Supporting Information for

Solvent-dependent Ln(III) clusters assembled by immobilization of CO_2 in the air: zero-field single-molecule magnets and magnetic refrigerant materials

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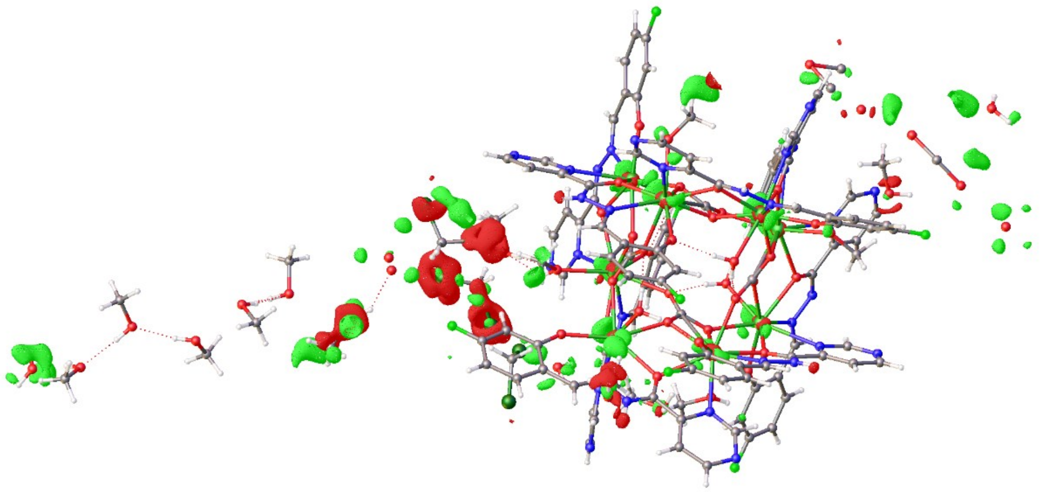

Fig. S1. Diagram showing the residual density plot of the X-ray structure of **3**.

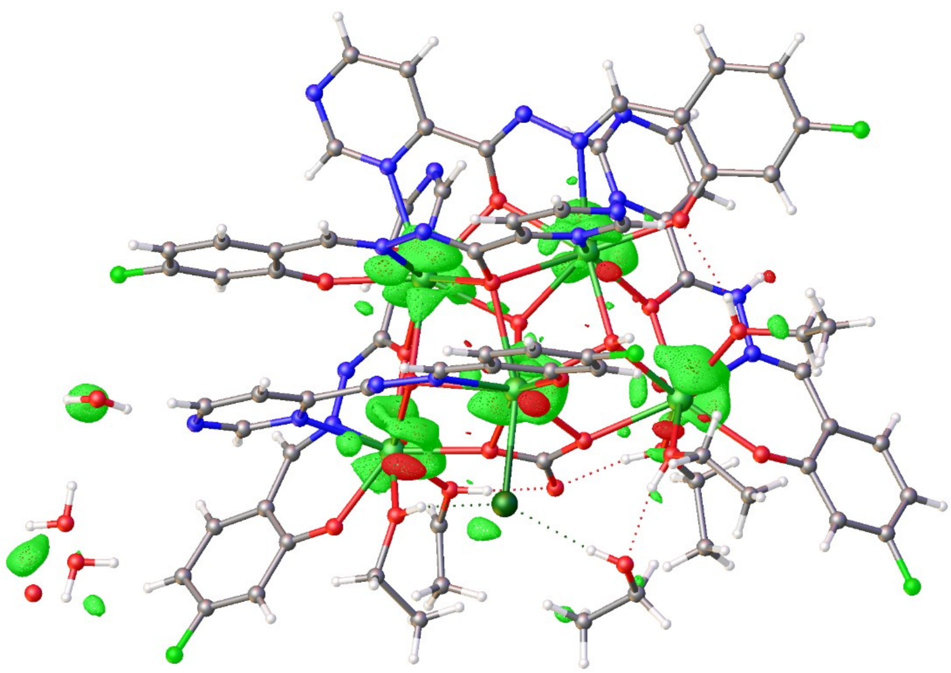

Fig. S2. Diagram showing the residual density plot of the X-ray structure of **4**.

Table S1. Selected bond lengths (Å) and angles (°) for **1**.

bond lengths (Å)			
Dy1-N1	2.481(5)	Dy1-N19	2.548(6)
Dy1-O1	2.205(4)	Dy1-O1W	2.342(5)
Dy1-O2	2.336(4)	Dy1-O10	2.523(4)
Dy1-O11	2.311(4)	Dy1-O14	2.346(5)
Dy2-N3	2.568(5)	Dy2-N5	2.500(6)
Dy2-N11	2.690(5)	Dy2-O2	2.421(4)
Dy2-O3	2.199(4)	Dy2-O4	2.489(4)
Dy2-O6	2.384(4)	Dy2-O10	2.584(4)
Dy2-O17	2.341(4)	Dy3-N7	2.696(5)
Dy3-N9	2.513(5)	Dy3-N15	2.577(5)
Dy3-O4	2.567(4)	Dy3-O5	2.276(4)
Dy3-O6	2.367(4)	Dy3-O8	2.401(4)
Dy3-O17	2.383(4)	Dy3-O18	2.289(4)
Dy4-N13	2.495(6)	Dy4-O7	2.210(5)
Dy4-O8	2.353(4)	Dy4-O12	2.357(4)
Dy4-O18	2.401(5)	Dy4-O19	2.379(5)
Dy4-O20	2.399(5)	Dy4-O21	2.412(4)
Dy5-N21	2.493(6)	Dy5-O4	2.495(4)
Dy5-O9	2.279(4)	Dy5-O10	2.409(4)
Dy5-O11	2.402(4)	Dy5-O12	2.429(5)
Dy5-O15	2.356(5)	Dy5-O17	2.517(4)
Dy5-O18	2.398(4)		
bond angles (°)			
O1-Dy1-N1	72.73(17)	O2-Dy1-N1	65.83(16)
O10-Dy1-N19	64.07(15)	O11-Dy1-O14	76.65(16)
O3-Dy2-N5	72.54(17)	O6-Dy2-N11	61.17(15)
O17-Dy2-O6	71.38(14)	O17- Dy2- O10	75.52(14)
O5-Dy3-N9	72.90(17)	O4-Dy3-N7	60.56(14)
O6-Dy3-N9	63.71(16)	O8-Dy3-N15	63.88(16)
O7-Dy4-N13	72.76(18)	O8-Dy4-N13	64.73(17)
O8-Dy4-O12	91.33(16)	O9-Dy5-N21	70.92(18)
O4-Dy5-O17	57.97(14)	O11-Dy5-O12	53.59(15)
O11-Dy5-O10	69.51(15)	O9-Dy5-O12	95.95(17)
Dy1-O2-Dy2	118.79(17)	Dy2-O4-Dy3	95.79(14)
Dy2-O4-Dy5	96.81(14)	Dy5-O4-Dy3	92.31(14)
Dy3-O6-Dy2	104.30(16)	Dy4-O8-Dy3	111.25(18)
Dy1-O10-Dy2	106.59(15)	Dy5-O10-Dy1	106.04(17)
Dy5-O10-Dy2	96.51(15)	Dy1-O11-Dy5	113.47(19)
Dy4-O12-Dy5	111.53(17)	Dy2-O17-Dy3	105.13(16)
Dy2-O17-Dy5	100.16(16)	Dy3-O17-Dy5	96.30(14)
Dy3-O18-Dy4	113.55(18)	Dy3-O18-Dy5	102.33(16)
Dy4-O18-Dy5	111.11(17)		

