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A series of 3D lanthanide frameworks constructed from aromatic multi- carboxylate ligand: structural diversity, luminescence and magnetic properties

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1 Additional Figures

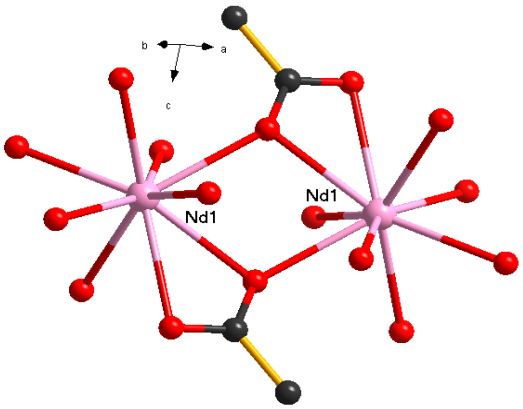

Fig. S1. llustration of an individual dinuclear Nd_2 unit doubly linked by the carboxylic group from Hddp ligands viewed approximately down the *a c*-plane in **1.**

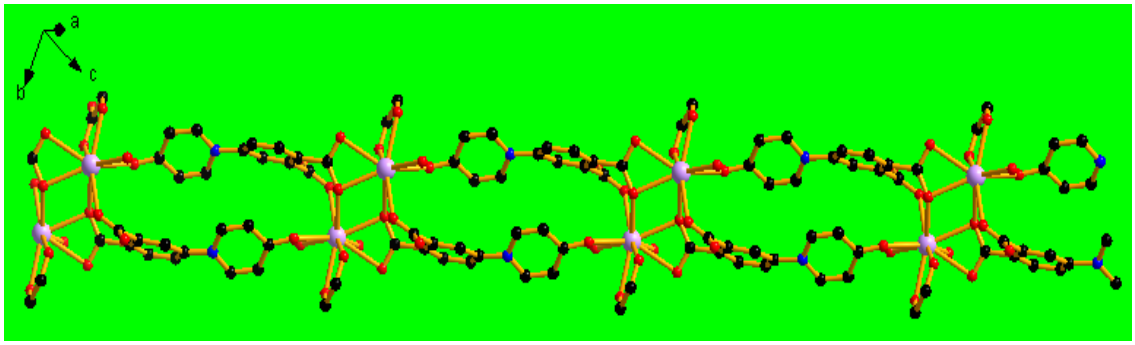

Fig. S2. llustration of 1D double chain linked by the carboxylic group from Hddp ligands viewed along the 011 direction in **1**.

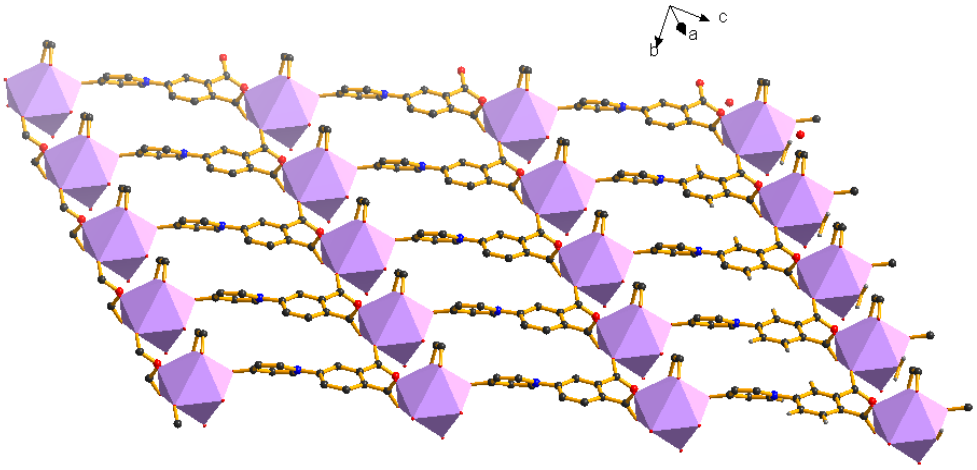

Fig. S3. 2D lattice layer constructed from DPPA and Nd(III) ions viewed down ac plane

