8)
O71–Gd1–N31	64.7(4)	Fe1–O4–Gd12	105.1(3)
N1–Gd1–N31	128.1(5)	C10–O6–Fe1	123.0(8)
O41–Gd1–Fe11	35.2(2)	C10–O6–Gd12	124.9(7)
O1–Gd1–Fe11	106.3(2)	Fe1–O6–Gd12	105.3(3)
O3–Gd1–Fe11	123.6(2)	C2–O2–Gd1	121.8(8)
O61–Gd1–Fe11	33.2(2)	C3–N1–C4	115.9(11)
O2–Gd1–Fe11	72.4(2)	C3–N1–Gd1	107.9(9)
O71–Gd1–Fe11	154.6(2)	C4–N1–Gd1	109.2(8)
N1–Gd1–Fe11	106.0(3)	O4–C6–C7	112.0(12)
N31–Gd1–Fe11	95.4(3)	C13–O7–Gd12	121.0(10)
O41–Gd1–Fe1	101.5(2)	O10–N4–O103	120.01(2)
O1–Gd1–Fe1	32.9(2)	O10–N4–O104	119.99(2)
O3–Gd1–Fe1	33.1(2)	O103–N4–O104	120.00(2)
O61–Gd1–Fe1	116.4(2)	C7–N2–C8	110.0(18)
O2–Gd1–Fe1	164.0(2)	C7–N2–Fe1	104.2(10)
O71–Gd1–Fe1	82.4(2)	C8–N2–Fe1	105.1(10)
N1–Gd1–Fe1	99.4(2)	O6–C10–C11	111.8(12)
N31–Gd1–Fe1	109.2(4)	C11–N3–C12	122.3(16)
Fe11–Gd1–Fe1	120.78(5)	C11–N3–Gd12	113.7(11)
O6–Fe1–O3	106.4(4)	C12–N3–Gd12	114.3(11)
O6–Fe1–O5	90.3(4)	N1–C4–C5	107.3(11)
O3–Fe1–O5	92.6(4)	O5–C9–C8	110.0(14)
O6–Fe1–O1	100.3(4)	C13–C12–N3	117.6(16)
O3–Fe1–O1	78.8(3)	O3–C5–C4	109.4(11)

O5–Fe1–O1	167.8(4)	C9–C8–N2	112.1(16)
O6–Fe1–O4	79.0(3)	N1–C3–C2	110.5(12)
O3–Fe1–O4	169.9(4)	N2–C7–C6	117.6(17)
O5–Fe1–O4	95.9(4)	O2–C2–C3	108.3(12)
O1–Fe1–O4	91.9(3)	N3–C11–C10	118.2(16)
O6–Fe1–N2	154.8(4)	C12–C13–O7	112.9(18)