Table S2. Selected bond lengths (Å) and angles (°) for **2**.

bond lengths (Å)			
Dy1-Cl1	2.7605(7)	Dy1-O1	2.1585(19)
Dy1-O2	2.3389(18)	Dy1-O8	2.3664(18)
Dy1-O13	2.4364(18)	Dy1-O14	2.4310(18)
Dy1-N1	2.450(2)	Dy1-N15	2.523(2)
Dy2-O3	2.149(2)	Dy2-O4	2.3359(18)
Dy2-O10	2.3608(18)	Dy2-O14	2.4198(18)
Dy2-O15	2.4431(18)	Dy2-N5	2.458(2)
Dy2-N19	2.519(2)	Dy2-O1W	2.450(2)
Dy3-O5	2.1610(19)	Dy3-O6	2.3446(17)
Dy3-O12	2.3548(18)	Dy3-O13	2.4329(18)
Dy3-O15	2.4825(18)	Dy3-N9	2.446(2)
Dy3-N23	2.551(2)	Dy3-Cl2	2.7155(7)
Dy4-O2	2.3452(18)	Dy4-O7	2.1561(19)
Dy4-O8	2.3395(18)	Dy4-O16	2.4820(18)
Dy4-O17	2.4404(18)	Dy4-O19	2.4048(19)
Dy4-N3	2.541(2)	Dy4-N13	2.494(2)
Dy5-O2W	2.409(2)	Dy5-O4	2.3551(18)
Dy5-O9	2.1650(19)	Dy5-O10	2.3176(18)
Dy5-O17	2.4703(18)	Dy5-O18	2.3925(18)
Dy5-N7	2.508(2)	Dy5-N17	2.460(2)
Dy6-O6	2.3308(17)	Dy6-O11	2.1652(18)
Dy6-O12	2.3331(17)	Dy6-O16	2.4770(18)
Dy6-O18	2.4114(18)	Dy6-O20	2.3748(19)
Dy6-N11	2.568(2)	Dy6-N21	2.449(2)
bond angles (°)			
O1-Dy1-N1	74.96(7)	O8-Dy1-N15	66.08(7)
O2-Dy1-O8	66.30(6)	O3-Dy2-N5	74.82(8)
O4-Dy2-O10	67.02(6)	O3-Dy2-N19	82.05(8)
O5-Dy3-N23	86.80(7)	O5-Dy3-Cl2	95.43(6)
O7-Dy4-N13	73.17(7)	O2-Dy4-N3	65.44(7)
O17-Dy4-O16	53.48(6)	O8-Dy4-O2	66.63(6)
O9-Dy5-N17	74.89(9)	O4-Dy5-N7	65.13(8)
O6-Dy6-N11	65.17(7)	O11-Dy6-N21	75.06(7)
Dy1-O2-Dy4	113.70(7)	Dy2-O4-Dy5	112.40(7)
Dy6-O6-Dy3	113.30(7)	Dy4-O8-Dy1	112.89(7)
Dy5-O10-Dy2	112.87(7)	Dy6-O12-Dy3	112.83(7)
Dy3-O13-Dy1	172.05(9)	Dy2-O14-Dy1	171.21(9)
Dy2-O15-Dy3	171.68(9)	Dy6-O16-Dy4	173.27(8)
Dy4-O17-Dy5	167.96(9)	Dy5-O18-Dy6	165.64(9)

Table S3. Selected bond lengths (Å) and angles (°) for **3**.