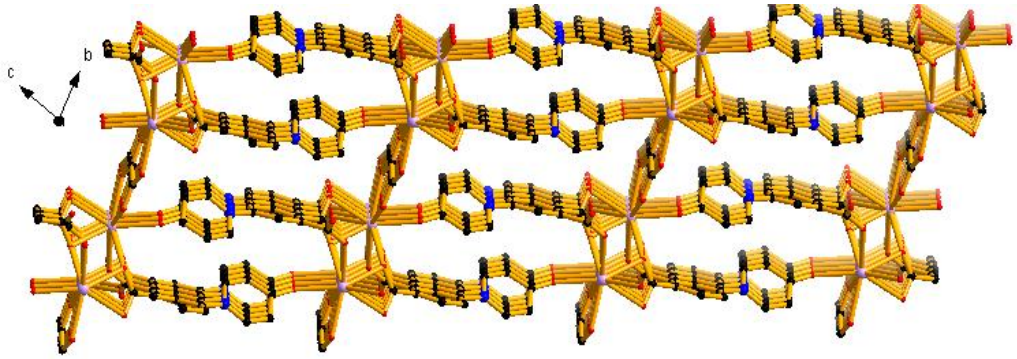

Fig. S4 Prospective view of 3D porous framework with open channels viewed along the [011] direction in **1**.

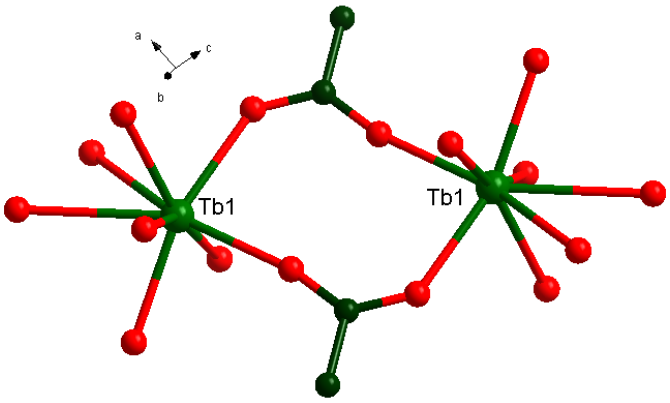

Fig. S5. View of an individual dinuclear Tb_2 units linked by the carboxylic group from HDDP ligands viewed approximately down the *ac*-plane in **3**.

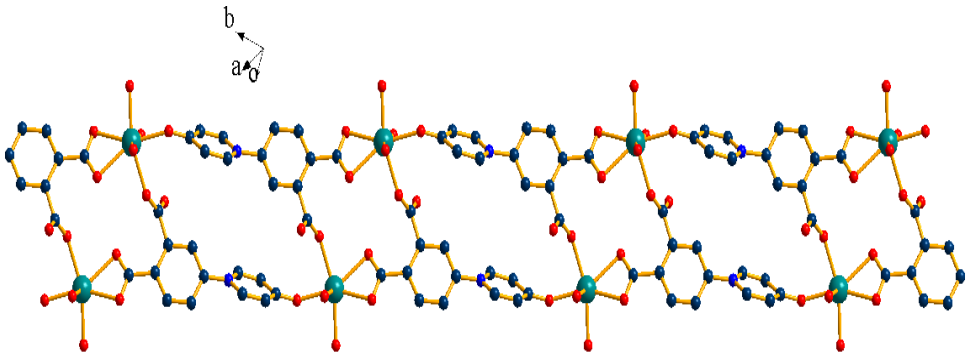

Fig. S6. Projective view of 1D double chain structure of **3** viewed along a b plane