Complex **3**			
O15–Y3–O21	106.6(3)	O9–Fe1–N12	80.1(5)
O15–Y3–O18	90.4(3)	O8–Fe1–N12	77.6(4)
O21–Y3–O18	66.1(3)	O10–Fe1–Y2	41.1(3)
O15–Y3–O17	66.6(3)	O7–Fe1–Y2	109.5(3)
O21–Y3–O17	88.0(3)	O32–Fe1–Y2	147.3(3)
O18–Y3–O17	139.3(3)	O9–Fe1–Y2	83.8(3)
O15–Y3–O19	84.9(4)	O8–Fe1–Y2	39.4(3)
O21–Y3–O19	157.7(4)	N12–Fe1–Y2	112.4(3)
O18–Y3–O19	134.2(4)	O10–Fe1–Y1	109.6(3)
O17–Y3–O19	79.1(3)	O7–Fe1–Y1	37.9(3)
O15–Y3–O20	159.2(4)	O32–Fe1–Y1	39.3(2)
O21–Y3–O20	87.3(3)	O9–Fe1–Y1	131.3(3)
O18–Y3–O20	81.0(3)	O8–Fe1–Y1	131.1(3)
O17–Y3–O20	130.8(3)	N12–Fe1–Y1	95.8(3)
O19–Y3–O20	87.6(3)	Y2–Fe1–Y1	139.28(7)
O15–Y3–N7	82.4(4)	O24–Fe3–O18	107.0(4)
O21–Y3–N7	133.4(4)	O24–Fe3–O21	102.2(4)
O18–Y3–N7	68.2(4)	O18–Fe3–O21	78.2(4)
O17–Y3–N7	135.0(3)	O24–Fe3–O22	89.1(4)
O19–Y3–N7	66.0(4)	O18–Fe3–O22	92.3(4)
O20–Y3–N7	76.8(4)	O21–Fe3–O22	166.9(4)
O15–Y3–N8	130.9(4)	O24–Fe3–O23	78.6(4)
O21–Y3–N8	82.4(4)	O18–Fe3–O23	170.3(4)
O18–Y3–N8	134.7(4)	O21–Fe3–O23	93.0(4)
O17–Y3–N8	65.7(4)	O22–Fe3–O23	95.7(4)
O19–Y3–N8	75.8(5)	O24–Fe3–N6	153.0(4)
O20–Y3–N8	65.1(4)	O18–Fe3–N6	98.5(4)
N7–Y3–N8	126.4(5)	O21–Fe3–N6	91.6(4)
O15–Y3–Fe2	35.1(2)	O22–Fe3–N6	80.9(5)
O21–Y3–Fe2	105.9(2)	O23–Fe3–N6	77.6(4)
O18–Y3–Fe2	122.9(2)	O24–Fe3–Y4	41.0(3)
O17–Y3–Fe2	33.1(2)	O18–Fe3–Y4	147.5(3)
O19–Y3–Fe2	72.4(2)	O21–Fe3–Y4	109.3(3)

O20–Y3–F2	155.6(2)	O22–Fe3–Y4	83.5(3)
N7–Y3–Fe2	106.2(3)	O23–Fe3–Y4	39.6(3)
N8–Y3–Fe2	95.8(3)	N6–Fe3–Y4	112.5(3)
O15–Y3–Fe3	100.9(2)	O24–Fe3–Y3	109.9(3)
O21–Y3–Fe3	33.0(2)	O18–Fe3–Y3	39.9(3)
O18–Y3–Fe3	33.1(2)	O21–Fe3–Y3	38.3(3)
O17–Y3–Fe3	116.0(2)	O22–Fe3–Y3	131.4(3)
O19–Y3–Fe3	165.0(3)	O23–Fe3–Y3	131.1(3)
O20–Y3–Fe3	82.2(2)	N6–Fe3–Y3	95.4(3)
N7–Y3–Fe3	100.8(3)	Y4–Fe3–Y3	139.45(7)
N8–Y3–Fe3	109.4(3)	O33–Fe4–O26	106.5(4)
Fe2–Y3–Fe3	119.94(6)	O33–Fe4–O27	102.1(4)
O14–Y2–O8	106.8(3)	O26–Fe4–O27	77.8(4)
O14–Y2–O12	66.5(3)	O33–Fe4–O30	88.9(4)
O8–Y2–O12	90.5(3)	O26–Fe4–O30	92.5(4)
O14–Y2–O10	88.1(3)	O27–Fe4–O30	166.9(4)
O8–Y2–O10	66.5(3)	O33–Fe4–O29	78.9(4)
O12–Y2–O10	139.6(3)	O26–Fe4–O29	170.3(4)
O14–Y2–O13	157.5(4)	O27–Fe4–O29	93.4(4)
O8–Y2–O1	84.7(4)	O30–Fe4–O29	95.6(4)
O12–Y2–O13	134.1(3)	O33–Fe4–N3	153.8(5)
O10–Y2–O13	78.7(3)	O26–Fe4–N3	98.1(4)
O14–Y2–O11	86.9(3)	O27–Fe4–N3	91.6(5)
O8–Y2–O11	159.0(4)	O30–Fe4–N3	81.1(5)
O12–Y2–O11	80.2(3)	O29–Fe4–N3	78.0(4)
O10–Y2–O11	131.3(3)	O33–Fe4–Y1	41.5(3)
O13–Y2–O11	88.3(3)	O26–Fe4–Y1	147.6(3)
O14–Y2–N10	133.1(4)	O27–Fe4–Y1	109.4(3)
O8–Y2–N10	82.6(4)	O30–Fe4–Y1	83.5(3)
O12–Y2–N10	67.6(4)	O29–Fe4–Y1	39.4(3)
O10–Y2–N10	135.3(4)	N3–Fe4–Y1	112.9(4)
O13–Y2–N10	66.5(4)	O33–Fe4–Y4	109.5(3)
O11–Y2–N10	76.5(4)	O26–Fe4–Y4	39.7(3)
O14–Y2–N11	81.5(4)	O27–Fe4–4	38.1(3)
O8–Y2–N11	131.2(4)	O30–Fe4–Y4	131.4(3)
O12–Y2–N11	134.1(4)	O29–Fe4–Y4	131.2(3)
O10–Y2–N11	65.9(4)	N3–Fe4–Y4	95.1(4)
O13–Y2–N11	76.5(5)	Y1–Fe4–Y4	139.35(6)
O11–Y2–N11	65.4(4)	C34–O18–Fe3	131.7(8)
N10–Y2–N11	126.9(4)	C34–O18–Y3	121.3(8)
O14–Y2–Fe1	105.8(2)	Fe3–O18–Y3	106.9(4)