bond lengths (Å)			
Gd1-N1	2.513(3)	Gd1-N31	2.675(3)
Gd1-O2	2.408(2)	Gd1-O16	2.476(2)
Gd1-O17	2.587(2)	Gd1-O18	2.399(2)
Gd1-O28	2.428(2)	Gd1-O29	2.481(3)
Gd1-O46	2.279(2)	Gd1-O29W	2.481(3)
Gd2-N3	2.662(3)	Gd2-N5	2.461(3)
Gd2-O1W	2.432(2)	Gd2-O2	2.352(2)
Gd2-O3	2.236(2)	Gd2-O4	2.353(2)
Gd2-O17	2.333(2)	Gd2-O27	2.356(2)
Gd3-N7	2.658(3)	Gd3-N9	2.521(3)
Gd3-O4	2.465(2)	Gd3-O5	2.288(2)
Gd3-O6	2.376(2)	Gd3-O25	2.442(2)
Gd3-O26	2.542(2)	Gd3-O27	2.410(2)
Gd3-O32	2.477(3)	Gd3-O32W	2.477(3)
Gd4-N11	2.631(3)	Gd4-N13	2.480(3)
Gd4-O3W	2.421(2)	Gd4-O6	2.422(2)
Gd4-O7	2.252(2)	Gd4-O8	2.388(2)
Gd4-O24	2.333(2)	Gd4-O26	2.330(2)
Gd5-N15	2.672(3)	Gd5-N17	2.540(3)
Gd5-O8	2.475(2)	Gd5-O9	2.313(2)
Gd5-O10	2.433(2)	Gd5-O22	2.397(2)
Gd5-O23	2.581(2)	Gd5-O24	2.387(2)
Gd5-O31	2.421(3)	Gd6-N19	2.616(3)
Gd6-N21	2.532(3)	Gd6-O2W	2.422(2)
Gd6-O10	2.439(2)	Gd6-O11	2.218(2)
Gd6-O12	2.396(2)	Gd6-O21	2.375(2)
Gd6-O23	2.348(2)	Gd7-N23	2.610(3)
Gd7-N25	2.521(3)	Gd7-O12	2.471(2)
Gd7-O13	2.307(2)	Gd7-O14	2.390(2)
Gd7-O19	2.418(2)	Gd7-O20	2.499(2)
Gd7-O21	2.399(2)	Gd7-O30	2.545(2)
Gd8-N27	2.666(3)	Gd8-N29	2.479(3)
Gd8-O4W	2.424(2)	Gd8-O14	2.401(2)
Gd8-O15	2.235(2)	Gd8-O16	2.364(2)
Gd8-O18	2.342(2)	Gd8-O20	2.327(2)
bond angles (°)			
O2-Gd1-N1	62.86(8)	O2-Gd1-O28	71.91(8)
O46-Gd1-N1	72.65(9)	N1-Gd1-N31	71.36(9)
N5-Gd2-N3	75.99(9)	O3-Gd2-O2	86.12(9)
O4-Gd2-N3	81.05(8)	O4-Gd2-N5	65.56(8)
N9-Gd3-N7	71.69(9)	O4-Gd3-N7	62.18(7)
O5-Gd3-N7	75.57(8)	O5-Gd3-O4	73.69(7)
O7-Gd4-O6	83.18(8)	N13-Gd4-N11	80.26(9)
O6-Gd4-N11	62.58(8)	O7-Gd4-O6	83.18(8)
N17-Gd5-N15	72.61(9)	O9-Gd5-O8	72.35(8)
O9-Gd5-O22	72.26(8)	O10-Gd5-N17	63.28(8)
N21-Gd6-N19	78.39(9)	O10-Gd6-N19	62.97(8)
O11-Gd6-N19	85.71(9)	O11-Gd6-O23	86.63(8)
N25-Gd7-N23	71.29(9)	O12-Gd7-O30	79.58(7)
O13-Gd7-O12	72.73(8)	O14-Gd7-O19	75.05(7)
N29-Gd8-N27	75.69(9)	O14-Gd8-N27	62.87(8)
O15-Gd8-O14	87.18(8)	O18-Gd8-O16	66.29(7)

Gd2-O2-Gd1	112.34(9)	Gd2-O4-Gd3	110.86(8)
Gd3-O6-Gd4	111.56(8)	Gd4-O8-Gd5	110.70(9)
Gd5-O10-Gd6	113.31(8)	Gd6-O12-Gd7	111.92(8)
Gd7-O14-Gd8	110.76(9)	Gd8-O16-Gd1	111.57(8)
Gd2-O17-Gd1	106.88(8)	Gd8-O18-Gd1	115.23(9)
Gd8-O20-Gd7	109.48(9)	Gd6-O21-Gd7	115.30(9)
Gd7-O14-Gd8	110.76(9)	Gd8-O16-Gd1	111.57(8)
Gd2-O17-Gd1	106.88(8)	Gd8-O18-Gd1	115.23(9)
Gd8-O20-Gd7	109.48(9)	Gd6-O21-Gd7	115.30(9)
Gd6-O23-Gd5	111.25(8)	Gd4-O24-Gd5	115.91(9)
Gd4-O26-Gd3	108.98(8)	Gd2-O27-Gd3	112.71(9)

Table S4. Selected bond lengths (Å) and angles (°) for **4**.

bond lengths (Å)			
Gd1-N1	2.510(6)	Gd1-N7	2.530(5)
Gd1-O1	2.215(5)	Gd1-O2	2.366(4)
Gd1-O4	2.531(4)	Gd1-O11	2.316(4)
Gd1-O16	2.422(5)	Gd1-O17	2.360(5)
Gd2-N3	2.622(5)	Gd2-N9	2.549(5)
Gd2-N15	2.643(5)	Gd2-O2	2.438(4)
Gd2-O4	2.593(4)	Gd2-O5	2.241(4)
Gd2-O6	2.521(4)	Gd2-O8	2.405(4)
Gd2-O14	2.376(4)	Gd3-N11	2.683(6)
Gd3-N13	2.559(6)	Gd3-N19	2.599(5)
Gd3-O6	2.549(4)	Gd3-O7	2.324(5)
Gd3-O8	2.419(4)	Gd3-O10	2.419(4)
Gd3-O14	2.446(4)	Gd3-O15	2.317(4)
Gd4-N17	2.536(6)	Gd4-O9	2.222(5)
Gd4-O10	2.379(4)	Gd4-O12	2.372(5)
Gd4-O15	2.445(4)	Gd4-O18	2.426(5)
Gd4-O19	2.437(5)	Gd4-O20	2.424(5)
Cl1-Gd5	2.7564(19)	Gd5-N5	2.548(5)
Gd5-O3	2.281(4)	Gd5-O4	2.525(4)
Gd5-O6	2.482(4)	Gd5-O11	2.511(4)
Gd5-O14	2.524(4)	Gd5-O15	2.423(4)
bond angles (°)			
N7-Gd1-O4	65.22(16)	O2-Gd1-N1	64.75(17)
O1-Gd1-N1	71.68(19)	O11-Gd1-O4	66.91(14)
O5-Gd2-N9	72.13(16)	O6-Gd2-N9	61.87(15)
O8-Gd2-O6	64.97(14)	O14-Gd2-O6	59.88(14)
O6-Gd3-N11	61.21(15)	O7-Gd3-N13	72.57(18)
O8-Gd3-N13	62.59(17)	O8-Gd3-O14	70.68(14)
O10-Gd4-N17	64.23(16)	O9-Gd4-N17	71.64(19)
O12-Gd4-O10	94.97(15)	O4-Gd5-N5	62.83(15)
O3-Gd5-O12	110.13(16)	O11-Gd5-O4	64.25(13)
O12-Gd5-O11	51.89(14)	O14-Gd5-O4	74.29(13)
Gd1-O2-Gd2	116.71(16)	Gd1-O4-Gd2	105.90(15)
Gd5-O4-Gd1	110.20(15)	Gd5-O4-Gd2	94.34(14)
Gd2-O6-Gd3	97.41(13)	Gd5-O6-Gd2	97.22(14)
Gd5-O6-Gd3	92.99(13)	Gd2-O8-Gd3	104.32(15)
Gd4-O10-Gd3	112.08(16)	Gd1-O11-Gd5	118.37(17)
Gd4-O12-Gd5	112.15(18)	Gd2-O14-Gd3	104.38(16)
Gd2-O14-Gd5	99.97(15)	Gd3-O14-Gd5	94.47(14)
Gd3-O15-Gd4	113.31(17)	Gd3-O15-Gd5	100.66(15)
Gd5-O15-Gd4	111.54(18)		