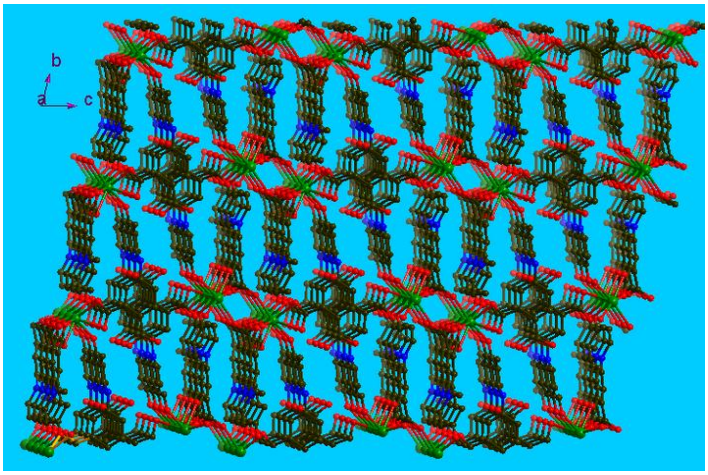

Fig. S7.Projective view of 3D packing structure of **3** viewed along *bc* plane

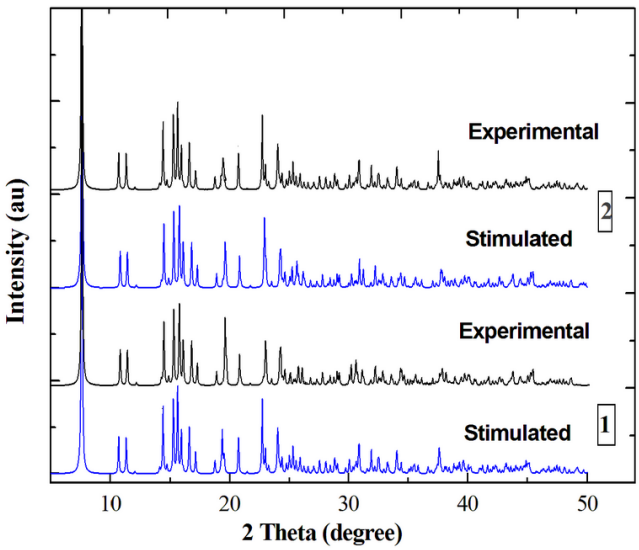

Fig. S8. Comparison of the experimental and simulated PXRD patterns for **1** and **2**

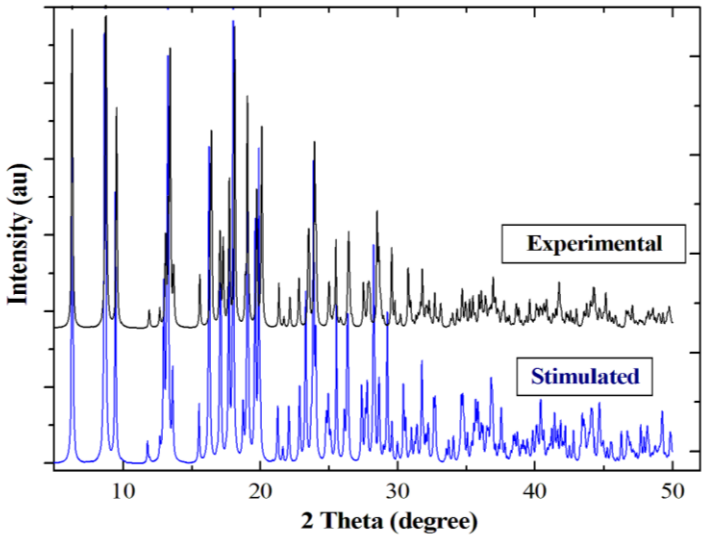

Fig. S9 The X-ray powder diffraction diagrams of microcrystalline powders of **3 (**Tb**)**