O8–Y2–Fe1	35.1(2)	C17–O12–Fe2	130.1(8)
O12–Y2–Fe1	123.0(3)	C17–O12–Y2	122.5(8)
O10–Y2–Fe1	33.0(2)	Fe2–O12–Y2	107.4(4)
O13–Y2–Fe1	72.3(2)	C22–O14–Fe2	118.3(8)
O11–Y2–Fe1	156.3(2)	C22–O14–Y2	128.8(9)
N10–Y2–Fe1	106.6(3)	Fe2–O14–Y2	109.2(4)
N11–Y2–Fe1	96.2(3)	C8–O32–Fe1	129.6(8)
O14–Y2–Fe2	33.1(2)	C8–O32–Y1	123.0(7)
O8–Y2–Fe2	101.1(2)	Fe1–O32–Y1	107.3(4)
O12–Y2–Fe2	33.4(2)	C9–O7–Fe1	120.3(9)
O10–Y2–Fe2	116.1(2)	C9–O7–Y1	126.9(9)
O13–Y2–Fe2	165.1(2)	Fe1–O7–Y1	109.1(4)
O11–Y2–Fe2	81.5(2)	C42–O26–Fe4	130.3(8)
N10–Y2–Fe2	100.4(3)	C42–O26–Y4	122.8(8)

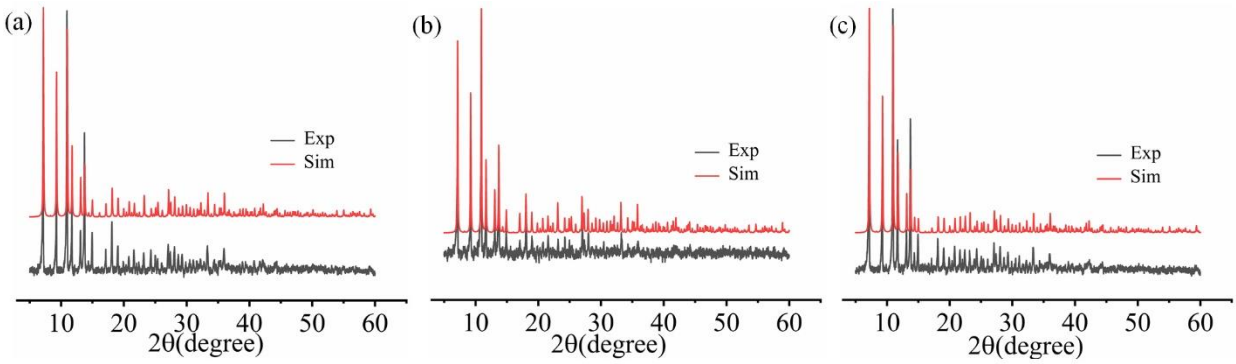

Fig. S10. Experimental and simulated PXRD patterns for complexes **1**-**3** (a-c).

