Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Octahedral lanthanide clusters containing a central PO_4^{3-} anion: structures, luminescent, magnetic and relaxometric properties

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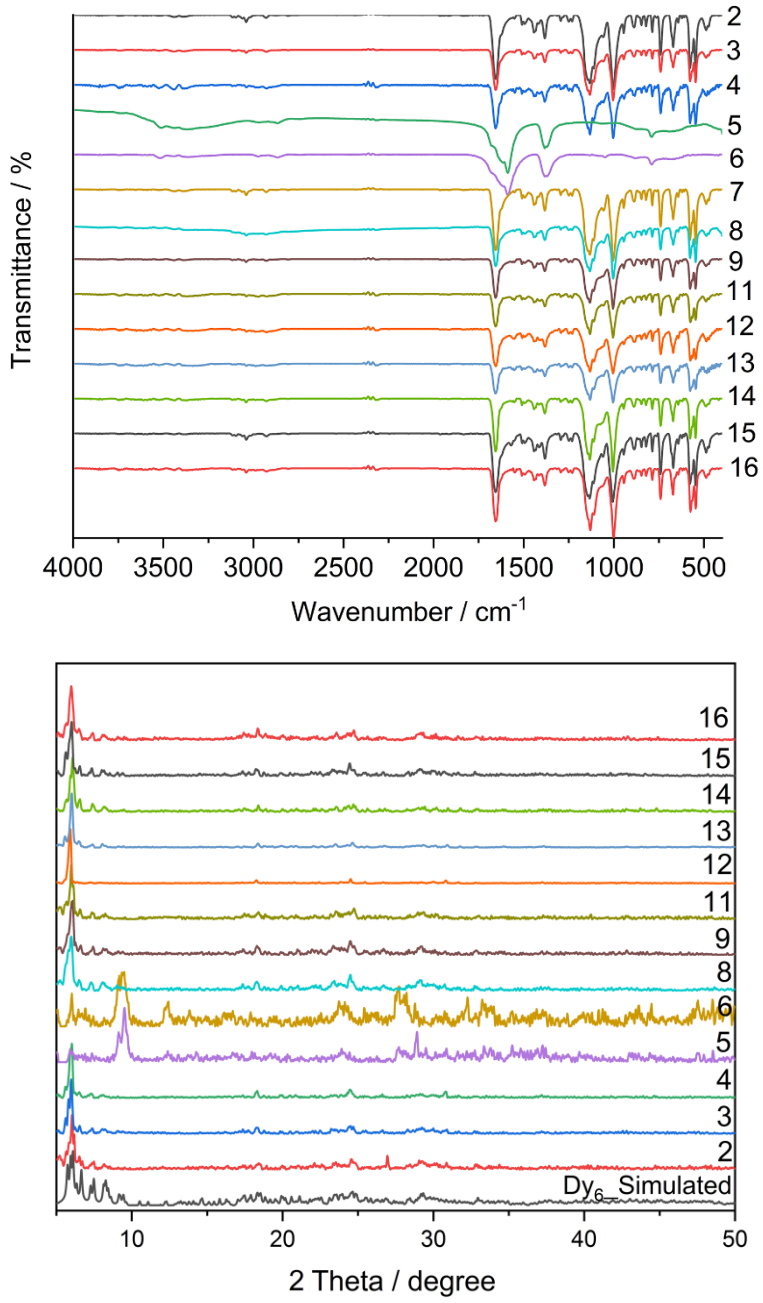


Fig. S1 IR spectra and PXRD patterns of solid products obtained under different experimental conditions given in Table S1.

Table S1 Products and productivities (based on $Dy(NO_3)_3 \cdot 6H_2O$) under different conditions.

Condition	$Dy(NO_3)_3 \cdot 6H_2O$ (mmol)	$AnPO_3H_2$ (mmol)	DMF/H_2O (mL/mL)	Time (h)	Temperature (°C)	Na_3PO_4 (mmol)	Product	Yield (mg, %)
1	0.1	0.2	3/0	24	120	/	/	/
2	0.1	0.2	3/0.5	24	120	/	**Dy_6**	49.3, 79.1
3	0.1	0.2	3/1	24	120	/	**Dy_6**	50.2, 80.5
4	0.1	0.2	3/1.5	24	120	/	**Dy_6**	45.4, 72.8
5	0.3	0.1	3/1	24	120	/	White Powder	/
6	0.2	0.1	3/1	24	120	/	White Powder	/
7	0.1	0.1	3/1	24	120	/	**Dy_6**	<1, <1.6%
8	0.1	0.3	3/1	24	120	/	**Dy_6**	45.6, 73.1
9	0.1	0.2	3/1	48	120	/	**Dy_6**	48.9, 78.4
10	0.1	0.2	3/1	6	120	/	/	/
11	0.1	0.2	3/1	12	120	/	**Dy_6**	32.5, 52.1
12	0.1	0.2	3/1	24	100	/	**Dy_6**	12, 19.2
13	0.1	0.2	3/1	24	110	/	**Dy_6**	30.9, 49.5
14	0.1	0.2	3/1	24	130	/	**Dy_6**	47.3, 75.9
15	0.1	0.2	3/1	24	140	/	**Dy_6**	48.1, 77.1
16	0.1	0.2	3/1	24	120	0.013	**Dy_6**	53.7, 86.1
17	0.1	0.2	4/0	24	120	0.013	/	/

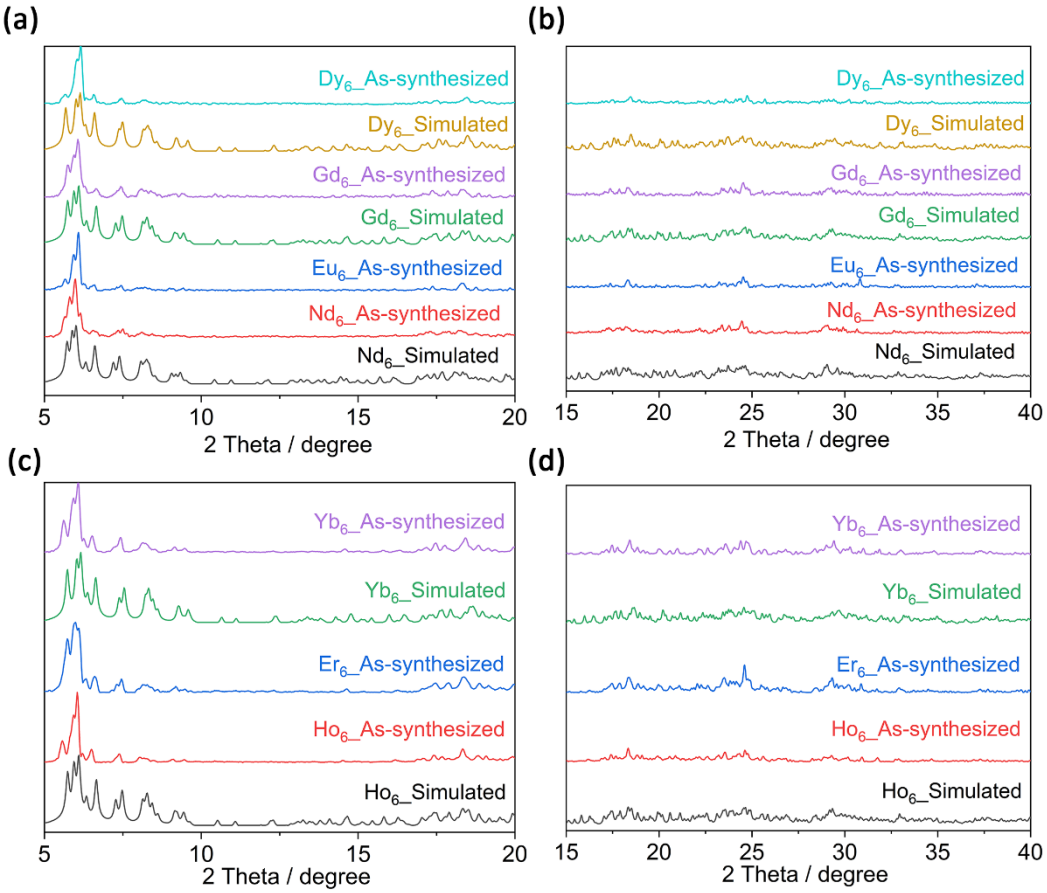


Fig. S2 Simulated and experimental PXRD patterns of **Ln_6**.