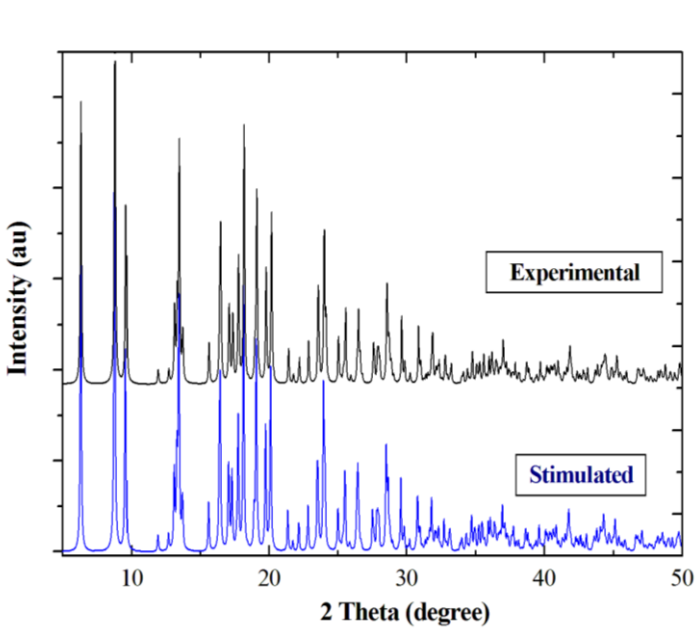

Fig. S10 The X-ray powder diffraction diagrams of microcrystalline powders of **4** (Yb)