Table S5. 9-coordinated Dy (III) ion geometry analysis by SHAPE 2.1 software for **1**.

Configuration	ABOXIY Dy2	ABOXIY Dy3	ABOXIY Dy5
Enneagon (D_{9h})	33.088	34.378	34.953
Octagonal pyramid (C_{8v})	21.903	21.837	22.916
Heptagonal bipyramid (D_{7h})	19.209	18.129	17.491
Johnson triangular cupola J3 (C_{3v})	13.894	14.294	14.176
Capped cube J8 (C_{4v})	10.606	9.925	8.713
Spherical-relaxed capped cube (C_{4v})	9.392	8.798	7.350
Capped square antiprism J10 (C_{4v})	2.364	2.070	2.797
Spherical capped square antiprism (C_{4v})	**1.284**	**1.109**	**1.834**
Tricapped trigonal prism J51 (D_{3h})	2.632	3.499	3.261
Spherical tricapped trigonal prism (D_{3h})	2.303	1.909	1.950
Tridiminished icosahedron J63 (C_{3v})	11.531	12.074	10.270
Hula-hoop (C_{2v})	10.326	11.759	8.438
Muffin (C_s)	1.848	1.540	2.467

Table S6. 8-coordinated Dy (III) ion geometry analysis by SHAPE 2.1 software for **1**.

Configuration	ABOXIY Dy1	ABOXIY Dy4
Octagon(D_{8h})	31.272	32.167
Heptagonal pyramid(C_{7v})	23.586	23.784
Cube (O_h)	14.761	13.867
Hexagonal bipyramid(D_{6h})	10.980	10.190
Square antiprism (D_{4d})	2.011	2.299
Triangular dodecahedron (D_{2d})	1.688	2.065
Johnson gyrobifastigium J26 (D_{2d})	12.710	12.861
Johnson elongated triangular bipyramid J14 (D_{3h})	27.858	27.171
Biaugmented trigonal prism J50 (C_{2v})	1.607	1.671
Biaugmented trigonal prism (C_{2v})	**1.118**	**0.975**
Snub diphenoid J84 (D_{2d})	3.715	4.125
Triakis tetrahedron (T_d)	11.541	10.653
Elongated trigonal bipyramid (D_{3h})	24.067	23.616

Table S7. 8-coordinated Dy (III) ion geometry analysis by SHAPE 2.1 software for **2**.

Configuration	ABOXIY Dy1	ABOXIY Dy2	ABOXIY Dy3	ABOXIY Dy4	ABOXIY Dy5	ABOXIY Dy6
Octagon(D_{8h})	31.475	32.237	31.620	31.799	32.086	32.687
Heptagonal pyramid(C_{7v})	22.636	22.021	22.817	22.041	22.129	21.894
Cube (O_h)	16.027	16.256	16.408	15.345	15.756	16.351
Hexagonal bipyramid(D_{6h})	12.487	12.416	13.230	11.247	12.202	13.610
Square antiprism (D_{4d})	4.186	4.031	4.002	4.655	4.269	4.440
Triangular dodecahedron (D_{2d})	**2.897**	2.897	**3.072**	**2.865**	2.858	3.315
Johnson gyrobifastigium J26 (D_{2d})	14.255	13.306	14.640	12.723	13.031	13.715
Johnson elongated triangular bipyramid J14 (D_{3h})	26.665	26.428	26.951	25.170	25.447	25.671
Biaugmented trigonal prism J50 (C_{2v})	3.676	2.901	3.494	3.252	2.884	**2.835**
Biaugmented trigonal prism (C_{2v})	3.325	**2.841**	3.235	3.312	**2.797**	2.877
Snub diphenoid J84 (D_{2d})	5.288	4.779	5.186	4.939	4.807	4.663
Triakis tetrahedron (T_d)	13.280	12.883	13.986	11.708	12.730	13.921
Elongated trigonal bipyramid (D_{3h})	24.024	23.897	24.569	22.471	22.912	23.473

Table S8. 8-coordinated Gd(III) ion geometry analysis by SHAPE 2.1 software for **3**.

Configuration	ABOXIY Gd2	ABOXIY Gd4	ABOXIY Gd6	ABOXIY Gd8
Octagon(D_{8h})	29.670	29.894	28.185	29.554
Heptagonal pyramid(C_{7v})	23.744	23.652	24.178	24.417
Cube (O_h)	14.025	15.325	15.016	14.553
Hexagonal bipyramid(D_{6h})	9.734	11.502	9.825	10.797
Square antiprism (D_{4d})	2.675	2.544	**1.714**	2.202
Triangular dodecahedron (D_{2d})	2.591	**1.909**	1.920	**1.759**
Johnson gyrobifastigium J26 (D_{2d})	12.264	12.633	13.395	12.476
Johnson elongated triangular bipyramid J14 (D_{3h})	26.748	27.998	26.118	28.386
Biaugmented trigonal prism J50 (C_{2v})	2.647	2.758	2.327	3.093
Biaugmented trigonal prism (C_{2v})	**2.306**	2.295	1.754	2.061
Snub diphenoid J84 (D_{2d})	4.238	3.907	4.012	3.510
Triakis tetrahedron (T_d)	10.359	12.103	10.292	11.466
Elongated trigonal bipyramid (D_{3h})	23.276	24.267	23.305	24.223

Table S9. 9-coordinated Gd(III) ion geometry analysis by SHAPE 2.1 software for **3**.

