Electronic Supporting Information

Table S1 Selected bond angles (°) for **1**

O1-Dy1-O7	82.04(13)	O6-Dy1-O5	73.19(11)
O1-Dy1-O4	74.72(12)	O1-Dy1-O1W	78.00(13)
O7-Dy1-O4	97.92(14)	O7-Dy1-O1W	145.06(12)
O1-Dy1-O8	145.99(11)	O4-Dy1-O1W	104.01(13)
O7-Dy1-O8	90.00(12)	O8-Dy1-O1W	90.76(11)
O4-Dy1-O8	139.28(11)	O6-Dy1-O1W	141.44(11)
O1-Dy1-O6	133.63(14)	O5-Dy1-O1W	69.35(11)
O7-Dy1-O6	71.25(12)	O1-Dy1-O9	76.47(11)
O4-Dy1-O6	72.39(13)	O7-Dy1-O9	71.54(12)
O8-Dy1-O6	72.63(12)	O4-Dy1-O9	150.45(11)
O1-Dy1-O5	125.45(12)	O8-Dy1-O9	69.65(10)
O7-Dy1-O5	144.41(11)	O6-Dy1-O9	125.99(11)
O4-Dy1-O5	72.52(12)	O5-Dy1-O9	131.64(10)
O8-Dy1-O5	77.96(10)	O1W-Dy1-O9	76.05(11)

Table S2 Selected bond angles (°) for **2**

O1-Gd1-O7	80.73(13)	O6-Gd1-O5	73.60(11)
O1-Gd1-O4	74.78(12)	O1-Gd1-O1W	78.59(12)
O7-Gd1-O4	100.18(12)	O7-Gd1-O1W	144.77(11)
O1-Gd1-O8	145.97(11)	O4-Gd1-O1W	101.48(12)
O7-Gd1-O8	87.07(12)	O8-Gd1-O1W	94.40(11)
O4-Gd1-O8	138.97(11)	O6-Gd1-O1W	142.84(12)
O1-Gd1-O6	130.98(13)	O1W-Gd1-O5	69.70(10)
O7-Gd1-O6	70.79(12)	O1-Gd1-O9	76.57(11)
O6-Gd1-O4	72.19(12)	O7-Gd1-O9	71.17(11)
O6-Gd1-O8	72.39(11)	O4-Gd1-O9	151.08(11)
O1-Gd1-O5	127.75(11)	O8-Gd1-O9	69.43(10)
O7-Gd1-O5	144.15(11)	O6-Gd1-O9	126.47(11)
O4-Gd1-O5	72.33(12)	O5-Gd1-O9	130.65(10)
O8-Gd1-O5	78.37(10)	O1W-Gd1-O9	76.45(10)

Table S3 Selected bond angles (°) for **3**

O4-Dy1-O1	145.96(15)	O7-Dy2-O10	144.62(15)
O4-Dy1-O13	75.54(15)	O7-Dy2-O19	82.91(15)
O1-Dy1-O13	78.75(14)	O10-Dy2-O19	106.73(14)
O4-Dy1-O17	81.37(14)	O7-Dy2-O22	111.54(14)
O1-Dy1-O17	107.84(14)	O10-Dy2-O22	80.19(14)
O13-Dy1-O17	143.36(14)	O19-Dy2-O22	145.14(13)
O4-Dy1-O14	110.17(14)	O7-Dy2-O24	72.55(14)
O1-Dy1-O14	83.42(15)	O10-Dy2-O24	141.54(14)
O13-Dy1-O14	74.29(14)	O19-Dy2-O24	82.02(14)
O17-Dy1-O14	141.35(14)	O22-Dy2-O24	73.22(14)
O4-Dy1-O16	71.75(14)	O7-Dy2-O23	140.48(15)
O1-Dy1-O16	141.19(15)	O10-Dy2-O23	73.63(14)
O13-Dy1-O16	117.31(13)	O19-Dy2-O23	72.62(14)
O17-Dy1-O16	80.67(15)	O22-Dy2-O23	77.04(13)
O14-Dy1-O16	69.31(15)	O24-Dy2-O23	73.67(13)
O4-Dy1-O18	78.02(14)	O7-Dy2-O21	75.31(15)
O1-Dy1-O18	74.83(15)	O10-Dy2-O21	78.08(14)
O13-Dy1-O18	77.27(13)	O19-Dy2-O21	144.28(14)
O17-Dy1-O18	70.31(14)	O22-Dy2-O21	70.29(14)
O14-Dy1-O18	146.98(14)	O24-Dy2-O21	116.72(13)
O16-Dy1-O18	140.69(15)	O23-Dy2-O21	139.71(15)
O4-Dy1-O15	139.34(14)	O7-Dy2-O20	77.07(14)
O1-Dy1-O15	73.46(13)	O10-Dy2-O20	74.68(14)
O13-Dy1-O15	140.48(14)	O19-Dy2-O20	70.31(13)
O17-Dy1-O15	73.26(13)	O22-Dy2-O20	142.36(14)
O14-Dy1-O15	75.09(13)	O24-Dy2-O20	140.97(14)
O16-Dy1-O15	73.16(13)	O23-Dy2-O20	120.55(13)
O18-Dy1-O15	120.29(13)	O21-Dy2-O20	77.36(13)