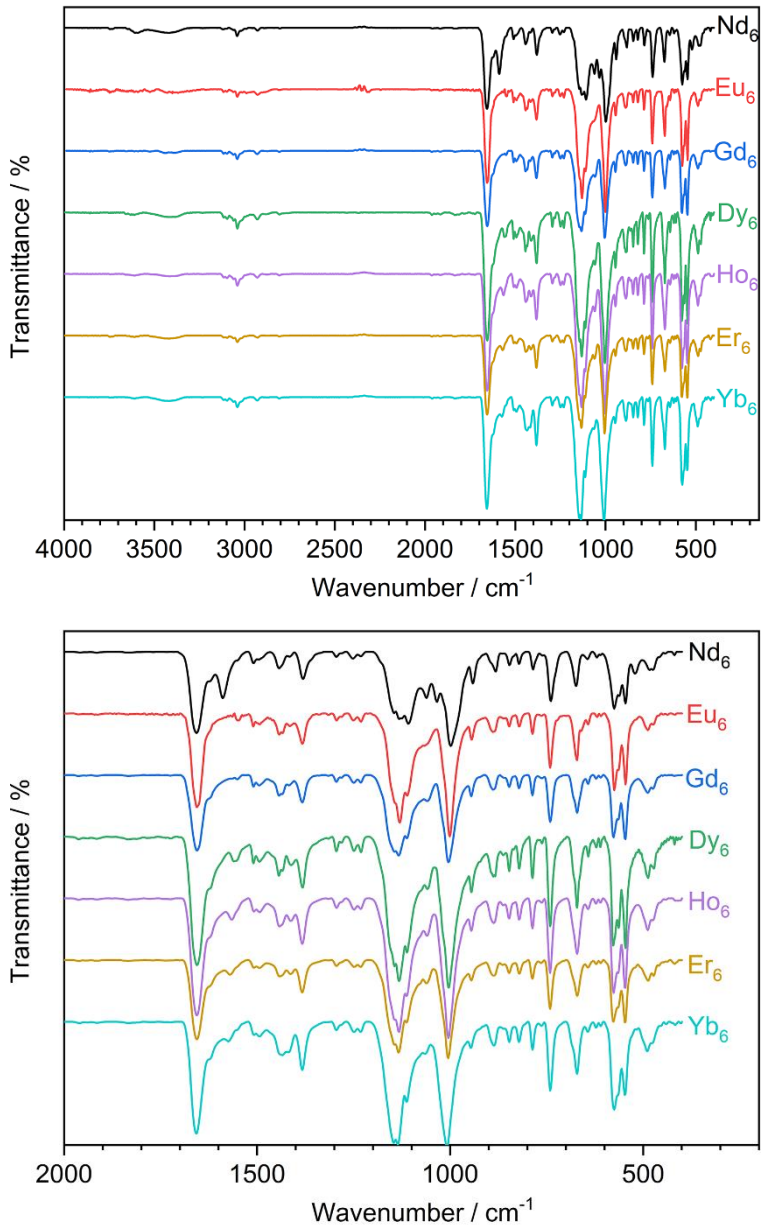


Fig. S3 The IR spectra of **Ln_6** in the range of 400 – 4000 cm^{-1} and 400 – 2000 cm^{-1}.

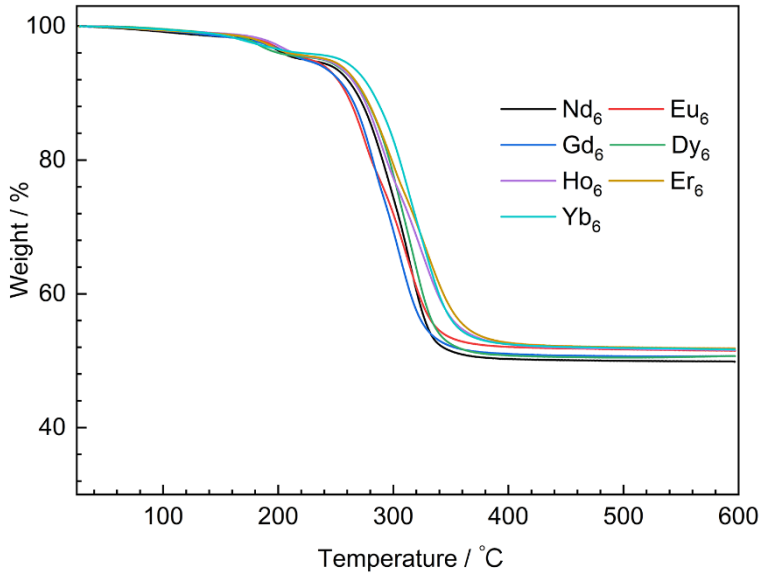


Fig. S4 TG curves of **Ln_6** at 30-600°C with a heating rate of 5°C/min.

Table S2 Calculated and experimental weight loss of **Ln_6**.

	Nd_6	**Eu_6**	**Gd_6**	**Dy_6**	**Ho_6**	**Er_6**	**Yb_6**
Temperature range/°C	30-130	30-132	30-134	30-136	30-136	30-137	30-137
Calculated weight loss (-2H_2O)/%	1.0	1.0	1.0	1.0	1.0	1.0	0.9
Experimental weight loss (-2H_2O)/%	1.3	1.0	1.0	0.9	1.2	1.0	1.0
Temperature range/°C	130-220	132-221	134-220	136-209	136-215	137-221	137-226
Calculated weight loss (-2DMF)/%	4.0	4.0	4.0	3.9	3.9	3.9	3.8
Experimental weight loss (-2DMF)/%	3.7	4.0	4.0	3.8	3.9	3.2	3.2

Table S3 Selected bond lengths (Å) and angles (°) for **Nd_6** at 193 K.

Nd1-O1	2.327(4)	O1-Nd1-O28	113.89(14)	O17-Nd4-O20	170.94(18)
Nd1-O4	2.348(5)	O4-Nd1-O28	115.10(15)	O14-Nd4-O20	88.35(16)
Nd1-O22	2.372(4)	O22-Nd1-O28	74.38(14)	O17-Nd4-O23	91.40(19)
Nd1-O19	2.393(5)	O19-Nd1-O28	79.19(15)	O14-Nd4-O23	177.18(16)
Nd1-O29	2.465(5)	O29-Nd1-O28	143.81(17)	O20-Nd4-O23	91.87(18)
Nd1-O28	2.532(4)	O1-Nd1-O25	74.77(14)	O17-Nd4-O32	94.7(4)
Nd1-O25	2.579(4)	O4-Nd1-O25	77.10(15)	O14-Nd4-O32	96.8(3)
Nd2-O7	2.307(5)	O22-Nd1-O25	112.36(15)	O20-Nd4-O32	94.0(3)
Nd2-O2	2.336(4)	O19-Nd1-O25	119.81(15)	O23-Nd4-O32	86.0(3)
Nd2-O10	2.351(5)	O29-Nd1-O25	157.66(16)	O17-Nd4-O28	92.49(16)
Nd2-O5	2.362(4)	O28-Nd1-O25	57.05(13)	O14-Nd4-O28	99.48(14)
Nd2-O30	2.394(8)	O7-Nd2-O2	93.33(18)	O20-Nd4-O28	79.96(15)
Nd2-O25	2.444(4)	O7-Nd2-O10	85.50(18)	O23-Nd4-O28	77.80(15)
Nd3-O13	2.321(4)	O2-Nd2-O10	175.52(16)	O32-Nd4-O28	162.4(3)
Nd3-O11	2.338(4)	O7-Nd2-O5	163.89(18)	O15-Nd5-O21	91.39(18)
Nd3-O8	2.358(5)	O2-Nd2-O5	94.60(17)	O15-Nd5-O3	171.87(15)
Nd3-O16	2.402(5)	O10-Nd2-O5	85.51(17)	O21-Nd5-O3	84.78(17)
Nd3-O31	2.477(5)	O7-Nd2-O30	76.7(4)	O15-Nd5-O9	93.75(18)
Nd3-O27	2.537(4)	O2-Nd2-O30	92.4(4)	O21-Nd5-O9	160.50(16)
Nd3-O26	2.582(4)	O10-Nd2-O30	91.5(4)	O3-Nd5-O9	87.62(17)
Nd4-O17	2.293(5)	O5-Nd2-O30	116.9(4)	O15-Nd5-O33	92.15(18)
Nd4-O14	2.312(4)	O7-Nd2-O25	90.28(16)	O21-Nd5-O33	81.5(2)
Nd4-O20	2.341(5)	O2-Nd2-O25	77.57(15)	O3-Nd5-O33	94.36(18)
Nd4-O23	2.369(5)	O10-Nd2-O25	98.09(14)	O9-Nd5-O33	117.08(19)
Nd4-O32	2.383(7)	O5-Nd2-O25	77.80(15)	O15-Nd5-O26	76.16(14)
Nd4-O28	2.414(4)	O30-Nd2-O25	163.2(3)	O21-Nd5-O26	85.60(15)
Nd5-O15	2.319(5)	O13-Nd3-O11	171.17(16)	O3-Nd5-O26	96.36(14)
Nd5-O21	2.326(5)	O13-Nd3-O8	90.44(17)	O9-Nd5-O26	77.42(15)
Nd5-O3	2.333(4)	O11-Nd3-O8	85.34(17)	O33-Nd5-O26	162.35(17)
Nd5-O9	2.362(5)	O13-Nd3-O16	90.82(18)	O6-Nd6-O24	88.16(17)
Nd5-O33	2.415(5)	O11-Nd3-O16	90.95(18)	O6-Nd6-O12	92.17(18)
Nd5-O26	2.481(4)	O8-Nd3-O16	162.81(18)	O24-Nd6-O12	178.62(15)
Nd6-O6	2.301(5)	O13-Nd3-O31	93.32(16)	O6-Nd6-O18	174.42(16)
Nd6-O24	2.342(4)	O11-Nd3-O31	78.52(16)	O24-Nd6-O18	87.02(16)
Nd6-O12	2.353(4)	O8-Nd3-O31	83.53(18)	O12-Nd6-O18	92.57(17)
Nd6-O18	2.357(4)	O16-Nd3-O31	79.28(17)	O6-Nd6-O34	92.08(17)
Nd6-O34	2.374(4)	O13-Nd3-O27	114.29(15)	O24-Nd6-O34	96.18(17)
Nd6-O27	2.415(4)	O11-Nd3-O27	74.53(14)	O12-Nd6-O34	85.15(16)
O1-Nd1-O4	91.89(18)	O8-Nd3-O27	117.85(15)	O18-Nd6-O34	91.25(16)
O1-Nd1-O22	171.58(16)	O16-Nd3-O27	76.99(14)	O6-Nd6-O27	95.83(15)
O4-Nd1-O22	85.60(18)	O31-Nd3-O27	143.46(15)	O24-Nd6-O27	101.60(15)
O1-Nd1-O19	90.44(17)	O13-Nd3-O26	75.15(14)	O12-Nd6-O27	77.03(13)
O4-Nd1-O19	162.88(17)	O11-Nd3-O26	111.53(14)	O18-Nd6-O27	82.39(14)

O22-Nd1-O19	89.65(17)	O8-Nd3-O26	79.20(16)	O34-Nd6-O27	160.73(16)
O1-Nd1-O29	95.06(17)	O16-Nd3-O26	117.64(16)	Nd1-O28-Nd4	136.36(15)
O4-Nd1-O29	83.53(18)	O31-Nd3-O26	159.05(15)	Nd1-O25-Nd2	135.84(13)
O22-Nd1-O29	76.68(17)	O27-Nd3-O26	56.93(12)	Nd6-O26-Nd5	135.50(16)
O19-Nd1-O29	79.36(18)	O17-Nd4-O14	87.98(17)	Nd6-O27-Nd3	136.28(15)