Table S5. Crystal field parameters obtained from ab initio calculation for complex **1**.

k	Q	Complex **1**
	-2	-0.4473E+00
	-1	-0.8947E+00
2	0	-0.2901E+01
	1	0.2074E+01
	2	-0.8202E+01
	-4	-0.8086E-01
	-3	-0.5556E-01
	-2	-0.1485E-01
	-1	-0.2100E-01
4	0	-0.3960E-02
	1	-0.4091E-02
	2	0.1191E-01

	3	0.9513E-02
	4	-0.6752E-02
	-6	0.8563E-04
	-5	0.2966E-03
	-4	0.6324E-04
	-3	0.1154E-03
	-2	0.5773E-04
	-1	0.7302E-04
6	0	0.2875E-05
	1	-0.1387E-03
	2	0.5165E-05
	3	-0.8449E-04
	4	-0.4035E-04
	5	-0.5239E-03
	6	-0.2489E-03

Table S6. Ab initio calculated low-lying spin-free and spin-orbit energy states for complex **1**.

Spin-free states	Spin-orbit states
0.000	0.000
18.320	188.282
270.923	315.610
291.308	339.974
350.389	393.411
375.345	478.328
429.334	585.107
507.539	677.114

Table S7: Single_aniso computed energy of the KDs, g and wave-functions composition for Complex **1**.

Kramers doublets (KDs)	Energy (cm^{-1})	g_x	g_y	g_z	Wave function composition
1	0.000	0.0024	0.0062	19.82	98.56%|±15/2>+1.15%|±11/2>
2	188.282	0.203	0.225	17.00	92.28%|±13/2>+3.76%|±11/2> +2.62%|±9/2>
3	315.610	1.441	3.200	14.00	57.25%|±11/2>+15.45%|±9/2> +6.47%|±5/2>+9.08%|±3/2>5.0 5%|±7/2>

4	339.974	0.533	3.016	13.99	11.42%|±9/2>+20.27%|±7/2>+ 19.98%|±1/2>+12.46%|±3/2>+ 17.20%|±5/2>+18.02%|±11/2>
5	393.411	1.748	5.547	10.81	27.56%|±9/2>+26.18%|±7/2>+ 17.93%|±5/2>+13.94%|±3/2>+ 8.34%|±1/2>+3.49%|±11/2>+2. 30%|±13/2>
6	478.328	2.326	4.014	9.83	22.26%|±9/2>+7.67%|±7/2>+1 7.66%|±5/2>+19.72%|±3/2>+1 8.74%|±1/2>+11.84%|±11/2>1. 93%|±13/2>
7	585.107	1.737	2.247	12.68	30.12%|±1/2>+13.01%|±3/2>+ 7.74%|±5/2>+26.38%|±7/2>+1 8.34%|±9/2>+3.63%|±11/2>
8	677.114	0.347	1.304	17.51	18.54%|±1/2>+31.32%|±3/2>+ 32.69%|±5/2>+14.36%|±7/2>+ 2.25%|±9/2>

Table S8: Single_aniso computed energy and g tensor of the ground and first excited KDs for four Dy centers in Complex **1**.

Complex 1		**Energy (cm^{-1})**	g_x	g_y	g_z
Dy1	ground state	0.000	0.002	0.006	19.82
	1st excited state	188.28	0.203	0.225	17.002
Dy2	ground state	0.000	0.001	0.005	19.71
	1st excited state	189.90	0.201	0.227	16.90
Dy3	ground state	0.000	0.001	0.005	19.83
	1st excited state	189.28	0.201	0.219	17.01
Dy4	ground state	0.000	0.001	0.005	19.83
	1st excited state	189.91	0.203	0.221	16.97

Table S9. Fitting and BS-DFT calculated parameters for complexes **1-3**.