Table S4 Selected bond angles (°) for **4**

O3-Gd1-O4	69.40(13)	O3A-Gd1-O3	143.30(18)
O5-Gd1-O3	114.08(13)	O5-Gd1-O6A	76.00(15)
O3-Gd1-O6	70.95(12)	O3-Gd1-O6A	143.61(12)
O5-Gd1-O6	70.66(15)	O6A-Gd1-O6	81.04(18)
O5-Gd1-O4	83.02(15)	O3-Gd1-O4A	79.78(13)
O6-Gd1-O4	116.52(13)	O5A-Gd1-O4	139.07(15)
O5-Gd1-O5A	135.7(2)	O6A-Gd1-O4	146.30(13)
O5A-Gd1-O3	80.18(13)	O4A-Gd1-O4	65.54(17)

Symmetry code: A: -x + 1, y, -z + 3/2

Table S5 The plane···plane distances and displacement angles of the stacking anthracene groups in **1-4** (these values are measured according to the related definitions in the paper: C. Janiak, *Dalton Trans.*, 2000, 3885.)

compound	**1**	**2**	**3**			**4**
plane···plane distance (Å)	3.443(1)	3.451(1)	3.367(1)	3.608(1)	3.660(1)	3.554(1)
centroid···centroid distance (Å)	3.757(1)	3.690(1)	3.737(1)	3.686(1)	3.689(1)	3.645(1)
displacement angle (^{o})	23.5(1)^o	20.7(1)^o	25.7(1)	11.8(1)^o	7.1(1)^o	12.8(1)

Table S6 The atoms were used to define the hfac planes of A, B and C around Dy(III) ions

Dy(III) ion	hfac plane of A	hfac plane of B	hfac plane of C
Dy1 in **1**	C31, C32, C33, O8, O9	C26, C27, C28, O6, O7	C21, C22, C23, O4, O5
Gd1 in **2**	C31, C32, C33, O8, O9	C26, C27, C28, O6, O7	C21, C22, C23, O4, O5
Dy1 in **3**	C50, C51, C52, O17, O18	C45, C46, C47, O15, O16	C40, C41, C42, O13, O14
Dy2 in **3**	C98, C99, C100, O21, O22	C103, C104, C105, O23, O24	C93, C94, C95, O19, O20
Gd1 in **4**	C21, C22, C23, O4, O5	C26, C26A, C27, O6, O6A	C21A, C22A, C23A, O4A, O5A

Table S7 Dihedral angle (^{o}) between hfac planes (A, B and C)

	A *vs.* B	A *vs.* C	B *vs.* C
around Dy1 in **1**	43.7(1)	57.6(1)	79.5(1)
around Gd1 in **2**	36.9(1)	57.5(1)	86.6(1)
around Dy1 in **3**	86.2(1)	13.6(1)	80.2(1)
around Dy2 in **3**	83.3(1)	15.1(1)	88.7(1)
around Gd1 in **4**	82.2(1)	17.8(1)	82.2(1)

Table S8 Solid-state emission data of **1-4** at room temperature

Compound	λ_{max} (nm)
1	487, 530, 575
2	487, 530
3	487, 529, 574
4	487, 530

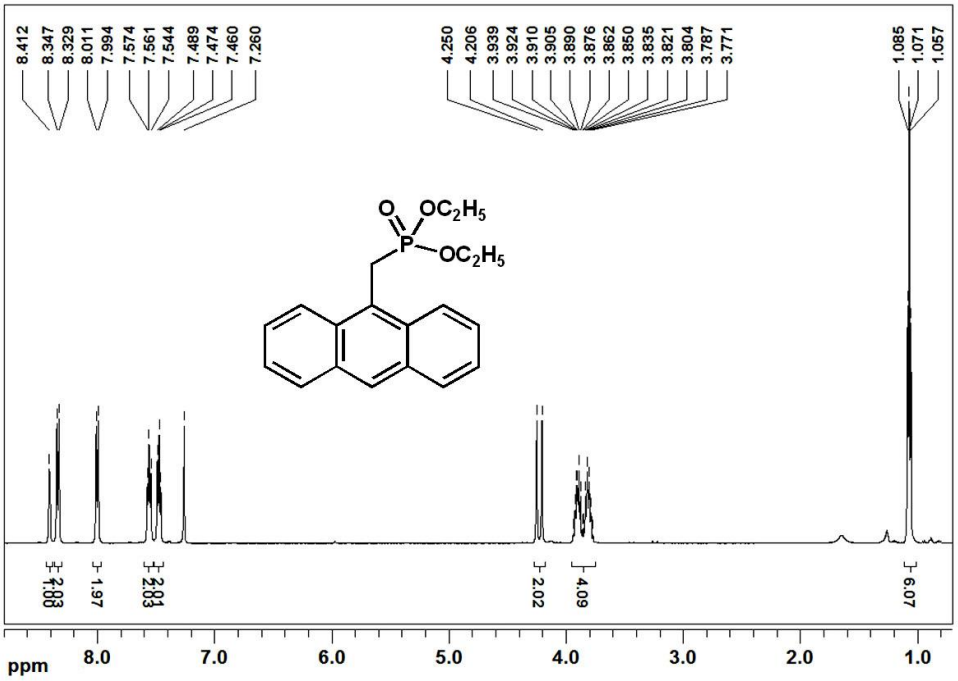

Fig. S1 ^{1}H NMR spectrum of depma (500 MHz, $CDCl_3$).