Table S4 Selected bond lengths (Å) and angles (°) for **Gd_6** at 193 K

Gd1-O1	2.278(5)	O1-Gd1-O28	114.12(16)	O17-Gd4-O20	171.6(2)
Gd1-O4	2.291(5)	O4-Gd1-O28	116.30(17)	O14-Gd4-O20	87.88(19)
Gd1-O22	2.300(5)	O22-Gd1-O28	74.43(17)	O17-Gd4-O23	90.5(2)
Gd1-O19	2.343(5)	O19-Gd1-O28	78.35(17)	O14-Gd4-O23	177.4(2)
Gd1-O29	2.372(5)	O29-Gd1-O28	144.14(19)	O20-Gd4-O23	93.3(2)
Gd1-O28	2.471(4)	O1-Gd1-O25	75.49(16)	O17-Gd4-O32	96.1(5)
Gd1-O25	2.512(5)	O4-Gd1-O25	76.75(18)	O14-Gd4-O32	99.7(5)
Gd2-O7	2.248(5)	O22-Gd1-O25	111.81(17)	O20-Gd4-O32	91.8(5)
Gd2-O2	2.259(5)	O19-Gd1-O25	119.92(17)	O23-Gd4-O32	82.6(5)
Gd2-O5	2.288(5)	O29-Gd1-O25	156.85(18)	O17-Gd4-O28	93.00(18)
Gd2-O10	2.292(5)	O28-Gd1-O25	58.10(14)	O14-Gd4-O28	99.86(16)
Gd2-O30	2.337(8)	O7-Gd2-O2	92.5(2)	O20-Gd4-O28	80.50(16)
Gd2-O25	2.392(4)	O7-Gd2-O5	166.11(18)	O23-Gd4-O28	78.05(17)
Gd3-O13	2.274(5)	O2-Gd2-O5	94.28(19)	O32-Gd4-O28	158.7(5)
Gd3-O11	2.280(5)	O7-Gd2-O10	86.59(19)	O21-Gd5-O15	91.62(19)
Gd3-O8	2.298(5)	O2-Gd2-O10	176.86(17)	O21-Gd5-O3	86.02(18)
Gd3-O16	2.330(5)	O5-Gd2-O10	86.01(19)	O15-Gd5-O3	174.47(17)
Gd3-O31	2.389(5)	O7-Gd2-O30	79.1(4)	O21-Gd5-O9	164.70(18)
Gd3-O27	2.488(4)	O2-Gd2-O30	90.5(4)	O15-Gd5-O9	93.15(19)
Gd3-O26	2.508(5)	O5-Gd2-O30	112.9(4)	O3-Gd5-O9	87.90(18)
Gd4-O17	2.235(5)	O10-Gd2-O30	92.3(4)	O21-Gd5-O33	84.7(2)
Gd4-O14	2.257(5)	O7-Gd2-O25	90.57(17)	O15-Gd5-O33	90.0(2)
Gd4-O20	2.279(5)	O2-Gd2-O25	78.70(16)	O3-Gd5-O33	94.71(19)
Gd4-O23	2.288(5)	O5-Gd2-O25	78.90(17)	O9-Gd5-O33	109.8(2)
Gd4-O32	2.327(8)	O10-Gd2-O25	98.30(16)	O21-Gd5-O26	88.69(17)
Gd4-O28	2.367(4)	O30-Gd2-O25	164.8(4)	O15-Gd5-O26	77.08(16)
Gd5-O21	2.249(5)	O13-Gd3-O11	170.37(18)	O3-Gd5-O26	97.84(15)
Gd5-O15	2.251(5)	O13-Gd3-O8	91.09(19)	O9-Gd5-O26	78.25(17)
Gd5-O3	2.278(4)	O11-Gd3-O8	84.80(19)	O33-Gd5-O26	165.39(18)
Gd5-O9	2.283(5)	O13-Gd3-O16	90.19(19)	O6-Gd6-O24	88.7(2)
Gd5-O33	2.330(6)	O11-Gd3-O16	91.26(19)	O6-Gd6-O12	90.9(2)
Gd5-O26	2.397(4)	O8-Gd3-O16	163.15(19)	O24-Gd6-O12	178.05(18)
Gd6-O6	2.262(5)	O13-Gd3-O31	91.46(18)	O6-Gd6-O18	173.8(2)
Gd6-O24	2.265(5)	O11-Gd3-O31	79.48(18)	O24-Gd6-O18	86.38(19)
Gd6-O12	2.289(5)	O8-Gd3-O31	84.15(19)	O12-Gd6-O18	93.93(18)
Gd6-O18	2.291(4)	O16-Gd3-O31	79.02(19)	O6-Gd6-O34	92.58(19)

Gd6-O34	2.293(5)	O13-Gd3-O27	114.86(17)	O24-Gd6-O34	96.4(2)
Gd6-O27	2.355(4)	O11-Gd3-O27	74.71(17)	O12-Gd6-O34	85.50(19)
O1-Gd1-O4	92.1(2)	O8-Gd3-O27	117.81(16)	O18-Gd6-O34	91.66(18)
O1-Gd1-O22	171.27(18)	O16-Gd3-O27	76.57(16)	O6-Gd6-O27	95.48(17)
O4-Gd1-O22	85.2(2)	O31-Gd3-O27	143.75(17)	O24-Gd6-O27	100.05(18)
O1-Gd1-O19	89.16(19)	O13-Gd3-O26	75.73(16)	O12-Gd6-O27	78.10(17)
O4-Gd1-O19	163.0(2)	O11-Gd3-O26	111.74(16)	O18-Gd6-O27	81.74(15)
O22-Gd1-O19	91.0(2)	O8-Gd3-O26	77.93(17)	O34-Gd6-O27	161.80(19)
O1-Gd1-O29	93.07(19)	O16-Gd3-O26	118.60(17)	Gd1-O25-Gd2	136.26(20)
O4-Gd1-O29	83.8(2)	O31-Gd3-O26	157.62(17)	Gd1-O28-Gd4	137.19(20)
O22-Gd1-O29	78.4(2)	O27-Gd3-O26	58.27(14)	Gd3-O26-Gd5	136.76(20)
O19-Gd1-O29	79.2(2)	O17-Gd4-O14	88.0(2)	Gd3-O27-Gd6	136.80(21)

Table S5 Selected bond lengths (Å) and angles (°) for **Dy_6** at 193 K

Dy1-O25	2.520(9)	O9-Dy1-O25	73.0(3)	O24-Dy4-O34	112.9(4)
Dy1-O31	2.335(9)	O13-Dy1-O25	110.5(3)	O15-Dy4-O34	92.1(3)
Dy1-O11	2.291(6)	O(23-Dy1-O25	112.6(3)	O21-Dy4-O34	96.1(3)
Dy1-O23	2.261(7)	O11-Dy1-O25	79.2(3)	O18-Dy4-O26	86.3(3)
Dy1-O13	2.233(6)	O31-Dy1-O25	146.9(3)	O24-Dy4-O26	73.7(3)
Dy1-O9	2.224(6)	O9-Dy1-O26	108.7(3)	O15-Dy4-O26	75.9(3)
Dy1-O26	2.595(10)	O13-Dy1-O26	73.2(3)	O21-Dy4-O26	95.9(3)
Dy2-O25	2.548(10)	O23-Dy1-O26	75.2(3)	O34-Dy4-O26	166.6(4)
Dy2-O7	2.231(6)	O11-Dy1-O26	116.8(3)	O12-Dy5-O1	92.1(3)
Dy2-O2	2.223(6)	O31-Dy1-O26	158.2(3)	O12-Dy5-O14	87.5(3)
Dy2-O10	2.205(6)	O25-Dy1-O26	53.9(3)	O1-Dy5-O14	177.1(2)
Dy2-O29	2.161(19)	O29-Dy2-O6	89.3(7)	O12-Dy5-O17	172.7(2)
Dy2-O6	2.186(7)	O29-Dy2-O10	109.8(7)	O1-Dy5-O17	92.7(2)
Dy3-O22	2.212(6)	O6-Dy2-O10	160.9(3)	O14-Dy5-O17	87.5(2)
Dy3-O5	2.278(6)	O29-Dy2-O2	98.0(11)	O12-Dy5-O32	85.9(3)
Dy3-O30	2.274(7)	O6-Dy2-O2	87.8(2)	O1-Dy5-O32	87.0(2)
Dy3-O20	2.252(7)	O10-Dy2-O2	88.0(2)	O14-Dy5-O32	95.8(2)
Dy3-O8	2.243(6)	O29-Dy2-O7	89.0(11)	O17-Dy5-O32	100.0(2)
Dy3-O27	2.324(6)	O6-Dy2-O7	87.8(2)	O12-Dy5-O28	94.2(3)
Dy4-O26	2.539(11)	O10-Dy2-O7	93.9(2)	O1-Dy5-O28	77.9(2)
Dy4-O34	2.262(12)	O2-Dy2-O7	171.7(2)	O14-Dy5-O28	99.3(2)
Dy4-O21	2.231(6)	O29-Dy2-O25	164.5(11)	O17-Dy5-O28	81.3(2)
Dy4-O15	2.220(6)	O6-Dy2-O25	87.1(3)	O32-Dy5-O28	164.9(2)
Dy4-O24	2.211(6)	O10-Dy2-O25	74.9(3)	O3-Dy6-O19	170.5(2)
Dy4-O18	2.194(7)	O2-Dy2-O25	96.9(2)	O3-Dy6-O16	92.2(2)
Dy5-O32	2.318(7)	O7-Dy2-O25	75.9(2)	O19-Dy6-O16	84.7(2)
Dy5-O17	2.254(6)	O22-Dy3-O8	89.1(3)	O3-Dy6-O4	89.1(2)
Dy5-O14	2.232(6)	O22-Dy3-O20	89.9(3)	O19-Dy6-O4	91.3(3)
Dy5-O1	2.220(6)	O8-Dy3-O20	178.1(2)	O16-Dy6-O4	163.6(2)