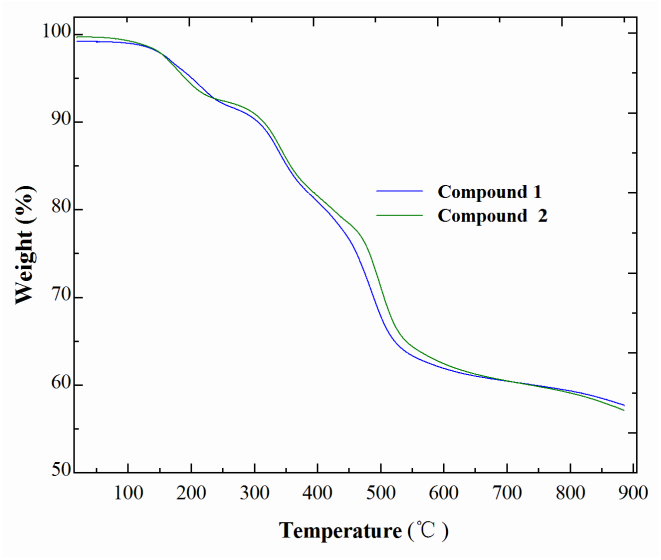

Fig. S 11. The TGA traces for compounds **1** and **2**

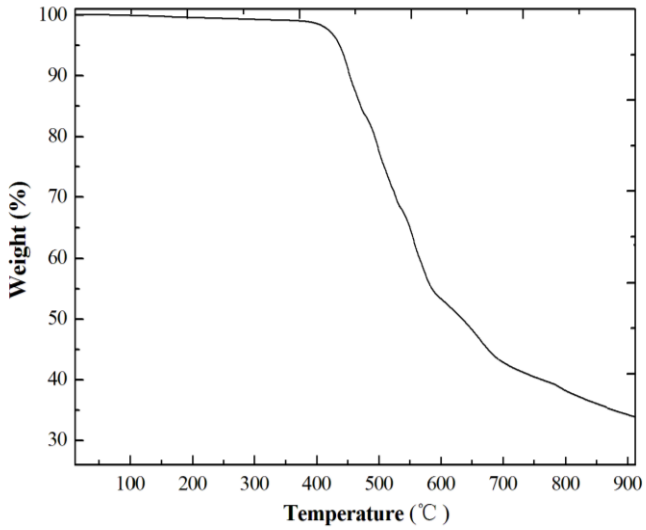

Fig. S12. The thermal gravimetric analysis (TGA) diagram for powder **3**

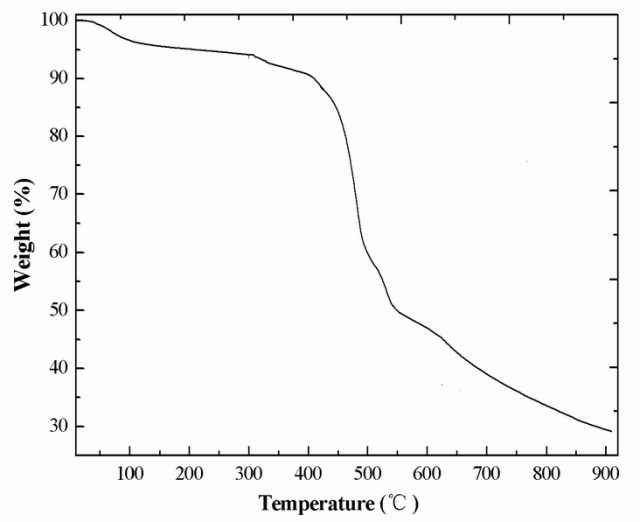

Fig. S13 The thermal gravimetric analysis (TGA) diagram for powder **4**

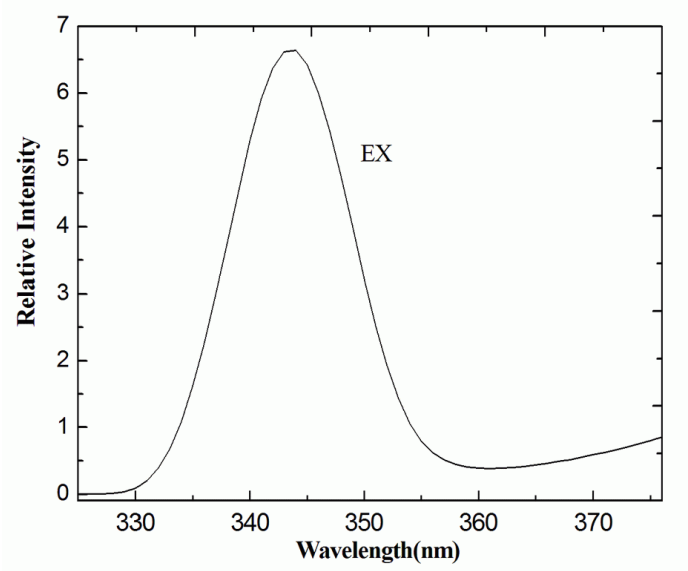

Fig. S14 Excitation spectrum of compound **1** in solid state.

Fitting of the compound 1 based on Sm^{3+} ion and equations employed

The ^6H ground term for Sm(II1) is split by spin-orbit coupling into six levels. The energies, *E(J)*, increase from $^6H_{5/2}$, these energy is

$$E(J) = \lambda[J(J+1) - {}^{35}/_{4}]/2 \qquad eq\ (S1)$$

The energy of the ground state is again taken as the origin. The spin-orbit coupling parameter is of the order of 200 cm^{-1}, such that the first excited state $^6H_{7/2}$ can be populated at room temperature and above. The expression of the magnetic susceptibility taking into account the six states arising from ^6H is:

$$\chi_M = \frac{\sum_{J={}^5/_2}^{{}^{15}/_2} (2J+1)\chi(J)\exp[-E(J)/kT]}{\sum_{J={}^5/_2}^{{}^{15}/_2} (2J+1)\exp[-E(J)/kT]} \qquad \ldots\ldots\ldots\ldots\ldots\ eq\ (1)$$