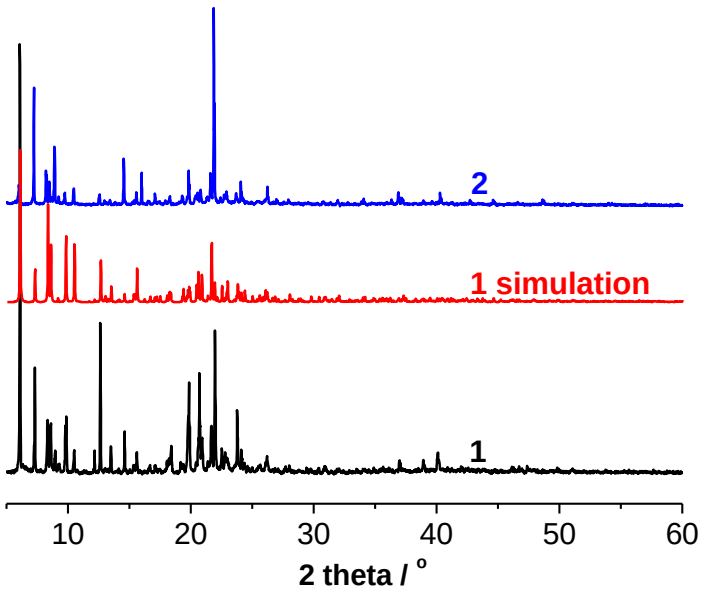

Fig. S2 Experimental XRD patterns of **1** and **2**, and simulated XRD pattern of **1**.

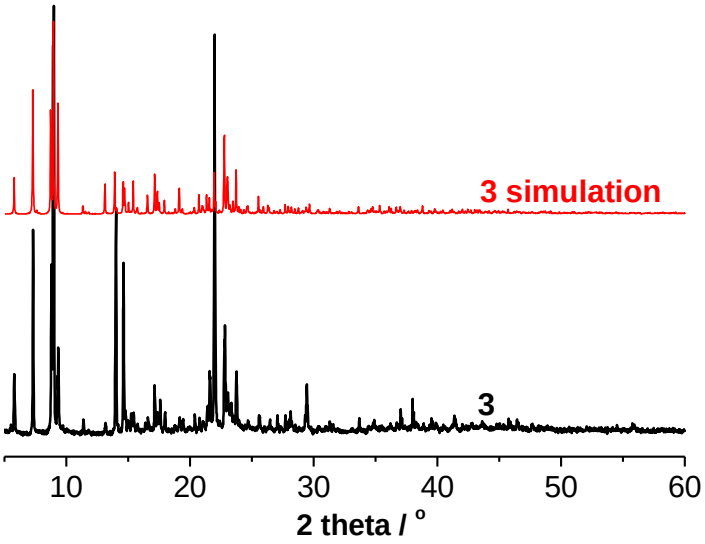

Fig. S3 Experimental and simulated XRD patterns of **3**.

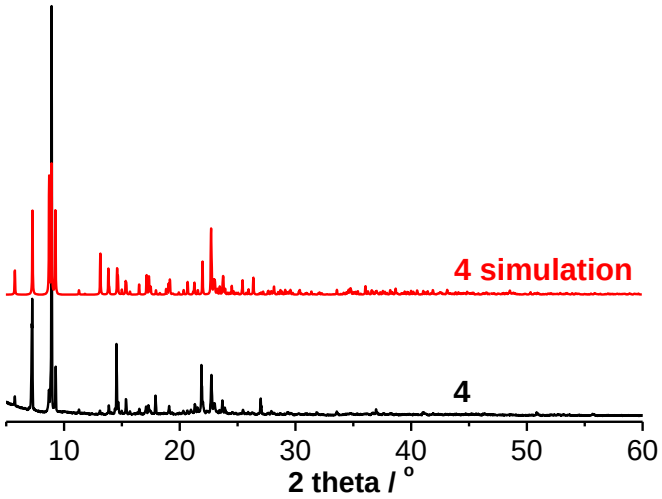

Fig. S4 Experimental and simulated XRD patterns of **4**.