Compounds	Fitting Parameters		BS-DFT Calculated	
	J_1 (cm^{-1})	J_2 (cm^{-1})	J_1 (cm^{-1})	J_2 (cm^{-1})
2	+0.30	+0.90	+0.15	+0.76
3	$J_{Fe\text{-}Fe}$ = -0.10 cm^{-1}		$J_{Fe\text{-}Fe}$ = -0.15 cm^{-1}	

The calculations were performed on the suitable fragment by replacing the adjacent lanthanide ion with diamagnetic Lu(III) ion in complex **2** whereas the whole molecule have been used for complex **3** as the magnetic exchange interactions between the Fe(III) centers were considered. The exchange interaction between the two Fe(III) centers in complex **3** are mediated through the diamagnetic Y(III) ion. Although, it is the interaction between the next nearest neighbor and is expected to be very weak as observed earlier, but not negligible. To extract the isotropic exchange coupling we have used the method of Yamaguchi where the exchange coupling is determined from the energies (E) and expectation values ($<S^2>$) of the triplet and broken symmetry singlet states.

$$J = \frac{-(E_T - E_{BSS})}{<S^2>_T - <S^2>_{BSS}} \quad \text{.....Eq. 1}$$

Table S10. Energy of the high spin and broken symmetry state for complexes **2-3**.

Spin State	Energy (Hatree)	$<S^2>$
Complex **2** (J_1)		
HS	-5429.21964058	42.0161
BS	-5429.21962406	7.0155
Complex **2** (J_2)		
HS	-5429.21836617	42.0161
BS	-5429.21824391	7.0152
Complex **3**		
HS	-10030.6583828	110
BS	-10030.6584387	10

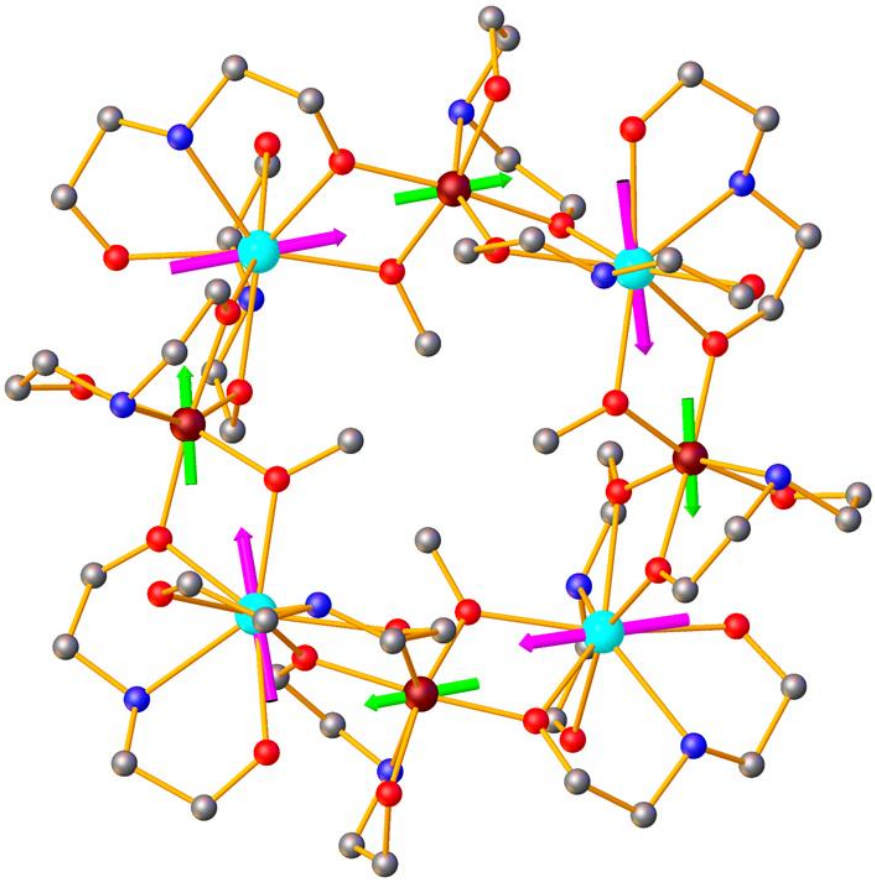

Fig. S11. The orientation of local anisotropy axis for each Dy(III) and Fe(III) centers in complex **1**.