Dy5-O12	2.188(7)	O22-Dy3-O30	90.5(2)	O3-Dy6-O33	90.0(2)
Dy5-O28	2.337(6)	O8-Dy3-O30	95.4(2)	O19-Dy6-O33	80.7(2)
Dy6-O28	2.479(7)	O20-Dy3-O30	86.3(2)	O16-Dy6-O33	84.9(2)
Dy6-O27	2.494(6)	O22-Dy3-O5	174.3(3)	O4-Dy6-O33	78.7(2)
Dy6-O33	2.354(7)	O8-Dy3-O5	85.7(2)	O3-Dy6-O28	76.6(2)
Dy6-O4	2.299(6)	O20-Dy3-O5	95.2(3)	O19-Dy6-O28	111.5(2)
Dy6-O16	2.279(6)	O30-Dy3-O5	92.4(2)	O16-Dy6-O28	78.4(2)
Dy6-O19	2.239(6)	O22-Dy3-O27	96.1(2)	O4-Dy6-O28	117.7(2)
Dy6-O3	2.228(6)	O8-Dy3-O27	100.3(2)	O33-Dy6-O28	158.1(2)
O9-Dy1-O13	176.3(2)	O20-Dy3-O27	78.2(2)	O3-Dy6-O27	114.2(2)
O9-Dy1-O23	87.5(3)	O30-Dy3-O27	163.0(2)	O19-Dy6-O27	75.1(2)
O13-Dy1-O23	90.0(2)	O5-Dy3-O27	82.3(2)	O16-Dy6-O27	116.6(2)
O9-Dy1-O11	91.8(3)	O18-Dy4-O24	158.8(3)	O4-Dy6-O27	77.5(2)
O13-Dy1-O11	90.0(3)	O18-Dy4-O15	91.2(2)	O33-Dy6-O27	145.4(2)
O23-Dy1-O11	167.3(2)	O24-Dy4-O15	91.0(2)	O28-Dy6-O27	56.4(2)
O9-Dy1-O31	81.2(3)	O18-Dy4-O21	87.9(2)	Dy1-O25-Dy2	133.34(37)
O13-Dy1-O31	96.0(3)	O24-Dy4-O21	86.9(2)	Dy1-O26-Dy4	134.41(41)
O23-Dy1-O31	86.2(3)	O15-Dy4-O21	171.8(2)	Dy6-O27-Dy3	135.55(26)
O11-Dy1-O31	81.2(3)	O18-Dy4-O34	88.1(4)	Dy6-O28-Dy5	135.96(27)

Table S6 Selected bond lengths (Å) and angles (°) for **Ho_6** at 193 K

Ho1-O1	2.228(6)	O1-Ho1-O28	111.2(3)	O32-Ho4-O14	102(3)
Ho1-O22	2.228(6)	O22-Ho1-O28	72.7(3)	O17-Ho4-O14	88.2(2)
Ho1-O4	2.253(7)	O4-Ho1-O28	112.4(3)	O32-Ho4-O23	86(3)
Ho1-O19	2.274(7)	O19-Ho1-O28	79.5(3)	O17-Ho4-O23	87.8(2)
Ho1-O29	2.322(8)	O29-Ho1-O28	147.5(3)	O14-Ho4-O23	172.2(2)
Ho1-O28	2.530(9)	O1-Ho1-O25	74.5(3)	O32-Ho4-O20	101(2)
Ho1-O25	2.570(9)	O22-Ho1-O25	107.8(3)	O17-Ho4-O20	161.1(3)
Ho2-O7	2.193(7)	O4-Ho1-O25	75.8(3)	O14-Ho4-O20	87.8(2)
Ho2-O5	2.215(6)	O19-Ho1-O25	116.5(3)	O23-Ho4-O20	93.8(2)
Ho2-O30	2.223(13)	O29-Ho1-O25	158.2(3)	O32-Ho4-O28	160(3)
Ho2-O2	2.246(6)	O28-Ho1-O25	53.4(3)	O17-Ho4-O28	87.9(3)
Ho2-O10	2.255(6)	O7-Ho2-O5	159.9(3)	O14-Ho4-O28	97.9(2)
Ho2-O25	2.495(10)	O7-Ho2-O30	82.5(9)	O23-Ho4-O28	75.3(2)
Ho3-O13	2.228(6)	O5-Ho2-O30	117.3(9)	O20-Ho4-O28	74.4(3)
Ho3-O11	2.237(6)	O7-Ho2-O2	91.0(2)	O21-Ho5-O15	92.8(3)
Ho3-O8	2.258(6)	O5-Ho2-O2	91.3(2)	O21-Ho5-O9	173.4(3)
Ho3-O16	2.286(6)	O30-Ho2-O2	93.2(9)	O15-Ho5-O9	91.7(3)
Ho3-O31	2.350(7)	O7-Ho2-O10	88.0(2)	O21-Ho5-O3	86.5(3)
Ho3-O27	2.495(6)	O5-Ho2-O10	87.4(2)	O15-Ho5-O3	177.4(2)
Ho3-O26	2.503(6)	O30-Ho2-O10	93.3(9)	O9-Ho5-O3	88.8(2)
Ho4-O32	2.145(16)	O2-Ho2-O10	173.2(2)	O21-Ho5-O33	85.6(3)
Ho4-O17	2.192(7)	O7-Ho2-O25	86.7(2)	O15-Ho5-O33	87.6(3)

Ho4-O14	2.223(6)	O5-Ho2-O25	74.5(3)	O9-Ho5-O33	99.4(2)
Ho4-O23	2.226(7)	O30-Ho2-O25	164.9(9)	O3-Ho5-O33	94.9(2)
Ho4-O20	2.227(6)	O2-Ho2-O25	76.5(3)	O21-Ho5-O26	94.9(2)
Ho4-O28	2.530(10)	O10-Ho2-O25	96.8(3)	O15-Ho5-O26	77.7(2)
Ho5-O21	2.170(6)	O13-Ho3-O11	170.2(2)	O9-Ho5-O26	81.3(2)
Ho5-O15	2.230(7)	O13-Ho3-O8	91.4(2)	O3-Ho5-O26	99.8(2)
Ho5-O9	2.235(6)	O11-Ho3-O8	85.8(2)	O33-Ho5-O26	165.3(2)
Ho5-O3	2.242(6)	O13-Ho3-O16	89.7(2)	O24-Ho6-O6	87.7(3)
Ho5-O33	2.325(7)	O11-Ho3-O16	90.4(3)	O24-Ho6-O12	178.4(3)
Ho5-O26	2.355(6)	O8-Ho3-O16	163.3(2)	O6-Ho6-O12	91.2(3)
Ho6-O24	2.212(6)	O13-Ho3-O31	89.7(2)	O24-Ho6-O18	86.9(2)
Ho6-O6	2.226(7)	O11-Ho3-O31	80.8(2)	O6-Ho6-O18	174.2(3)
Ho6-O12	2.231(6)	O8-Ho3-O31	85.2(2)	O12-Ho6-O18	94.1(3)
Ho6-O18	2.275(6)	O16-Ho3-O31	78.1(2)	O24-Ho6-O34	95.4(2)
Ho6-O34	2.278(6)	O13-Ho3-O27	114.6(2)	O6-Ho6-O34	90.9(3)
Ho6-O27	2.328(6)	O11-Ho3-O27	74.9(2)	O12-Ho6-O34	86.0(2)
O1-Ho1-O22	176.0(3)	O8-Ho3-O27	116.4(2)	O18-Ho6-O34	91.9(2)
O1-Ho1-O4	91.0(3)	O16-Ho3-O27	77.9(2)	O24-Ho6-O27	99.9(2)
O22-Ho1-O4	86.5(3)	O31-Ho3-O27	145.5(2)	O6-Ho6-O27	96.1(2)
O1-Ho1-O19	89.0(3)	O13-Ho3-O26	76.8(2)	O12-Ho6-O27	78.9(2)
O22-Ho1-O19	92.6(3)	O11-Ho3-O26	111.6(2)	O18-Ho6-O27	82.6(2)
O4-Ho1-O19	167.1(2)	O8-Ho3-O26	77.8(2)	O34-Ho6-O27	163.4(2)
O1-Ho1-O29	94.3(3)	O16-Ho3-O26	118.6(2)	Ho1-O25-Ho2	134.48(41)
O22-Ho1-O29	82.4(3)	O31-Ho3-O26	157.9(2)	Ho1-O28-Ho4	134.10(37)
O4-Ho1-O29	85.8(3)	O27-Ho3-O26	56.48(19)	Ho3-O26-Ho5	136.30(27)
O19-Ho1-O29	81.3(3)	O32-Ho4-O17	98(2)	Ho3-O27-Ho6	135.23(27)