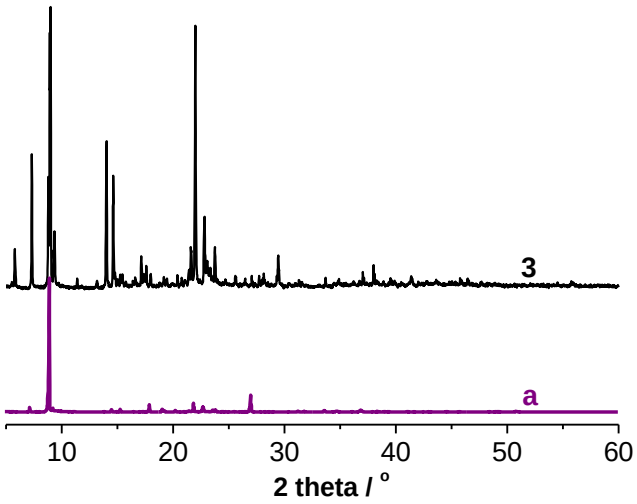

Fig. S5 The XRD patterns of **3** and **a** sample from the reaction of **1** and depma.

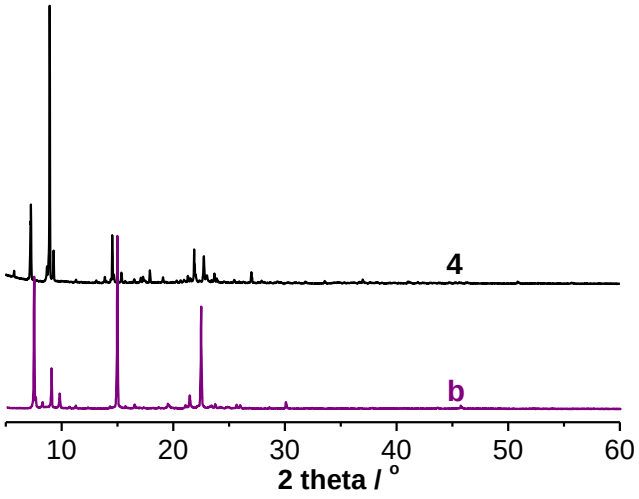

Fig. S6 The XRD patterns of **4** and **b** sample from the reaction of **2** and depma.

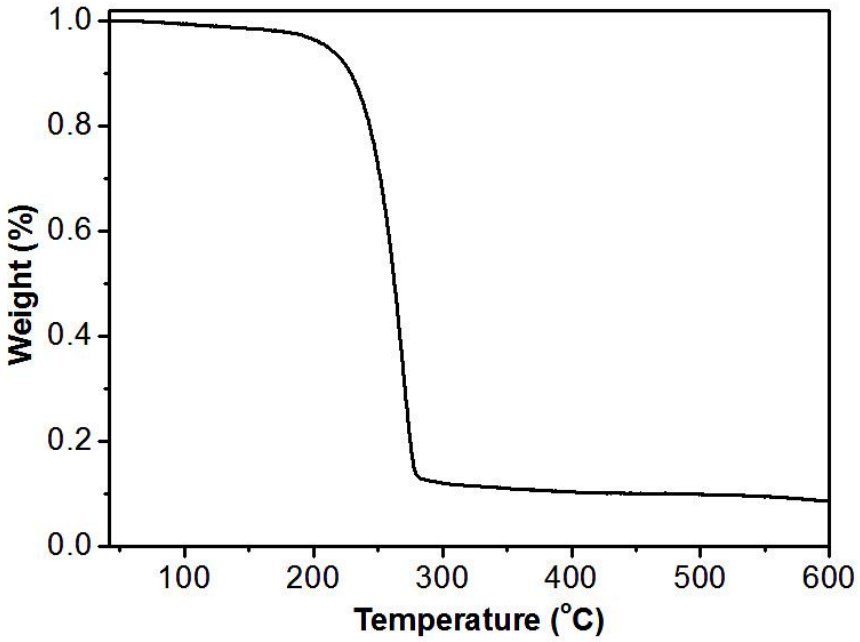

Fig. S7 TG curve of compound **1**.

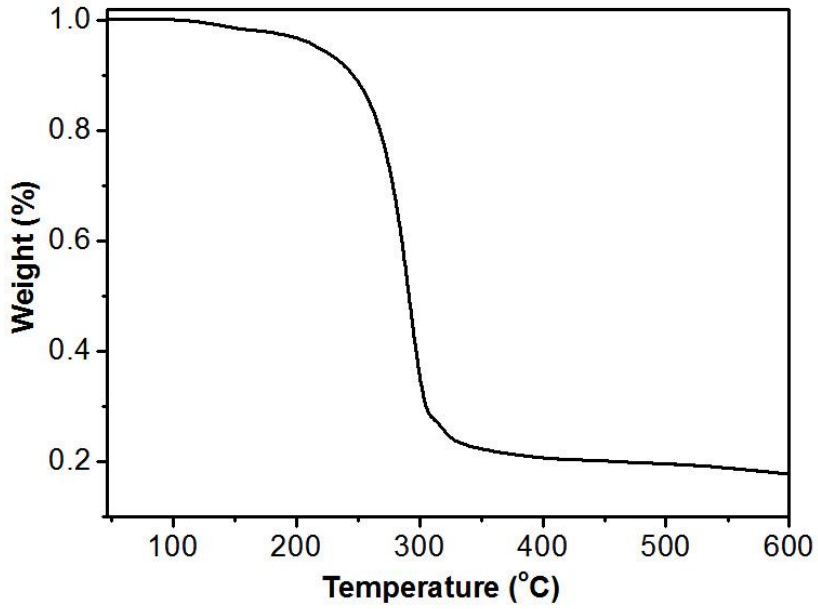

Fig. S8 TG curve of compound **2**.