The $\chi(J)$ is given by ***eq*** (2) and ***E(J)*** by eq (1). X_M may be expanded as:

$$\chi' = \frac{N\beta^2}{3kTx}\frac{a_1x+b_1+(a_2x+b_2)e^{-7x/2}+(a_3x+b_3)e^{-8x}+(a_4x+b_4)e^{-27x/2}+(a_5x+b_5)e^{-20x}+(a_6x+b_6)e^{-55x/2}}{3+4e^{-7x/2}+5e^{-8x}+6e^{-27x/2}+7e^{-20x}+8e^{-55x/2}}$$

$$x = J/kT \qquad eq\ (2)$$

Parameters and value are as follow

$a_1 = 2.143; b_1 = 7.347$
$a_2 = 42.92; b_2 = 1.641$
$a_3 = 283.7; b_3 = -0.6571$
$a_4 = 620.6; b_4 = -1.9400$
$a_5 = 1122; b_5 = -2.835$
$a_6 = 1813; b_6 = -3.556$

Equation (3) was assigned as a molecular field approximation

$$\chi = \frac{\chi'}{1-(2zj'/Ng^2\beta^2)\chi'} \qquad eq\ (3)$$

2 Supporting characterizations

IR spectra of complexes **1-4 .**

For **1**, IR (KBr pellet, cm^{-1}): 3384s, 3181br, 2973m, 1594s, 1529s, 1452s, 1410m, 1338s, 1279m, 1212s, 867m, 810s, 793s, 660s, 569m.

For **2**, IR: 3402s, 3122br, 2953m, 1623s, 1591s, 1413m, 1374s, 1279s, 1087s, 1245s, 929vs, 827s, 556m.

For **3**, IR: 3420vs, 1734s, 1626vs, 1612s, 1442s, 1423s, 1392s, 1329m, 1279s, 1068s, 832s, 763s, 698s.

For **4**, IR: 3415vs, 1762s, 1686vs, 1622s, 1417s,1392s, 1319m, 1273s, 1012vs, 873s, 810m, 663s.