Configuration	ABOXIY Gd1	ABOXIY Gd3	ABOXIY Gd5	ABOXIY Gd7
Enneagon (D_{9h})	29.591	32.030	33.151	32.030
Octagonal pyramid (C_{8v})	22.493	22.661	22.491	22.661
Heptagonal bipyramid (D_{7h})	14.835	16.977	15.623	16.977
Johnson triangular cupola J3 (C_{3v})	14.235	14.855	13.673	14.855
Capped cube J8 (C_{4v})	7.562	8.726	6.946	8.726
Spherical-relaxed capped cube (C_{4v})	6.564	7.706	5.864	7.706
Capped square antiprism J10 (C_{4v})	5.153	4.205	5.550	4.205
Spherical capped square antiprism (C_{4v})	4.206	2.976	4.234	2.976
Tricapped trigonal prism J51 (D_{3h})	5.792	5.563	6.039	5.563
Spherical tricapped trigonal prism (D_{3h})	4.801	3.588	5.210	3.588
Tridiminished icosahedron J63 (C_{3v})	11.496	11.290	10.567	11.290
Hula-hoop (C_{2v})	5.406	6.940	5.677	6.940
Muffin (C_s)	**2.640**	**1.711**	**2.747**	**1.711**

Table S10. 9-coordinated Gd(III) ion geometry analysis by SHAPE 2.1 software for **4**.

Configuration	ABOXIY Gd2	ABOXIY Gd3	ABOXIY Gd5
Enneagon (D_{9h})	33.595	34.341	33.579
Octagonal pyramid (C_{8v})	22.435	21.205	24.308
Heptagonal bipyramid (D_{7h})	18.998	18.338	16.240
Johnson triangular cupola J3 (C_{3v})	13.731	14.261	14.338
Capped cube J8 (C_{4v})	10.643	10.290	8.763
Spherical-relaxed capped cube (C_{4v})	9.435	9.057	7.001
Capped square antiprism J10 (C_{4v})	2.498	2.301	4.171
Spherical capped square antiprism (C_{4v})	**1.344**	**1.241**	3.425
Tricapped trigonal prism J51 (D_{3h})	2.820	3.789	4.816
Spherical tricapped trigonal prism (D_{3h})	2.189	1.657	3.752
Tridiminished icosahedron J63 (C_{3v})	11.989	11.651	11.097
Hula-hoop (C_{2v})	10.227	11.485	5.676
Muffin (C_s)	1.623	1.546	**3.112**

Table S11. 8-coordinated Gd(III) ion geometry analysis by SHAPE 2.1 software for **4**.

Configuration	ABOXIY Gd1	ABOXIY Gd4
Octagon(D_{8h})	31.759	33.619
Heptagonal pyramid(C_{7v})	22.934	23.092
Cube (O_h)	13.147	13.808
Hexagonal bipyramid(D_{6h})	10.425	10.972
Square antiprism (D_{4d})	2.401	3.145
Triangular dodecahedron (D_{2d})	1.922	2.438
Johnson gyrobifastigium J26 (D_{2d})	11.354	12.651
Johnson elongated triangular bipyramid J14 (D_{3h})	26.488	26.738
Biaugmented trigonal prism J50 (C_{2v})	2.076	1.847
Biaugmented trigonal prism (C_{2v})	**1.735**	**1.252**
Snub diphenoid J84 (D_{2d})	3.834	4.237
Triakis tetrahedron (T_d)	10.928	11.365
Elongated trigonal bipyramid (D_{3h})	22.526	23.085

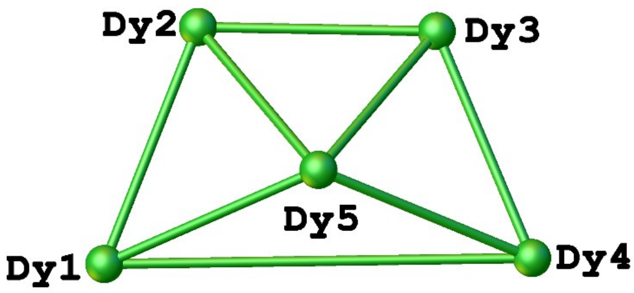

Fig. S3. The unique trapezoidal pyramid metal core in **1**.

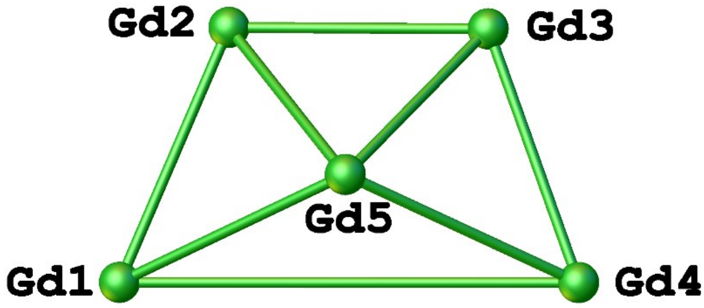

Fig. S4. The unique trapezoidal pyramid metal core in **4**.

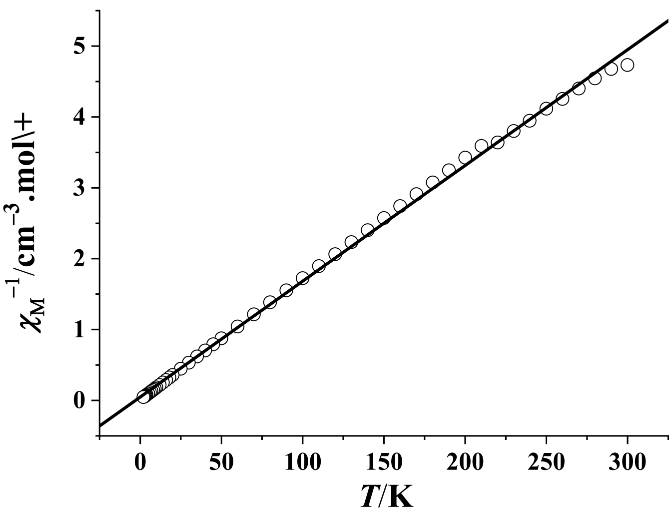

Fig. S5. $1/\chi_M$-T curve of **3**.