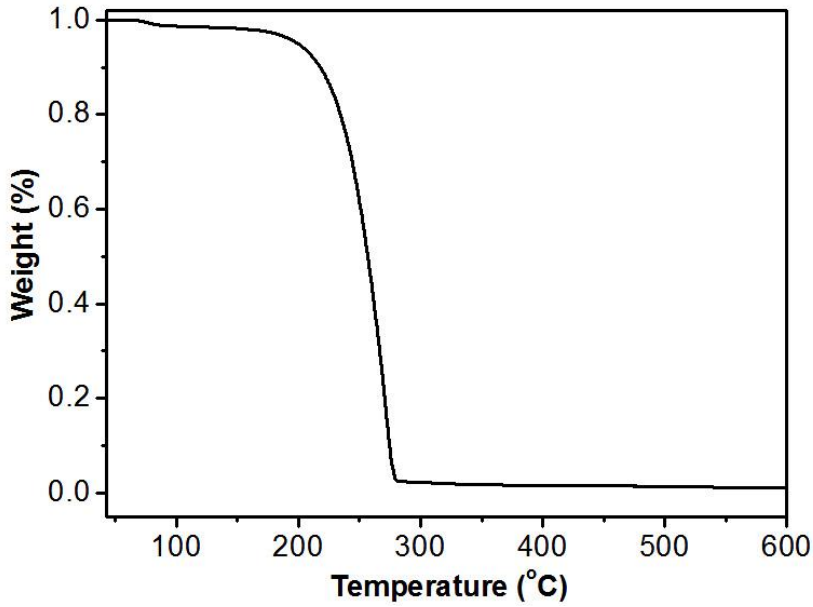

Fig. S9 TG curve of compound **3**.

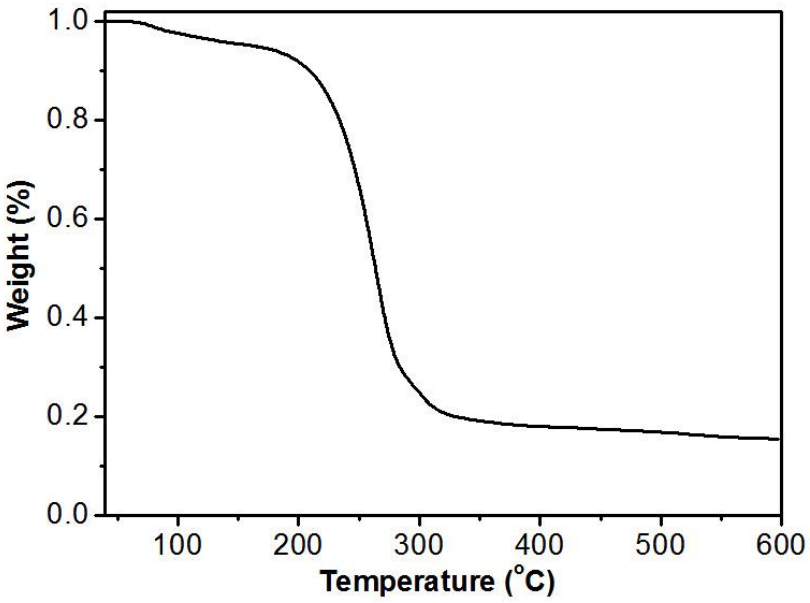

Fig. S10 TG curve of compound **4**.

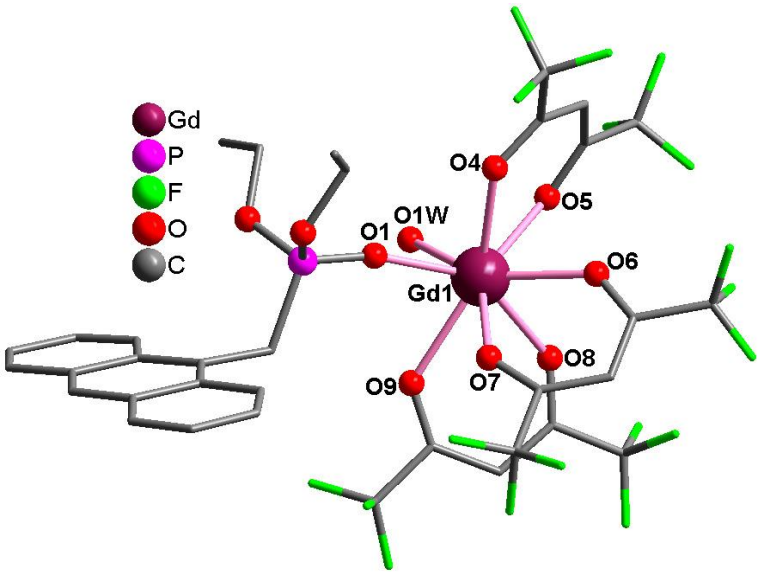

Fig. S11 Molecular structure of **2**. All H atoms were omitted for clarity.