Table S7 Selected bond lengths (Å) and angles (°) for **Yb_6** at 193 K

Yb1-O1	2.183(7)	O1-Yb1-O28	112.1(2)	O17-Yb4-O14	87.7(3)
Yb1-O22	2.188(7)	O22-Yb1-O28	74.2(3)	O20-Yb4-O14	88.4(3)
Yb1-O4	2.213(7)	O4-Yb1-O28	114.8(2)	O17-Yb4-O23	88.9(3)
Yb1-O19	2.242(7)	O19-Yb1-O28	78.2(2)	O20-Yb4-O23	94.4(3)
Yb1-O29	2.292(8)	O29-Yb1-O28	146.0(3)	O14-Yb4-O23	175.7(3)
Yb1-O28	2.456(7)	O1-Yb1-O25	74.2(2)	O17-Yb4-O32	93.6(6)
Yb1-O25	2.531(8)	O22-Yb1-O25	110.3(3)	O20-Yb4-O32	97.5(6)
Yb2-O7	2.149(7)	O4-Yb1-O25	75.1(3)	O14-Yb4-O32	99.2(7)
Yb2-O2	2.172(6)	O19-Yb1-O25	118.1(3)	O23-Yb4-O32	83.6(7)
Yb2-O5	2.172(7)	O29-Yb1-O25	156.9(3)	O17-Yb4-O28	91.5(3)
Yb2-O10	2.188(7)	O28-Yb1-O25	56.5(2)	O20-Yb4-O28	78.7(3)
Yb2-O30	2.233(11)	O7-Yb2-O2	92.1(3)	O14-Yb4-O28	98.8(2)
Yb2-O25	2.373(8)	O7-Yb2-O5	166.1(3)	O23-Yb4-O28	78.6(3)
Yb3-O13	2.178(6)	O2-Yb2-O5	91.9(3)	O32-Yb4-O28	161.5(7)
Yb3-O11	2.193(7)	O7-Yb2-O10	88.0(3)	O21-Yb5-O15	91.4(3)

Yb3-O8	2.225(7)	O2-Yb2-O10	177.4(3)	O21-Yb5-O3	87.6(3)
Yb3-O16	2.239(7)	O5-Yb2-O10	87.4(3)	O15-Yb5-O3	178.0(3)
Yb3-O31	2.302(7)	O7-Yb2-O30	86.0(7)	O21-Yb5-O9	173.6(3)
Yb3-O26	2.443(6)	O2-Yb2-O30	90.6(7)	O15-Yb5-O9	92.5(3)
Yb3-O27	2.477(6)	O5-Yb2-O30	107.4(7)	O3-Yb5-O9	88.3(3)
Yb4-O17	2.132(7)	O10-Yb2-O30	92.0(7)	O21-Yb5-O33	86.9(3)
Yb4-O20	2.163(7)	O7-Yb2-O25	90.2(3)	O15-Yb5-O33	87.0(3)
Yb4-O14	2.181(7)	O2-Yb2-O25	78.5(3)	O3-Yb5-O33	94.7(3)
Yb4-O23	2.187(7)	O5-Yb2-O25	77.6(3)	O9-Yb5-O33	98.4(3)
Yb4-O32	2.215(10)	O10-Yb2-O25	98.9(3)	O21-Yb5-O26	94.9(3)
Yb4-O28	2.369(8)	O30-Yb2-O25	168.3(8)	O15-Yb5-O26	78.1(2)
Yb5-O21	2.145(7)	O13-Yb3-O11	171.1(3)	O3-Yb5-O26	100.2(2)
Yb5-O15	2.171(6)	O13-Yb3-O8	91.7(3)	O9-Yb5-O26	81.0(3)
Yb5-O3	2.189(6)	O11-Yb3-O8	84.8(3)	O33-Yb5-O26	165.0(2)
Yb5-O9	2.200(7)	O13-Yb3-O16	88.4(3)	O6-Yb6-O24	89.5(3)
Yb5-O33	2.257(7)	O11-Yb3-O16	92.7(3)	O6-Yb6-O18	174.6(3)
Yb5-O26	2.298(6)	O8-Yb3-O16	164.0(2)	O24-Yb6-O18	86.2(2)
Yb6-O6	2.173(7)	O13-Yb3-O31	90.1(2)	O6-Yb6-O12	89.6(3)
Yb6-O24	2.200(7)	O11-Yb3-O31	81.4(3)	O24-Yb6-O12	178.5(3)
Yb6-O18	2.211(7)	O8-Yb3-O31	85.1(3)	O18-Yb6-O12	94.6(3)
Yb6-O12	2.212(7)	O16-Yb3-O31	79.0(3)	O6-Yb6-O34	91.4(3)
Yb6-O34	2.219(7)	O13-Yb3-O26	76.1(2)	O24-Yb6-O34	94.5(3)
Yb6-O27	2.283(6)	O11-Yb3-O26	111.1(2)	O18-Yb6-O34	92.2(3)
O1-Yb1-O22	173.6(2)	O8-Yb3-O26	78.0(2)	O12-Yb6-O34	86.7(3)
O1-Yb1-O4	90.3(3)	O16-Yb3-O26	117.5(2)	O6-Yb6-O27	95.9(3)
O22-Yb1-O4	86.6(3)	O31-Yb3-O26	157.6(2)	O24-Yb6-O27	100.0(2)
O1-Yb1-O19	89.2(3)	O13-Yb3-O27	113.7(2)	O18-Yb6-O27	81.7(2)
O22-Yb1-O19	92.5(3)	O11-Yb3-O27	75.1(2)	O12-Yb6-O27	78.9(2)
O4-Yb1-O19	166.0(3)	O8-Yb3-O27	117.4(2)	O34-Yb6-O27	163.8(3)
O1-Yb1-O29	93.6(3)	O16-Yb3-O27	76.9(2)	Yb1-O25-Yb2	136.31(35)
O22-Yb1-O29	80.6(3)	O31-Yb3-O27	145.2(2)	Yb1-O28-Yb4	135.45(36)
O4-Yb1-O29	85.6(3)	O26-Yb3-O27	57.1(2)	Yb3-O26-Yb5	137.10(27)
O19-Yb1-O29	80.5(3)	O17-Yb4-O20	168.8(3)	Yb3-O27-Yb6	135.98(27)

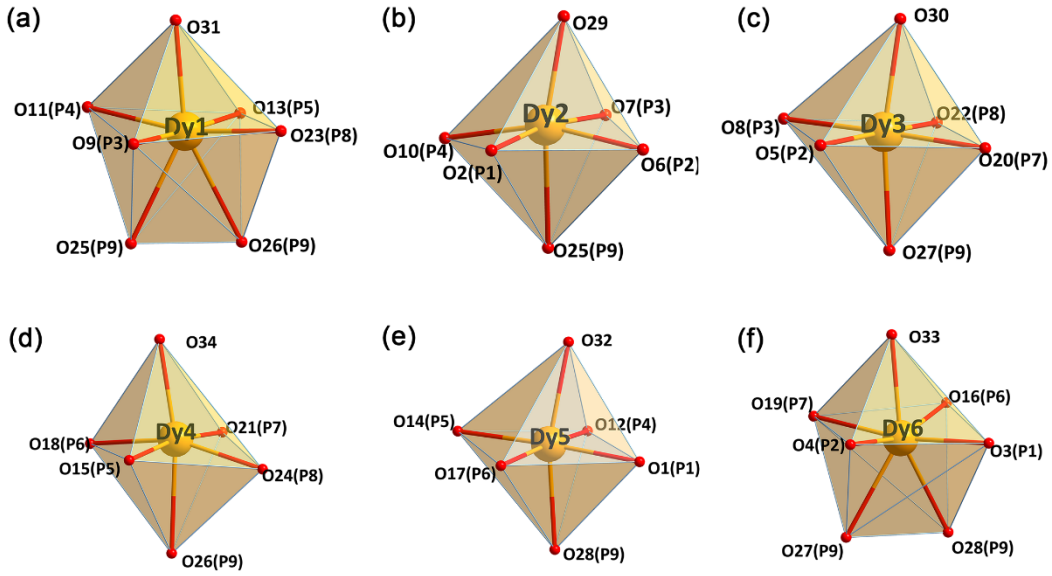


Fig. S5 Different coordination modes of Dy^{III} in **Dy_6**.

Table S8 Coordination geometry for **Dy_6** at 193 K.

Geometry	Dy1	Dy6
Heptagon (D_{7h})	30.996	31.471
Hexagonal pyramid (C_{6v})	21.074	22.158
Pentagonal bipyramid (D_{5h})	5.690	5.541
Capped octahedron (C_{3v})	2.930	2.485
Capped trigonal prism (C_{2v})	1.389	0.998
Johnson pentagonal bipyramid J13 (D_{5h})	8.532	8.469
Johnson elongated triangular pyramid J7 (C_{3v})	18.234	19.741

	Dy2	Dy3	Dy4	Dy5
Hexagon (D_{6h})	29.148	30.224	28.796	29.872
Pentagonal pyramid (C_{5v})	22.822	23.480	22.557	24.771
Octahedron (O_h)	1.346	0.894	1.587	0.973
Trigonal prism (D_{3h})	12.539	13.038	11.440	13.014
Johnson pentagonal pyramid J2 (C_{5v})	25.769	27.253	25.463	27.906

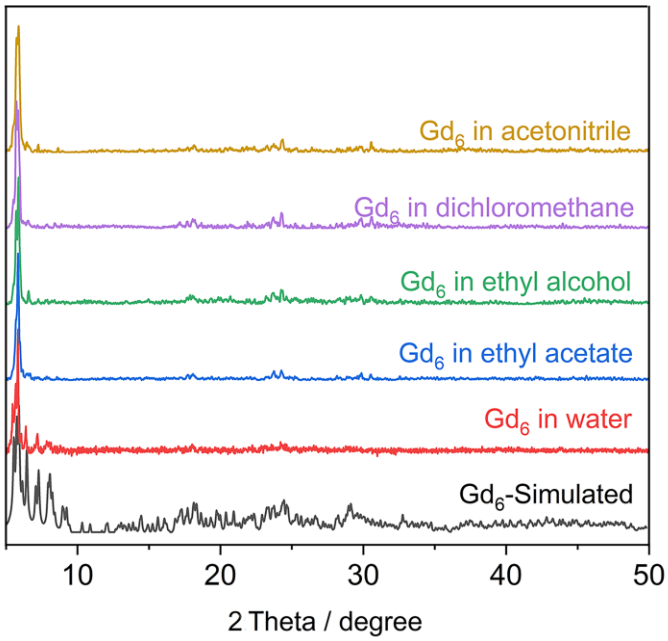


Fig. S6 PXRD spectra of **Gd_6** immersed in different solvents for 1 day.