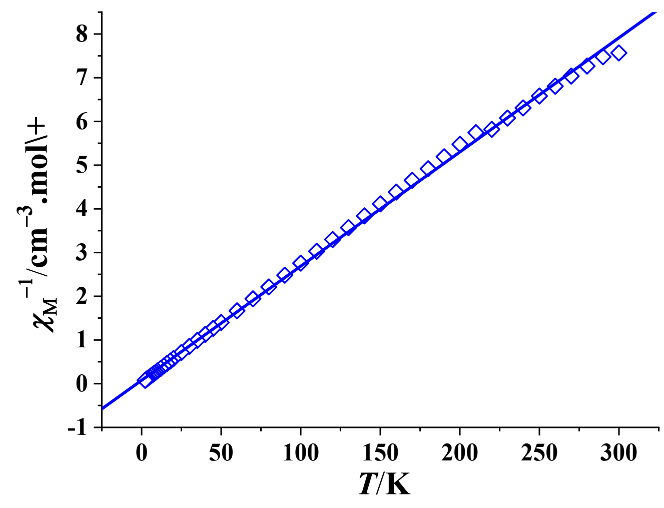

Fig. S6. $1/\chi_M$-T curve of **4**.

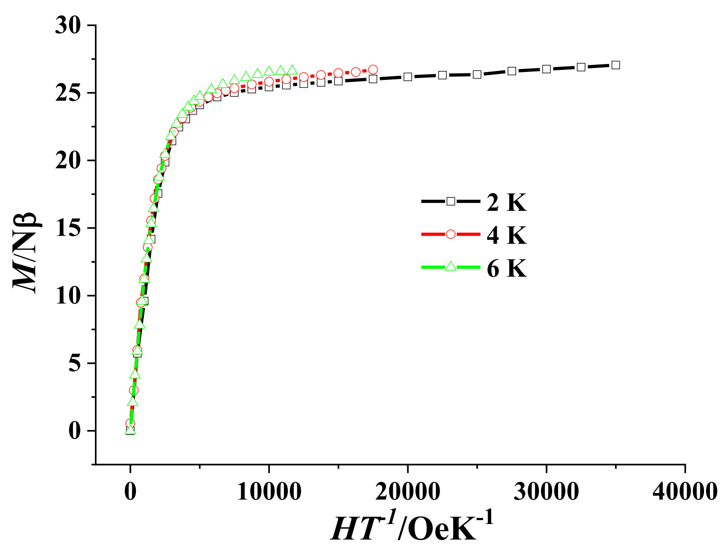

Fig. S7. *M versus H/T* plots at 2 K, 4 K and 6 K of **1**.

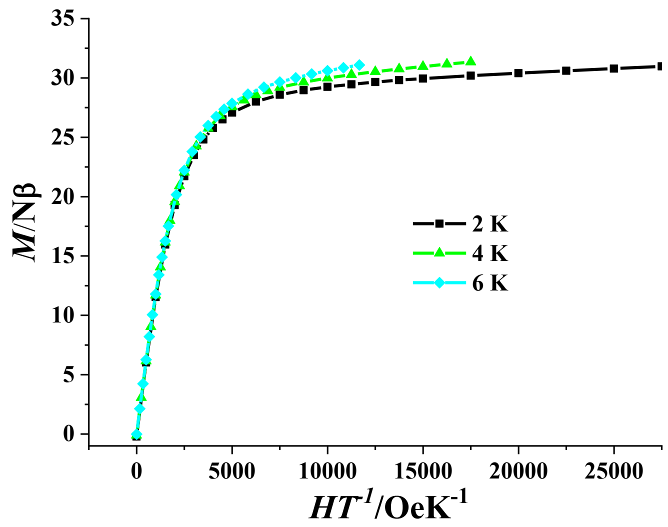

Fig. S8. *M versus H/T* plots at 2 K, 4 K and 6 K of **2**.

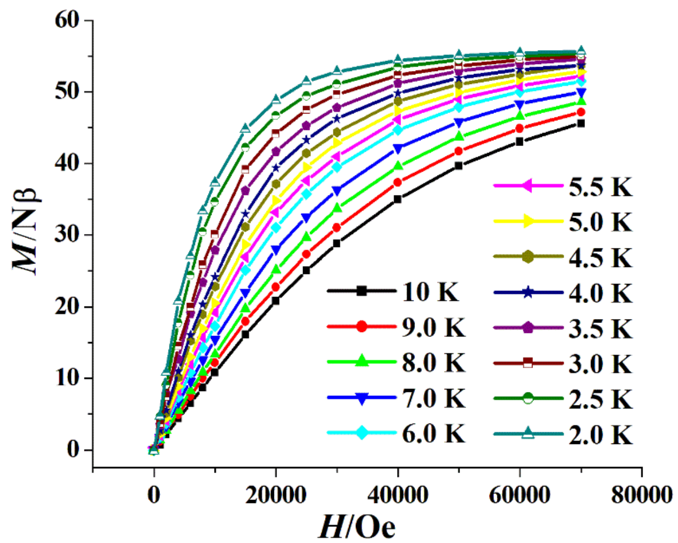

Fig. S9. *M versus H* plots at 2-10 K of **3**.

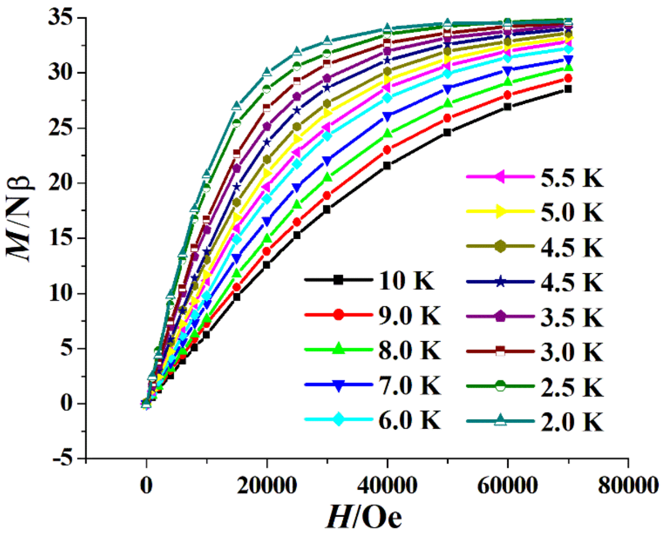

Fig. S10. *M versus H* plots at 2-10 K of **4**.