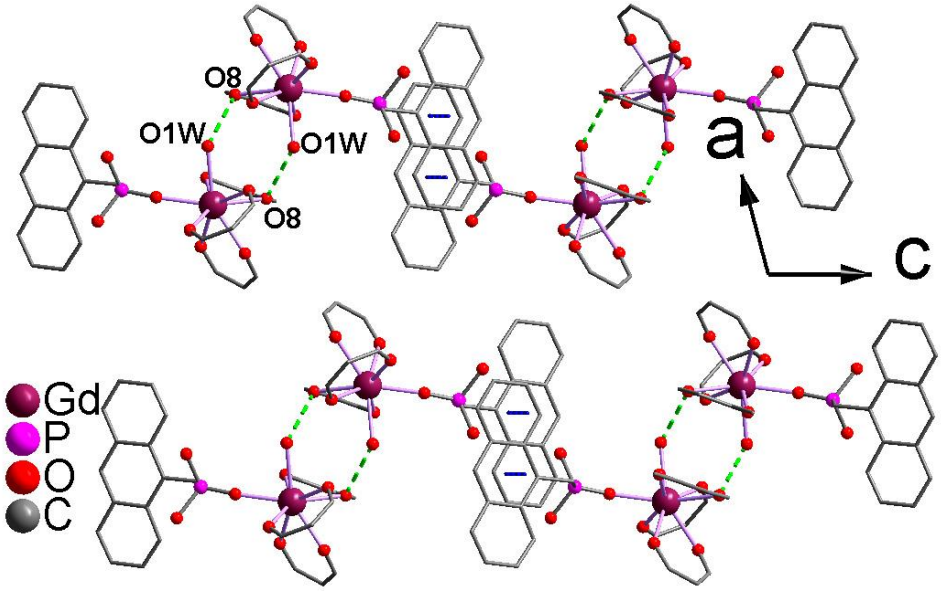

Fig. S12 The packing structure of **2**. All H atoms and CF_3 groups were omitted for clarity.

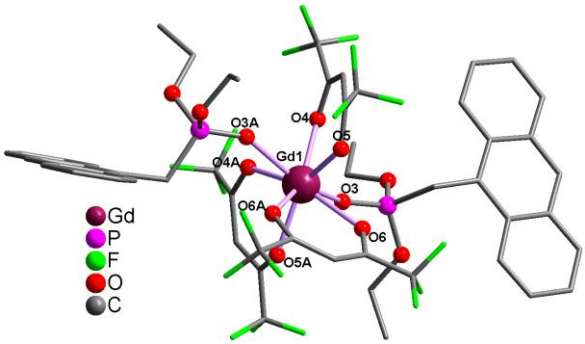

Fig. S13 Molecular structure of **4**. All H atoms and lattice water were omitted for clarity.

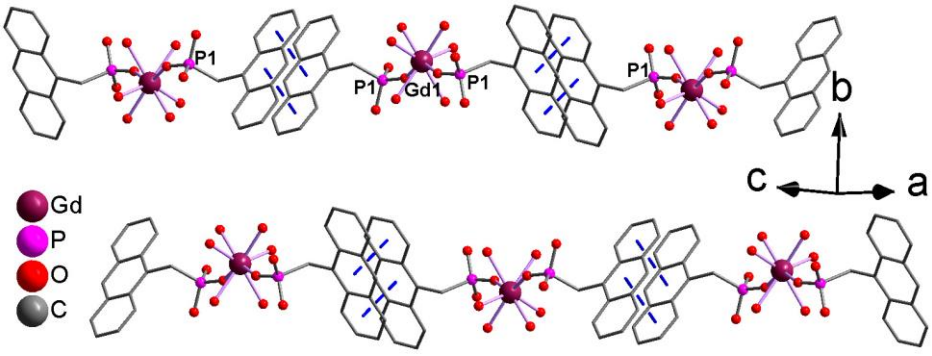

Fig. S14 Supramolecular chain in **4**. All H atoms, non-oxygen atoms of hfac ligands, and C_2H_5 groups attached to phosphonate oxygen atoms were omitted for clarity.