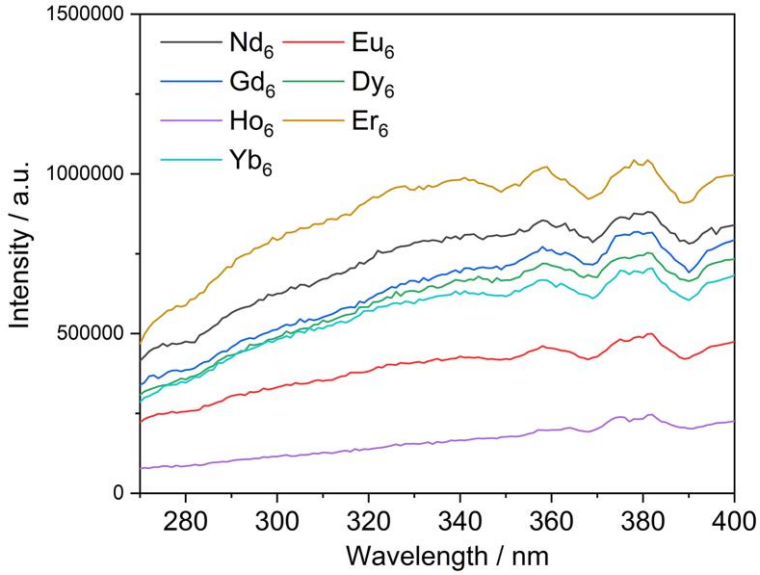


Fig. S7 Excitation spectra of **Ln_6** in the solid state (λ_{em}= 427 nm).

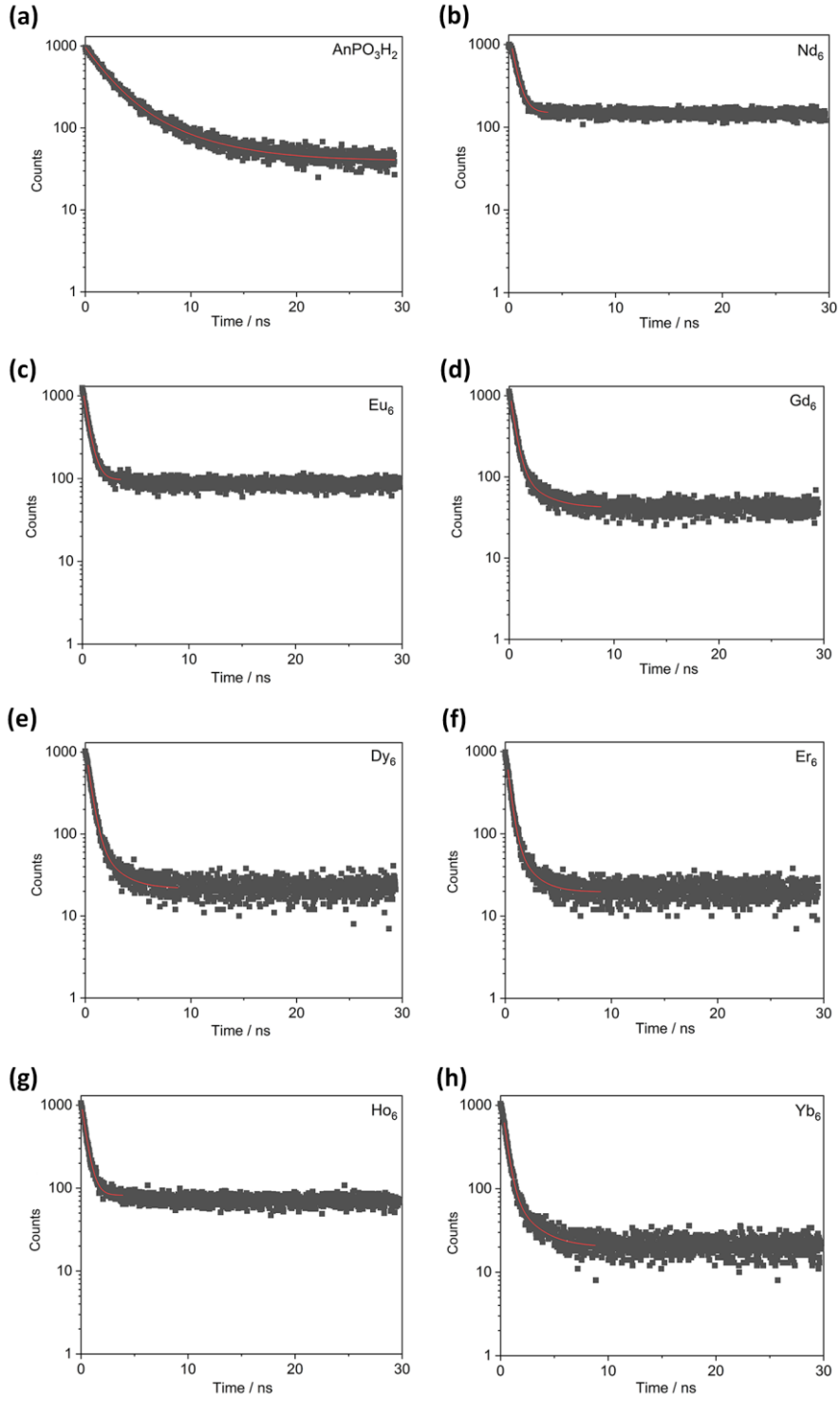


Fig. S8 Fluorescence decay curve (black dots) and fitting line (red line) for $AnPO_3H_2$ emitting at 444 nm and **Nd_6**-**Yb_6** emitting at 427 nm (λ_{ex} = 375 nm).

Table S9 The emission peak and life time of $AnPO_3H_2$ and compounds **Nd_6** - **Yb_6.**

	Nd_6	**Eu_6**	**Gd_6**	**Dy_6**	**Ho_6**	**Er_6**	**Yb_6**	$AnPO_3H_2$
λ/nm	427	427	427	427	427	427	427	444
τ1/ns	0.46 (83.2%)	0.44 (85.9%)	0.47 (66.1%)	0.44 (69.6%)	0.46 (89.8%)	0.37 (66.5%)	0.41 (68.0%)	1.96 (49.2%)
τ2/ns	1.33 (16.8%)	1.25 (14.1%)	1.98 (33.9%)	1.75 (30.4%)	1.31 (10.2%)	1.46 (33.5%)	1.91 (32.0%)	5.44 (50.8%)
τ_{av}/ns	0.61	0.55	0.98	0.84	0.55	0.74	0.89	3.73
X^2	0.984	0.915	1.068	1.033	1.079	1.087	0.926	0.916

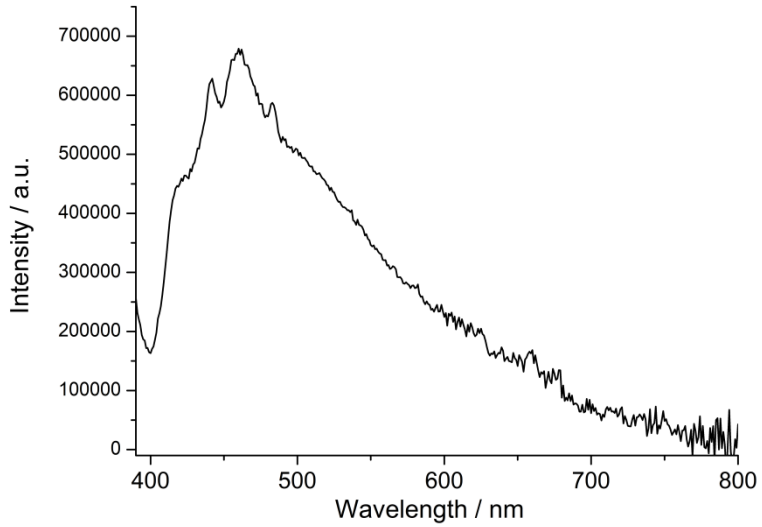


Fig. S9 Phosphorescent spectrum excited at 375 nm for **Gd_6** at 77 K.

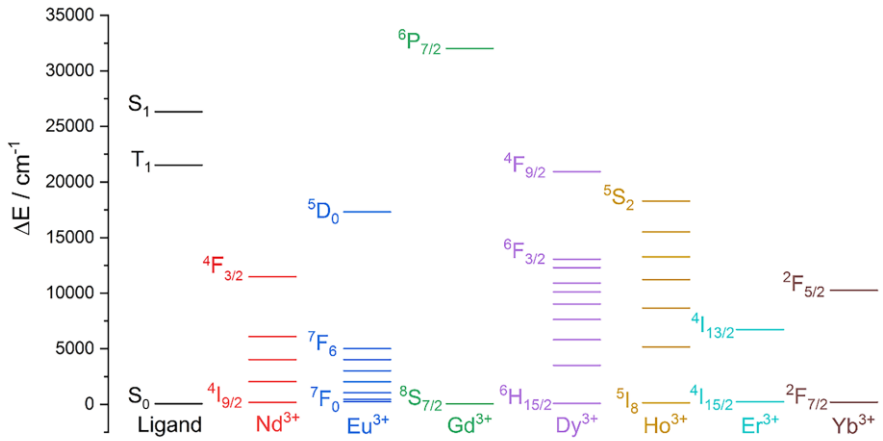


Fig. S10 Simplified energy diagram showing the lanthanide excited states and the estimated triplet state of $AnPO_3H_2$ in **Gd_6**.