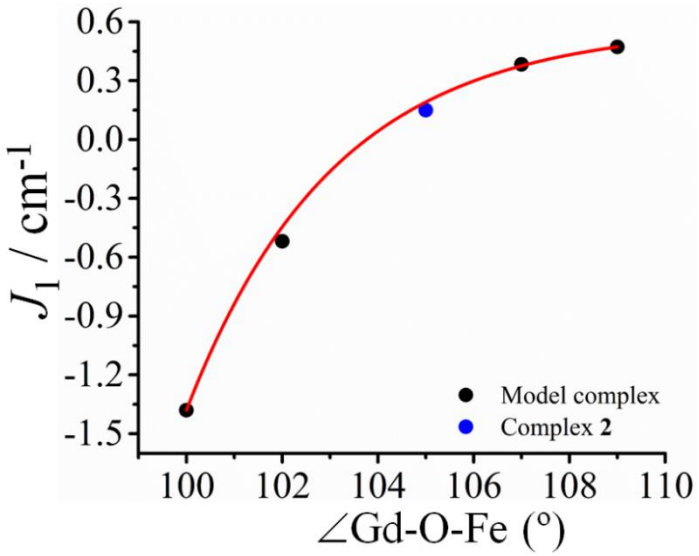

Figure S12. The variation of exchange coupling constant with the ∠Gd-O-Fe bridging angle for complex **2**.

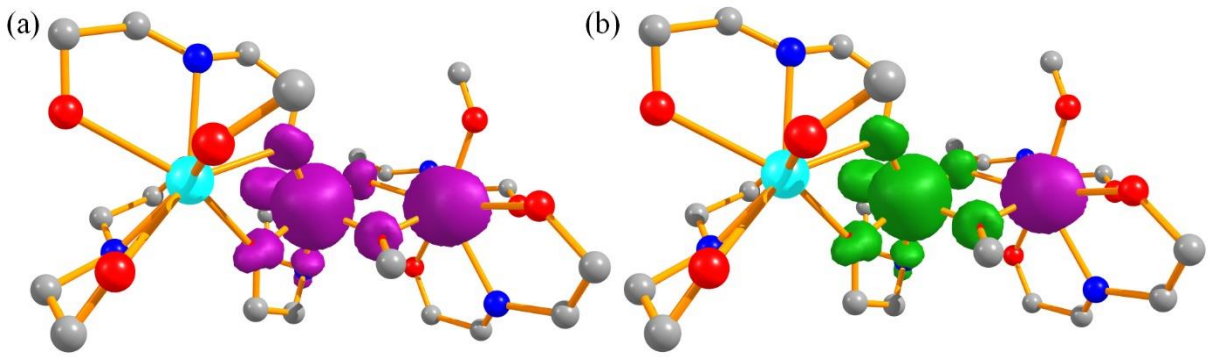

Fig. S13. The high spin and broken symmetry spin density plots for the fragment of complex **2**.