Table S12. The $-\Delta S_m$ maximum value for some Gd_n clusters (n ≥4) on ΔH at a given temperature.

cluster	$-\Delta S_m^{max}$ (J kg^{-1} K^{-1})	ΔH(T)	T (K)	reference
$[Gd_4(H_3L)_2(OAc)_3(F_6acac)_3]$	21.88	5	2.0	36
$[Gd_4(LH_2)_2(Piv)_4(\mu_3\text{-}O_2)_2(H_2O)_2]\cdot 2MeOH$	33.60	13	4	37
$[Gd_4(HL)_4(OAc)_2(H2O)_2]\cdot 2Et_3NH\cdot$solvents	20.8	7	2.0	38
$[Gd_4(\mu_4\text{-}O)L_2(PhCOO)_6]\cdot$solvent	22.88	7	3.0	66
$[Gd_5L_4(HL)(CO_3)O(OH)(EtOH)_5(H_2O)_2Cl]\cdot$solvents	27.58	7	2.5	this work
$[H_3O][Gd_6(PO_4)(AnPO_3)_8(DMF)_6]\cdot$solvents	25.92	7	2.5	67
$[Gd_7L_6(CH_3O)_8(OH)_4(NO_3)_2]NO_3\cdot$solvents	17.4	5	3.0	68
$[Gd_7(OH)_6(thmeH_2)_5(thmeH)(tpa)_6(MeCN)_2](NO_3)_2$	23.0	7	3.0	69
$[Gd_8L_8(CO_3)_4(MeOH)_4(H_2O)_4]\cdot$solvents	27.52	7	2.0	this work
$[Gd_8(\mu_3\text{–}OH)_4(CO_3)_2L_4(PhCOO)_8]\cdot$solvent	28.38	7	2.0	66
$[Gd_8(acac)_4(HL)_4(L)_2(\mu_3\text{-}O)_4(C_2H_5O)_4]\cdot$solvents	33.06	7	2.0	70
$[Gd_8(IN)_{14}(\mu_3\text{-}OH)_8(\mu_2\text{-}OH)_2(H_2O)_8]\cdot$solvents	31.77	7	2.0	71
$\{Gd_9L_4(OH)_{10}(OCH_3)_4(NO_3)_8(H_2O)_8\}(OH)\cdot 2H_2O$	40.60	7	2.0	72
$[Gd_9(acac)_{16}(\mu_3\text{-}OH)_8(\mu_4\text{-}OH)_2]OH\cdot 6H_2O$	20.98	9	2.0	73
$[Gd_{10}(3\text{-}TCA)_{22}(\mu_3\text{-}OH)_8(H_2O)_4]$	31.22	7	2.0	74
$[Gd_{10}(LH)_{10}(k^2\text{-}Piv)_{10}]\cdot$solvents	26.6	7	2.2	75
$[Gd_{12}(H_2L1)_4O_4(OH)_4(AcO)_{15}]\cdot(AcO)\cdot(CH_3OH)_6$	35.63	7	2.0	76
$[Gd_{14}(H_{0.5}L)_8O_3(OH)_{16}(NO_3)_{16}]\cdot$solvents	22.3	5	2.0	68
$Gd_{16}L_3(OH)_{18}(NO_3)_{12}(H_2O)_6$	34.05	7	2.0	77
$[Gd_{24}(DMC)_{36}(\mu_4\text{-}CO_3)_{18}(\mu_3\text{-}H_2O)_2]\cdot nH_2O$	46.12	7	2.5	25
$[(ClO_4)@Gd_{27}(\mu_3\text{-}OH)_{32}(CO_3)_8(CH_3CH_2COO)_{20}(H_2O)_{40}]\cdot(ClO_4)_{12}\cdot(H_2O)_{50}$	41.8	7	2.0	78
$[Gd_{28}(IN)_{25}(C_2O_4)_6(HCOO)(\mu_3\text{-}OH)_{36}(\mu_2\text{-}OH)_2(H_2O)_{36}]\cdot 8Br\cdot xH_2O$	37.5	7	2.0	79
$[Gd_{38}(\mu\text{-}O)(\mu_8\text{-}ClO_4)_6(\mu_3\text{-}OH)_{42}(CAA)_{37}(H_2O)_{36}(EtOH)_6](ClO_4)_{10}(OH)_{17}\cdot$solvents	37.9	7	1.8	80
$[Gd_{48}(\mu_4\text{-}O)_6(\mu_3\text{-}OH)_{84}(CAA)_{36}(NO_3)_6(H_2O)_{24}(EtOH)_{12}(NO_3)Cl_2]Cl_3\cdot$solvents	43.6	7	1.8	80

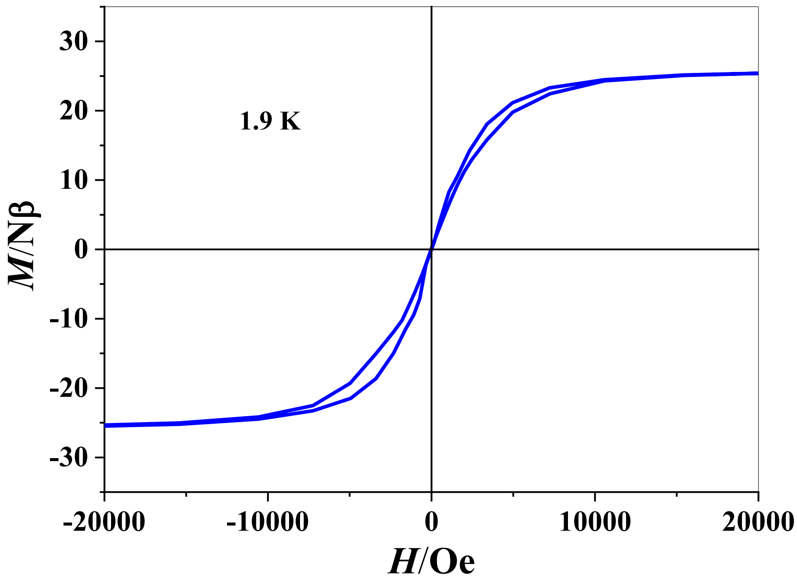

Fig. S11. Hysteresis loop for **1** at 1.9 K with a sweep rate of 100 Oe S^{-1}.