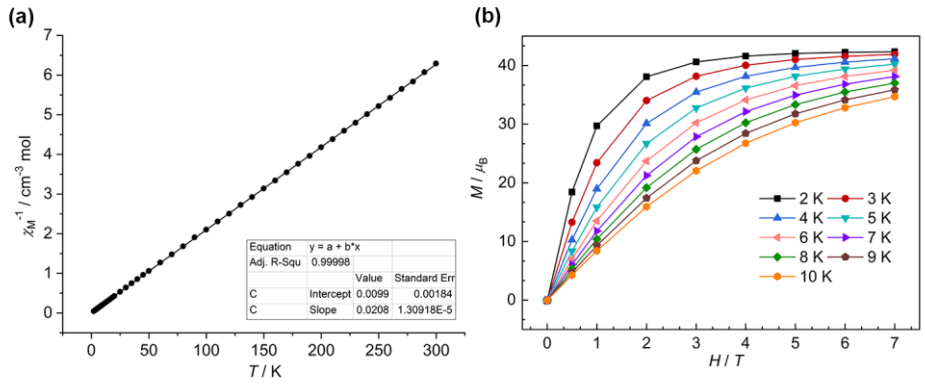


Fig. S11 (a) Temperature dependence of the χ_M^{-1} product at 1 kOe for **Gd_6**. (b) Molar magnetization(M) against magnetic field(H) for **Gd_6** from 0-7 T at 2-10 K.

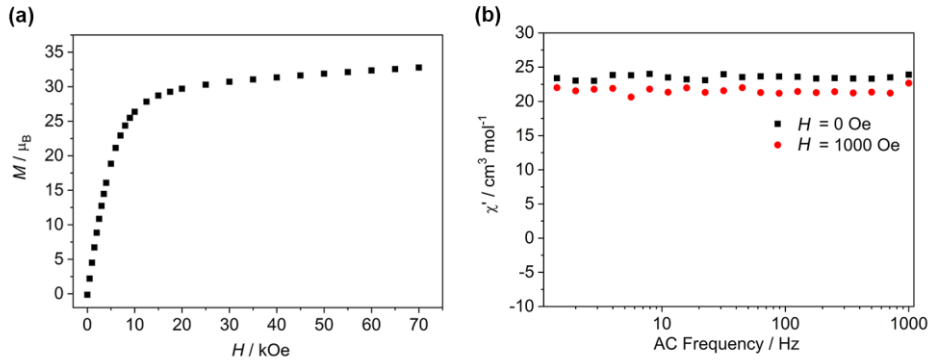


Fig. S12 (a) Molar magnetization (*M*) against magnetic field (*H*) for **Dy_6** from 0-70 kOe at 2 K. (b) Frequency dependence of the in-phase susceptibilities of **Dy_6**.

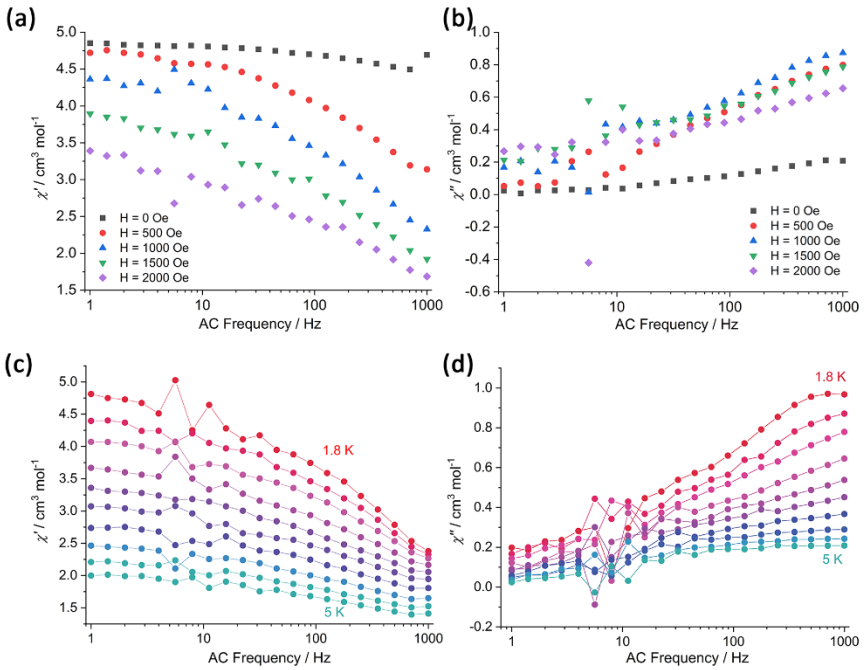


Fig. S13 Frequency dependence of the in-phase (a) and out-of-phase (b) ac-susceptibilities of **DyY_5** under different dc field at 1.8 K. Frequency dependence of the in-phase (c) and out-of-phase (d) ac-susceptibilities of **DyY_5** under 1kOe dc field at 1.8-5 K.

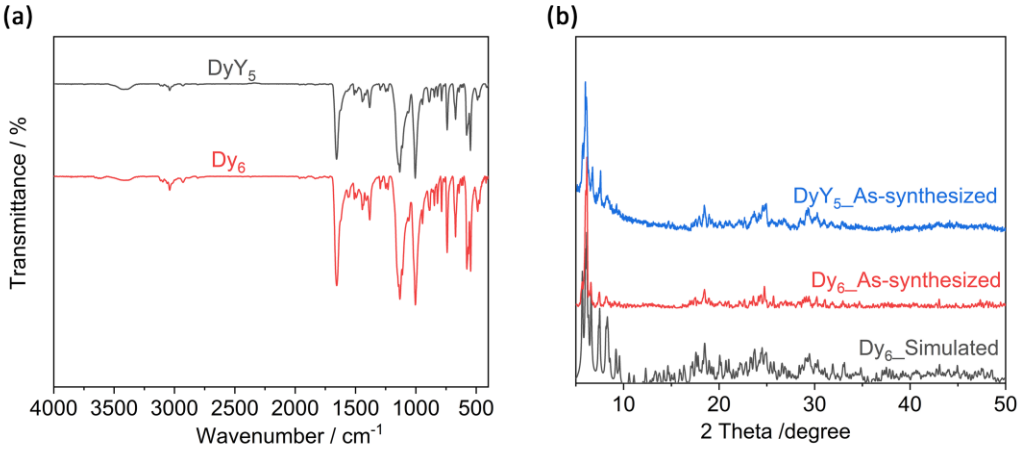


Fig. S14 (a) IR spectra of **DyY_5** and **Dy_6**. (b) PXRD patterns of **Dy_6** and **DyY_5**.

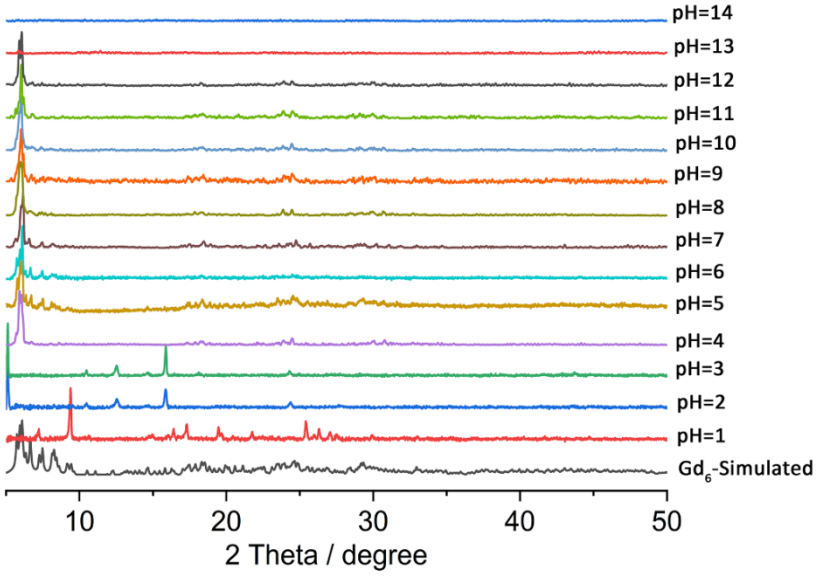


Fig. S15 PXRD patterns of **Gd_6** immersed in aqueous solutions with pH values of 1-14 for 1 day.

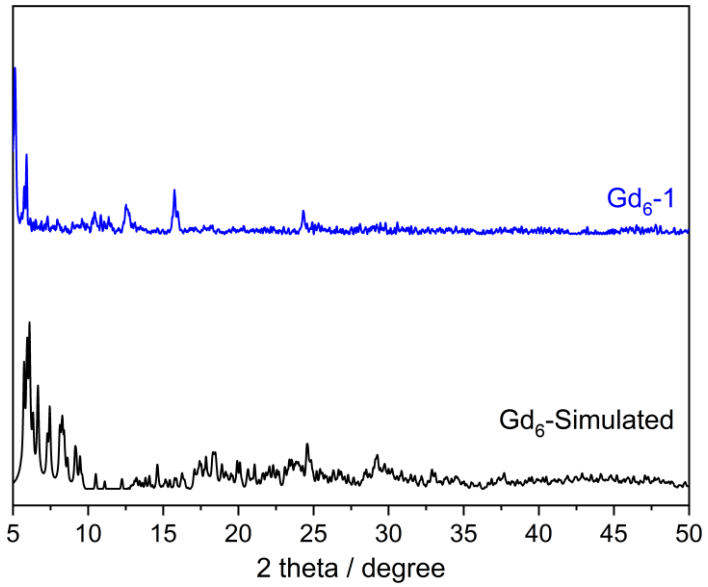


Fig. S16 PXRD patterns of **Gd_6** as well as **Gd_6-1**.