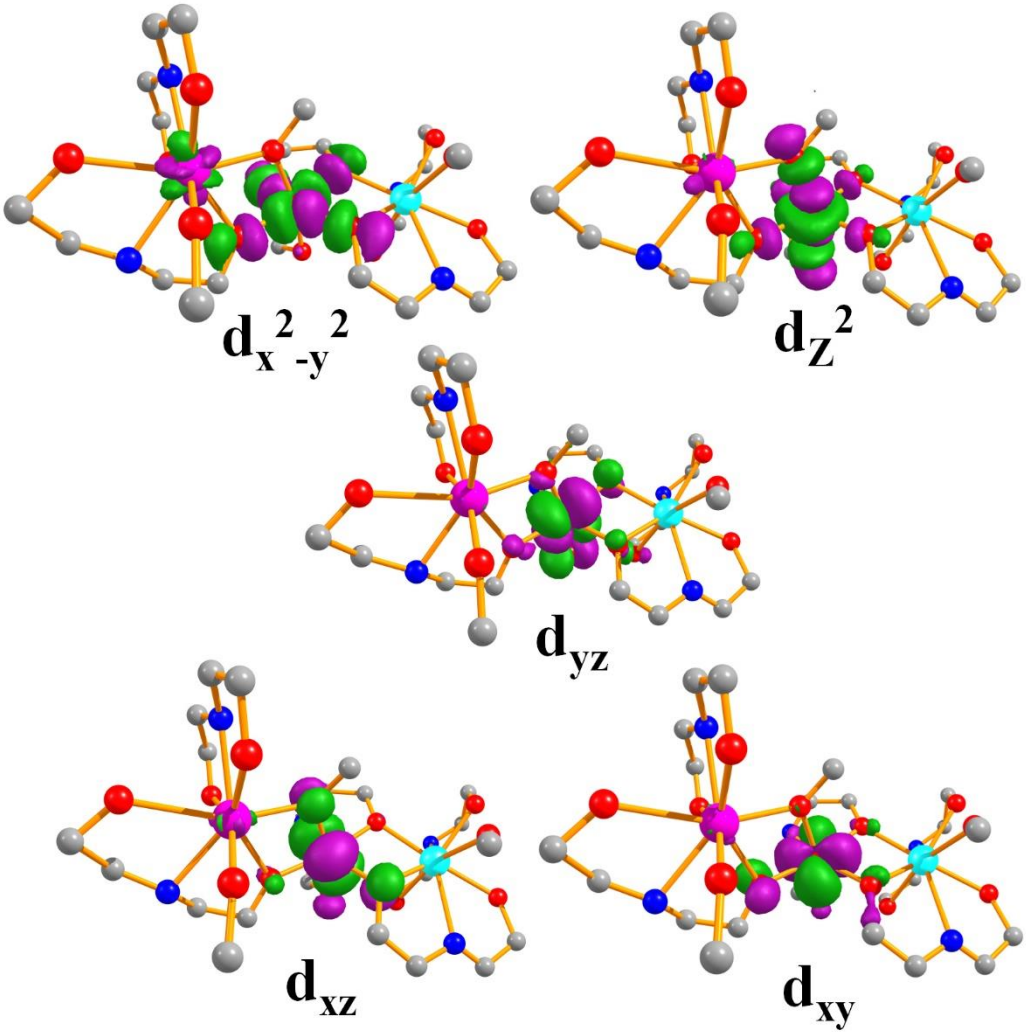

Fig. S14. Molecular orbital picture of the 3d orbitals of Fe^{III} for the fragment of complex **2**.