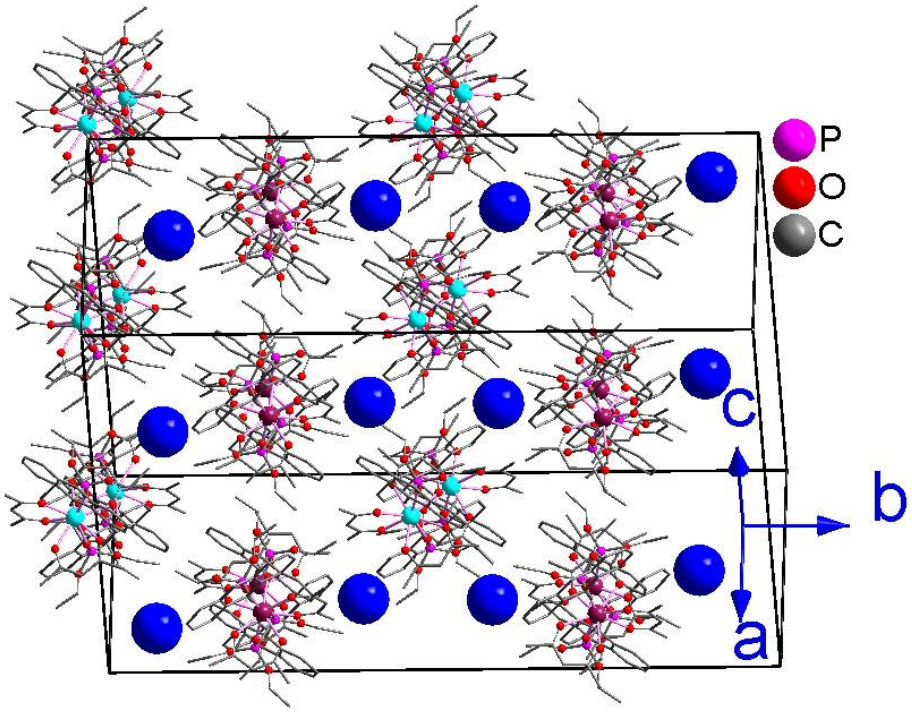

Fig. S15 The packing structure of **3**. Blue small balls are lattice water molecules, and all H atoms and F atoms were omitted for clarity. Color code: Dy1, purple; Dy2, cyan; lattice water, blue ball.

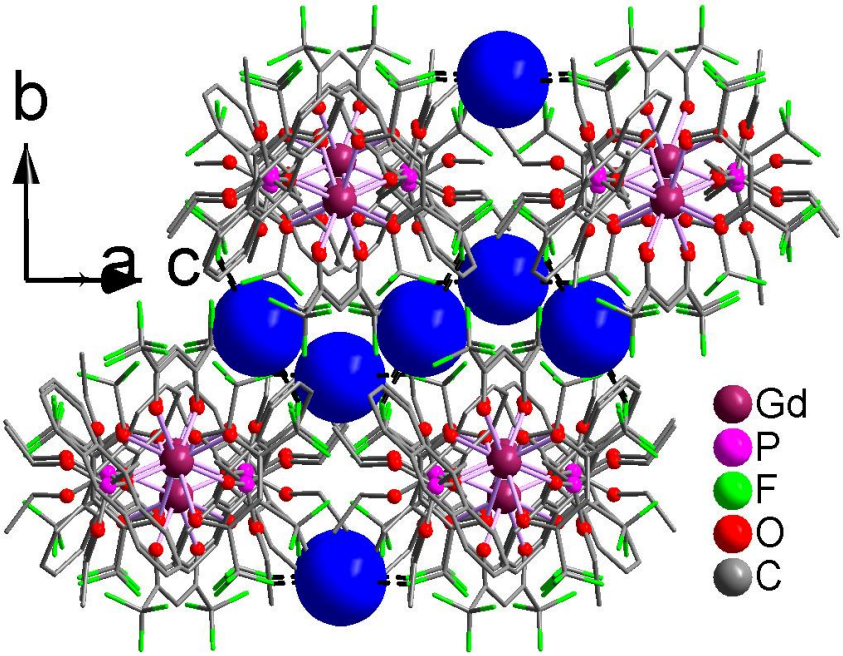

Fig. S16 The supramolecular three dimensional structure of **4**. Blue small balls are lattice water molecules, and all H atoms and F atoms were omitted for clarity. Blue balls represent lattice water.

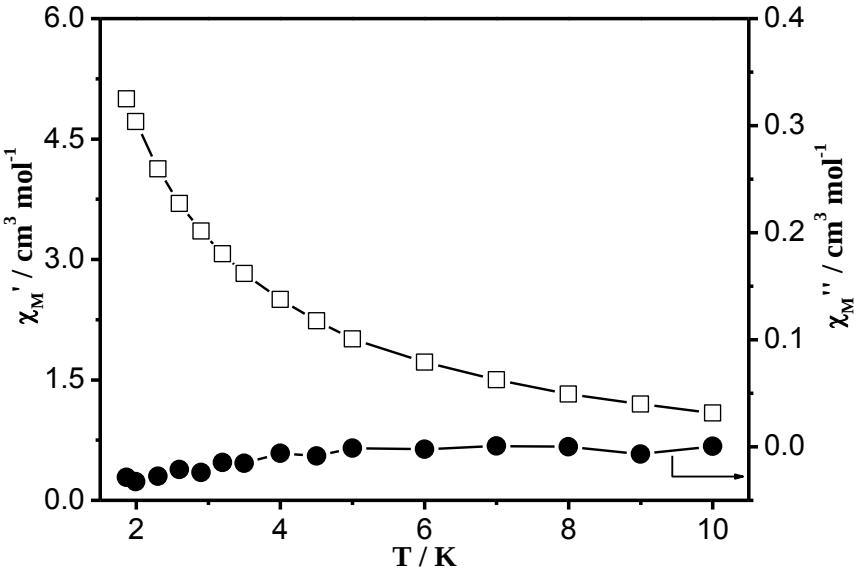

Fig. S17 Temperature dependence of ac susceptibilities of in-phase χ_M' and out-of-phase χ_M" for **1** under zero static field with a frequency of 1000 Hz in the temperature range of 1.8-10 K.