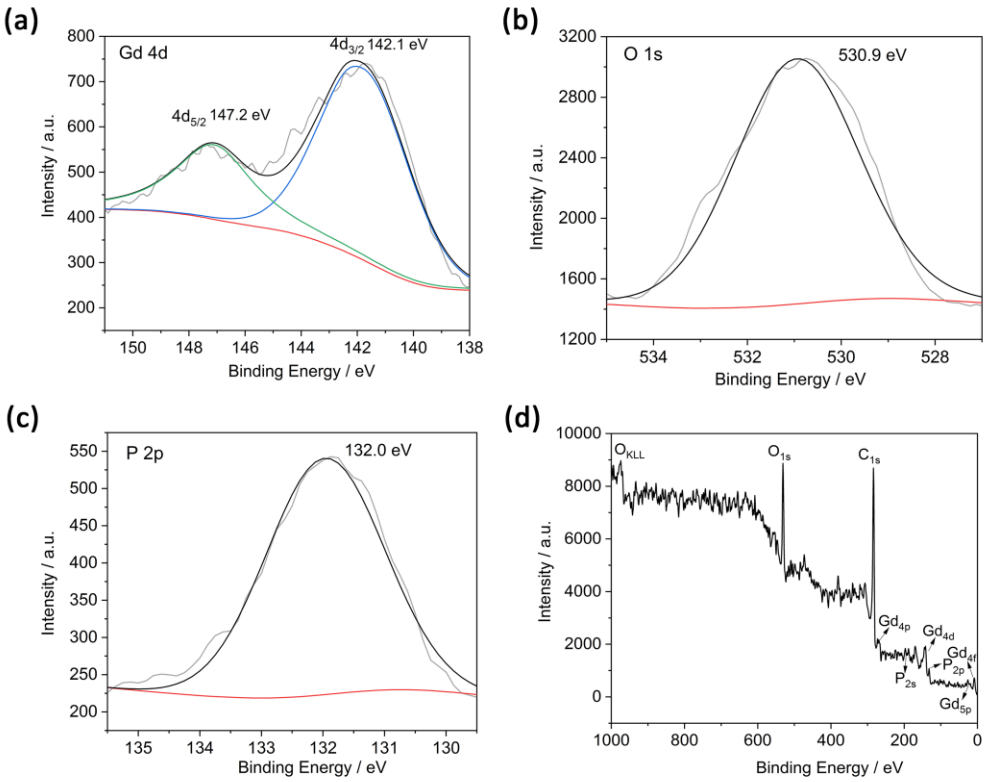


Fig. S17 XPS spectra of **Gd_6**.

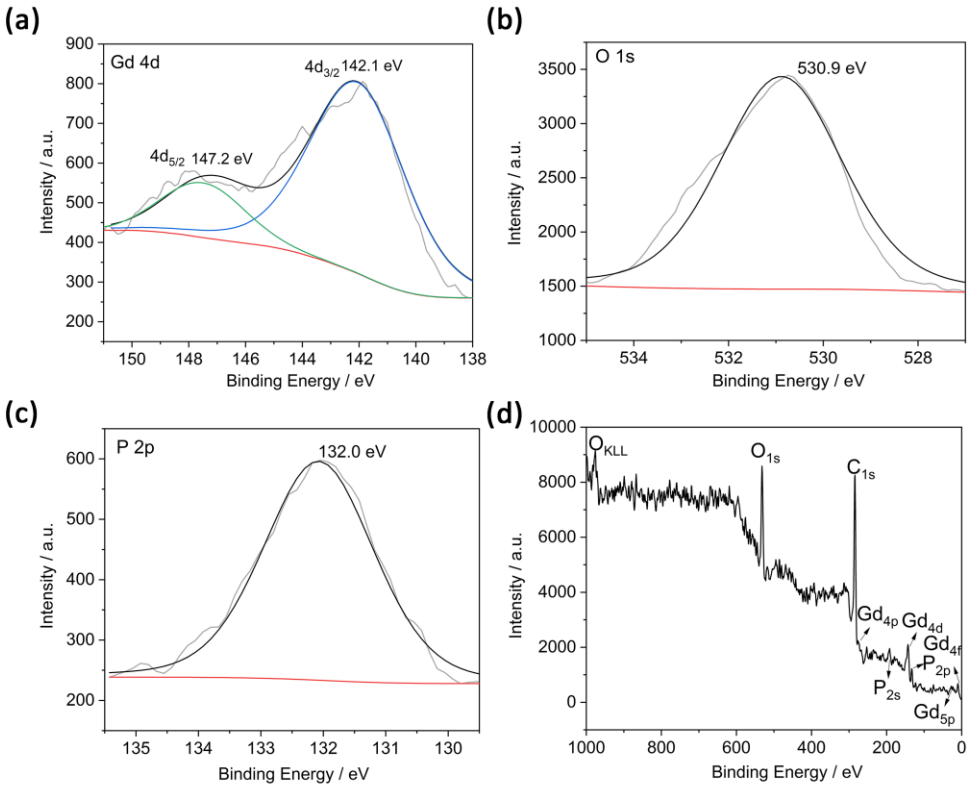
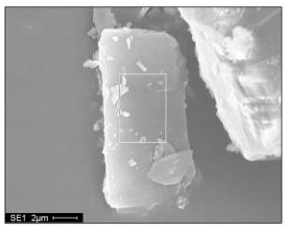
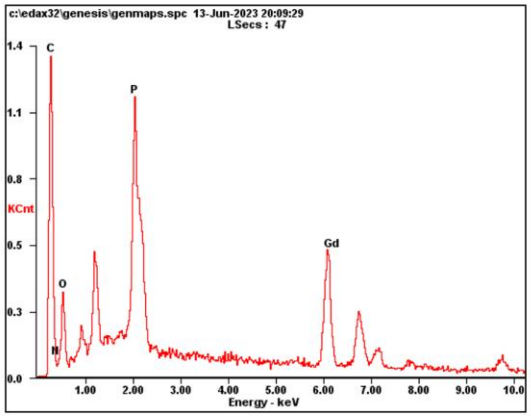


Fig. S18 XPS spectra of **Gd_6-1**.

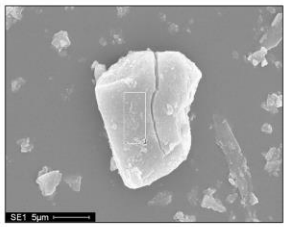
(a)



Element	Wt%	At%
CK	52.14	79.21
NK	02.63	03.43
OK	08.07	09.20
PK	08.13	04.79
GdL	29.03	03.37
Matrix	Correction	ZAF



(b)



Element	Wt%	At%
CK	33.85	69.42
NK	02.11	03.71
OK	06.45	09.93
PK	12.41	09.87
GdL	45.18	07.08
Matrix	Correction	ZAF

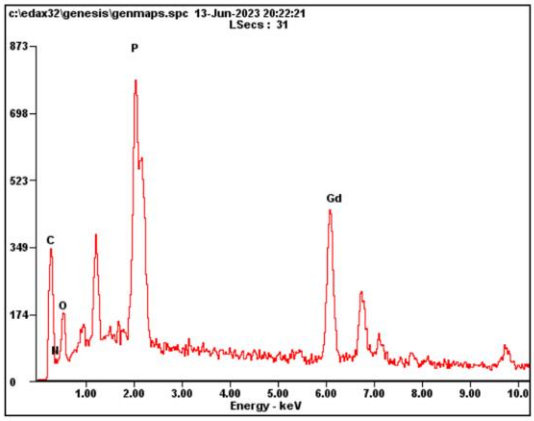


Fig. S19 EDS spectra of (a) **Gd_6** and (b) **Gd_6-1**.

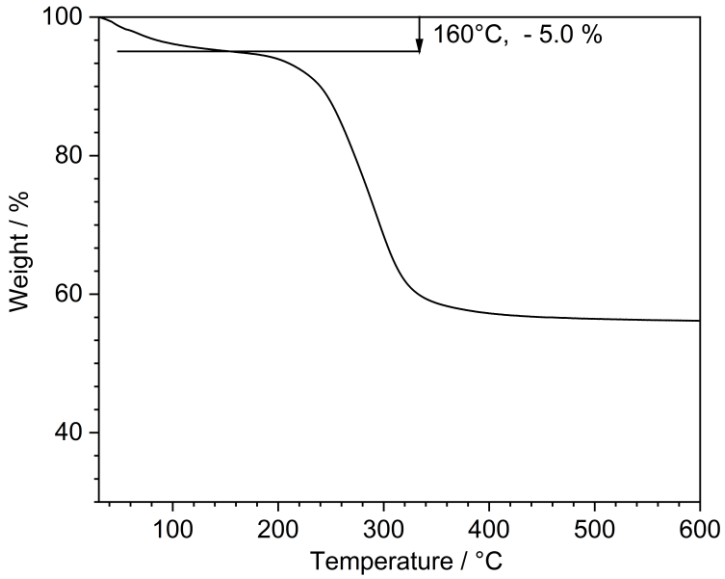


Fig. S20 TG curves of **Gd_6-1** at 30-600°C with a heating rate of 5°C/min under N_2 flow.

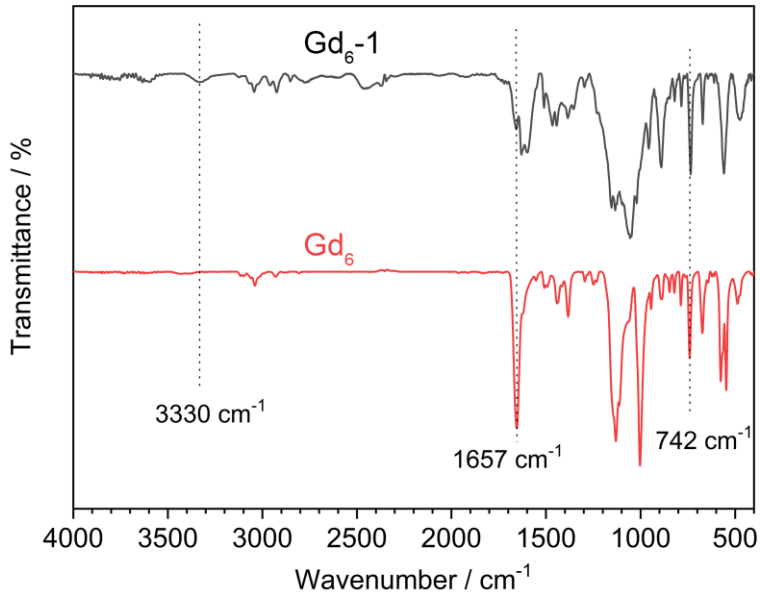


Fig. S21 IR spectra of **Gd_6** and **Gd_6-1**.