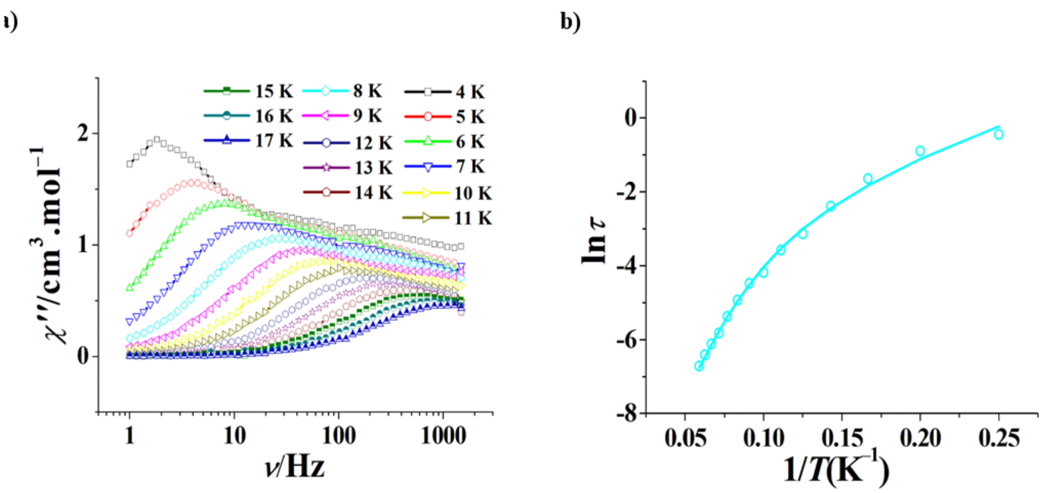

Fig. S12. Plots of χ'' *versus* T for **1** (H_{dc} = 1000 Oe) (a); plot of ln(τ) *versus* 1/T for **1** (H_{dc} = 1000 Oe) (b), the solid line represents the best fitting with Orbach *plus* Raman.

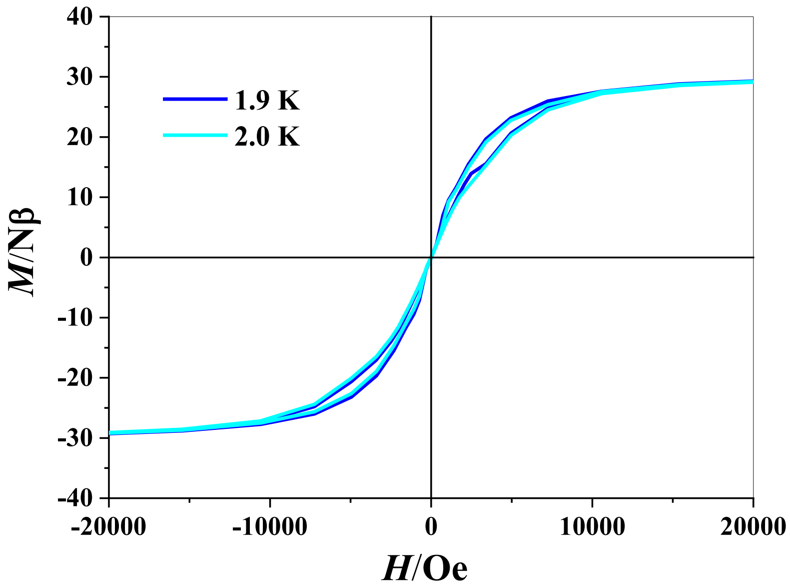

Fig. S13. Hysteresis loop for **2** at 1.9 K and 2.0 K with a sweep rate of 100 Oe S^{-1}.

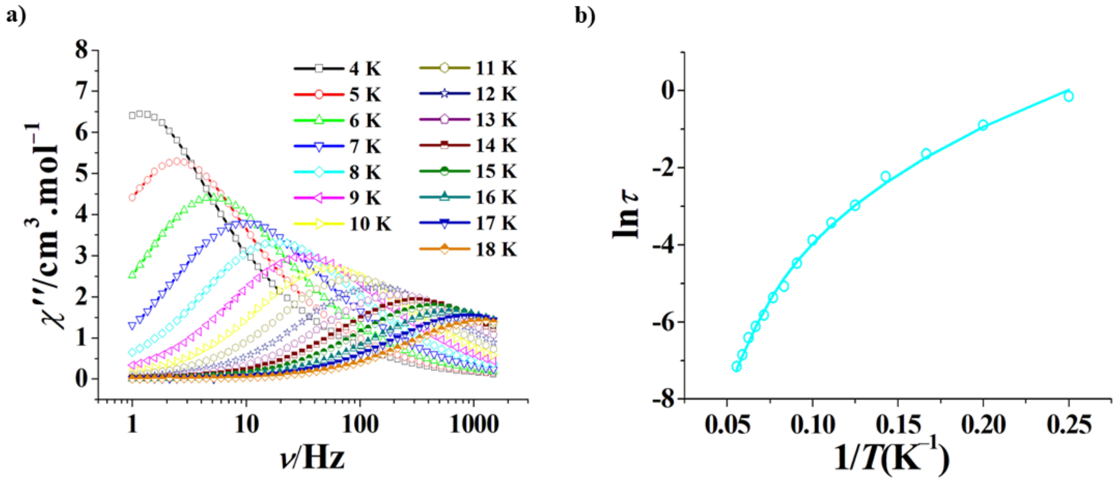

Fig. S14. Plots of χ'' *versus* T for **2** (H_{dc} = 1000 Oe) (a); plot of ln(τ) *versus* 1/T for **2** (H_{dc} = 1000 Oe) (b), the solid line represents the best fitting with Orbach *plus* Raman.