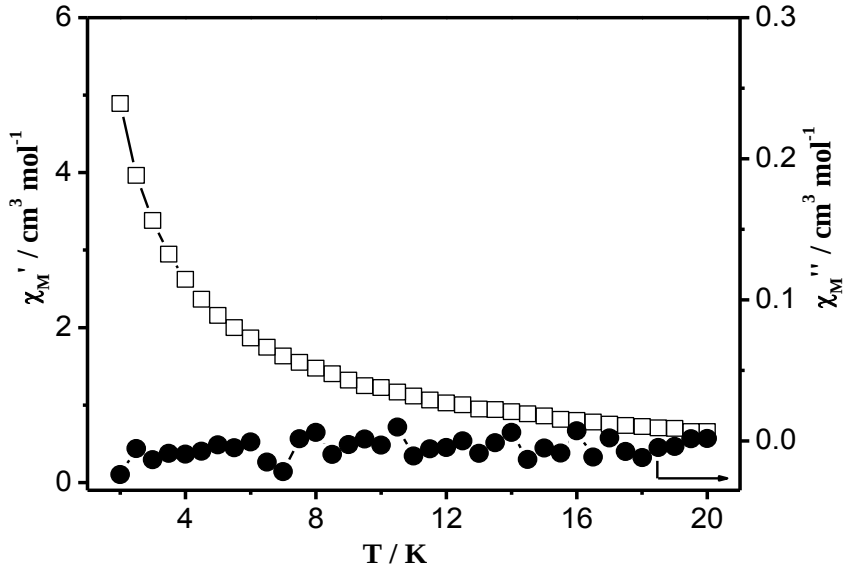

Fig. S18 Temperature dependence of ac susceptibilities of in-phase χ_M' and out-of-phase χ_M" for **3** under zero static field with a frequency of 1000 Hz in the temperature range of 1.8-20 K.

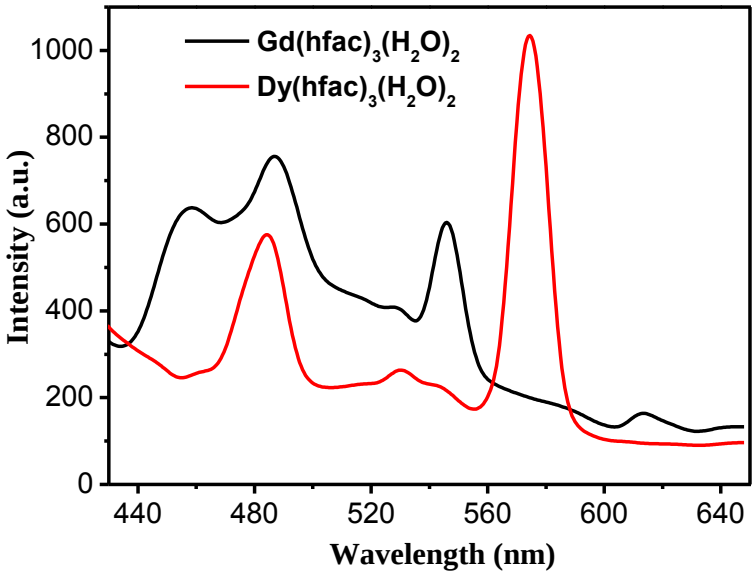

Fig. S19 Solid-state emission spectra for $Gd(hfac)_2(H_2O)_2$ and $Dy(hfac)_2(H_2O)_2$ under λ_{ex} = 370 nm at room temperature.

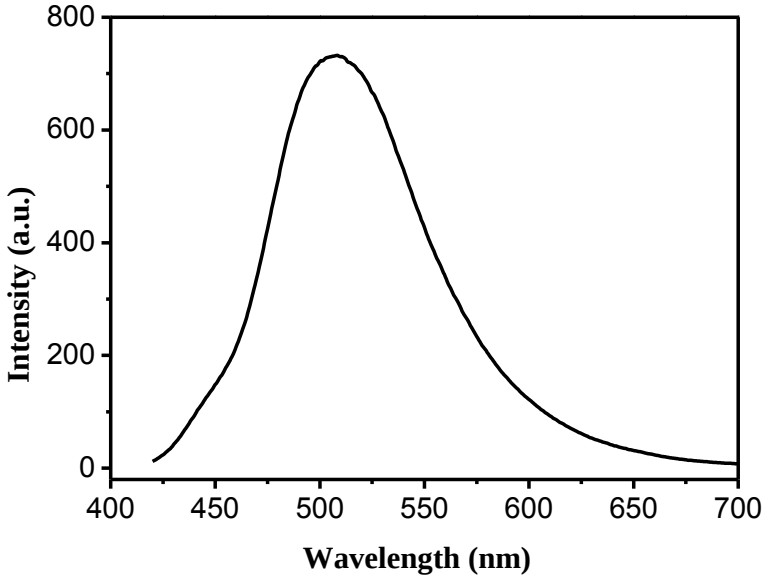

Fig. S20 Solid-state emission spectrum of depma under λ_{ex} = 370 nm at room temperature.