3 Additional Tables

Table S1 Selected bond lengths [Å] and angles [°] for complexes **1**–**4**

Polymer **1**					
Nd(1)-O(3)	2.443(2)	Nd(1)-O(6)	2.445(2)	Nd(1)-O(5)#1	2.460(2)
Nd(1)-O(7)#2	2.476(2)	Nd(1)-O(4)#3	2.498(2)	Nd(1)-O(1)	2.515(2)
Nd(1)-O(1W)	2.522(2)	Nd(1)-O(1)#4	2.573(2)	Nd(1)-O(2)#4	2.625(2)
O(3)-Nd(1)-O(6)	139.20(7)	O(3)-Nd(1)-O(5)#1	97.37(8)	O(6)-Nd(1)-O(5)#1	70.41(8)
O(3)-Nd(1)-O(7)#2	148.95(7)	O(6)-Nd(1)-O(7)#2	66.76(7)	O(5)#1-Nd(1)-O(7)#2	73.65(8)
O(3)-Nd(1)-O(4)#3	76.13(7)	O(6)-Nd(1)-O(4)#3	136.15(7)	O(5)#1-Nd(1)-O(4)#3	143.35(7)
O(7)#2-Nd(1)-O(4)#3	93.30(8)	O(3)-Nd(1)-O(1)	66.09(7)	O(6)-Nd(1)-O(1)	73.14(7)
O(5)#1-Nd(1)-O(1)	75.90(7)	O(7)#2-Nd(1)-O(1)	135.70(7)	O(4)#3-Nd(1)-O(1)	129.55(8)
O(3)-Nd(1)-O(1W)	71.19(8)	O(6)-Nd(1)-O(1W)	133.93(8)	O(5)#1-Nd(1)-O(1W)	72.09(8)
O(7)#2-Nd(1)-O(1W)	77.78(8)	O(4)#3-Nd(1)-O(1W)	71.70(8)	O(1)-Nd(1)-O(1W)	121.60(7)
O(3)-Nd(1)-O(1)#4	84.15(7)	O(6)-Nd(1)-O(1)#4	82.26(7)	O(5)#1-Nd(1)-O(1)#4	139.69(7)
O(7)#2-Nd(1)-O(1)#4	122.17(7)	O(4)#3-Nd(1)-O(1)#4	76.31(7)	O(1)-Nd(1)-O(1)#4	67.97(7)
O(1W)-Nd(1)-O(1)#4	143.27(7)	O(3)-Nd(1)-O(2)#4	125.90(7)	O(6)-Nd(1)-O(2)#4	69.82(7)
O(5)#1-Nd(1)-O(2)#4	135.55(8)	O(7)#2-Nd(1)-O(2)#4	73.07(7)	O(4)#3-Nd(1)-O(2)#4	67.01(7)
O(1)-Nd(1)-O(2)#4	110.11(6)	O(1W)-Nd(1)-O(2)#4	127.03(7)	O(1)#4-Nd(1)-O(2)#4	50.24(6)
Polymer **2**					
Sm(1)-O(1)	2.403(3)	Sm(1)-O(2)#2	2.470(3)	Sm(1)-O(4)#3	2.601(3)
Sm(1)-O(6)	2.414(3)	Sm(1)-O(1W)	2.479(3)	O(2)-Sm(1)#2	2.470(3)
Sm(1)-O(5)#1	2.425(3)	Sm(1)-O(3)	2.493(3)	O(3)-Sm(1)#3	2.524(3)
Sm(1)-O(7)	2.442(3)	Sm(1)-O(3)#3	2.524(3)	Sm(1)-C(1)#4	2.917(3)
O(1)-Sm(1)-O(6)	139.49(8)	O(7)-Sm(1)-O(3)#3	122.36(9)	O(5)#1-Sm(1)-O(1W)	72.38(10)
O(1)-Sm(1)-O(5)#1	97.04(10)	O(2)#2-Sm(1)-O(3)#3	76.18(9)	O(7)-Sm(1)-O(1W)	77.41(10)
O(6)-Sm(1)-O(5)#1	70.41(9)	O(1W)-Sm(1)-O(3)#3	143.06(9)	O(2)#2-Sm(1)-O(1W)	71.71(10)
O(1)-Sm(1)-O(7)	148.24(8)	O(3)-Sm(1)-O(3)#3	67.97(10)	O(1)-Sm(1)-O(3)	66.42(9)
O(6)-Sm(1)-O(7)	67.22(8)	O(1)-Sm(1)-O(4)#3	126.38(8)	O(6)-Sm(1)-O(3)	73.12(9)
O(5)#1-Sm(1)-O(7)	74.27(10)	O(6)-Sm(1)-O(4)#3	69.75(9)	O(5)#1-Sm(1)-O(3)	75.53(10)
O(1)-Sm(1)-O(2)#2	76.26(9)	O(5)#1-Sm(1)-O(4)#3	135.47(10)	O(7)-Sm(1)-O(3)	136.16(8)
O(6)-Sm(1)-O(2)#2	135.90(9)	O(7)-Sm(1)-O(4)#3	72.66(9)	O(2)#2-Sm(1)-O(3)	129.72(9)
O(5)#1-Sm(1)-O(2)#2	143.66(9)	O(2)#2-Sm(1)-O(4)#3	66.80(10)	O(1W)-Sm(1)-O(3)	121.72(10)
O(7)-Sm(1)-O(2)#2	92.65(9)	O(1W)-Sm(1)-O(4)#3	126.66(9)	O(1)-Sm(1)-O(3)#3	84.30(9)
O(1)-Sm(1)-O(1W)	70.86(10)	O(3)-Sm(1)-O(4)#3	110.41(9)	O(6)-Sm(1)-O(3)#3	82.42(9)
O(6)-Sm(1)-O(1W)	133.97(10)	O(3)#3-Sm(1)-O(4)#3	50.73(8)	O(5)#1-Sm(1)-O(3)#3	139.47(9)
Polymer **3**					
Tb(1)-O(10)#1	2.264(4)	Tb(1)-O(5)#2	2.291(4)	Tb(1)-O(9)#3	2.302(4)