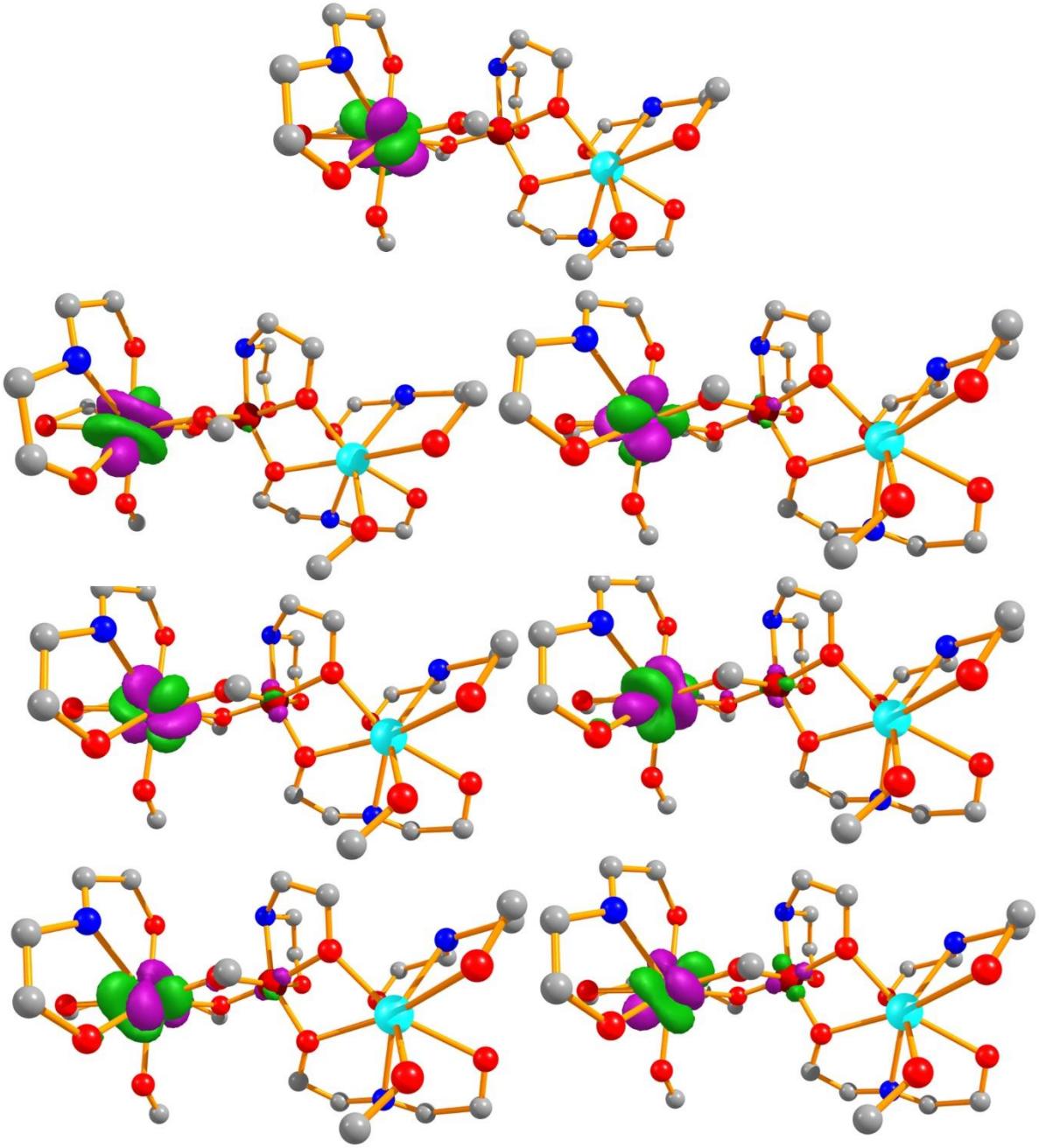

Fig. S15. Molecular orbital picture of the 4f orbitals of Gd^{III} ion for the fragment of complex **2**.

Table S11. Second Order Perturbation Theory NBO Analysis on Complexes **1** and **2**.

Complex **1**		
Donor NBO	Acceptor NBO	CT interaction (Kcal/mol)
Fe (s = 92.95%, p = 7.0%, d = 0.06%)	Dy (s = 93.70%, p = 5.06%, d = 1.20%)	16.34
Fe (s = 92.95%, p = 7.0%, d = 0.06%)	Dy (s = 67.45%, p = 8.39%, d = 6.40%)	4.52
Fe (s = 100%)	Dy (s = 0.11%, p = 98.42%, d = 1.43%)	3.11
Dy (s = 2.26%, p = 96.50%, d = 1.21%)	Fe (s = 92.95%, p = 7.0%, d = 0.06%)	28.54
Dy (s = 2.83%, p = 94.02%, d = 3.09%)	Fe (s = 92.95%, p = 7.0%, d = 0.06%)	8.28

Complex **2**		
Donor NBO	Acceptor NBO	CT interaction (Kcal/mol)
Fe (s = 92.07%, p = 7.88%, d = 0.05%)	Gd (s = 92.36%, p = 4.77%, d = 2.82%)	15.91
Fe (s = 92.07%, p = 7.88%, d = 0.05%)	Gd (s = 50.56%, p = 6.88%, d = 23.93%)	3.33
Fe (s = 92.07%, p = 7.88%, d = 0.05%)	Gd (s = 7.61%, p = 8.07%, d = 37.27%)	3.00