Tb(1)-O(6)	2.338(4)	Tb(1)-O(8)#4	2.402(4)	Tb(1)-O(1)	2.428(4)
Tb(1)-O(7)#4	2.477(4)	Tb(1)-O(2)	2.765(6)		
O(10)#1-Tb(1)-O(5)#2	83.09(16)	O(10)#1-Tb(1)-O(9)#3	78.59(15)	O(5)#2-Tb(1)-O(9)#3	84.05(15)
O(10)#1-Tb(1)-O(6)	80.75(14)	O(5)#2-Tb(1)-O(6)	85.64(13)	O(5)#2-Tb(1)-O(8)#4	81.39(14)
O(9)#3-Tb(1)-O(8)#4	79.92(14)	O(6)-Tb(1)-O(8)#4	117.78(14)	O(10)#1-Tb(1)-O(1)	76.11(16)
O(8)#4-Tb(1)-O(1)	122.32(15)	O(9)#3-Tb(1)-O(1)	103.47(17)	O(6)-Tb(1)-O(1)	79.03(15)
O(5)#2-Tb(1)-O(7)#4	114.17(15)	O(9)#3-Tb(1)-O(7)#4	122.82(14)	O(6)-Tb(1)-O(7)#4	79.32(13)
O(8)#4-Tb(1)-O(7)#4	53.03(12)	O(1)-Tb(1)-O(7)#4	81.38(15)	O(10)#1-Tb(1)-O(2)	106.78(17)
O(9)#3-Tb(1)-O(2)	73.40(16)	O(6)-Tb(1)-O(2)	120.73(14)	O(8)#4-Tb(1)-O(2)	79.59(15)
O(1)-Tb(1)-O(2)	48.89(16)	O(7)#4-Tb(1)-O(2)	68.27(16)		
Polymer **4**					
Yb(1)-O(5)#1	2.205(2)	Yb(1)-O(4)#2	2.221(2)	Yb(1)-O(6)	2.227(2)
Yb(1)-O(3)#3	2.280(2)	Yb(1)-O(7)#4	2.305(3)	Yb(1)-O(2)	2.353(2)
Yb(1)-O(1)	2.419(2)				
O(5)#1-Yb(1)-O(4)#2	84.33(9)	O(5)#1-Yb(1)-O(6)	79.94(9)	O(4)#2-Yb(1)-O(6)	87.02(9)
O(5)#1-Yb(1)-O(3)#3	80.70(9)	O(4)#2-Yb(1)-O(3)#3	85.56(8)	O(5)#1-Yb(1)-O(7)#4	78.52(10)
O(6)-Yb(1)-O(7)#4	94.48(10)	O(3)#3-Yb(1)-O(7)#4	87.10(10)	O(4)#2-Yb(1)-O(2)	81.52(9)
O(6)-Yb(1)-O(2)	79.59(9)	O(3)#3-Yb(1)-O(2)	117.66(9)	O(7)#4-Yb(1)-O(2)	116.19(10)
O(4)#2-Yb(1)-O(1)	114.54(9)	O(6)-Yb(1)-O(1)	122.00(8)	O(3)#3-Yb(1)-O(1)	78.07(8)
O(7)#4-Yb(1)-O(1)	79.58(9)	O(2)-Yb(1)-O(1)	54.21(7)		

Symmetry codes for **1**: #1, -x,-y+1,-z+1; #2, -x,-y+2,-z+1; #3, x-1,y+1,z; #4, -x+1,-y+2,-z+1; #5, x+1,y-1,z. for **2**: #1, x,y+1,z; #2, -x+2,-y-1,-z+2; #3, x+1,y+1,z; #4, x+1,y-1,z; #5, x-1,y-1,z; #6, x,y-1,z; #7, x-1,y+1,z; for **3**: #1, -x,-y+1,-z+1; #2, -x,-y+2,-z+1; #3, x-1,y+1,z; #4, -x+1,-y+2,-z+1; #5, x+1,y-1,z. for **4**: #1, x-1,y-1, z; #2, x-1,y,z; #3, -x+1,-y,-z+1; #4, x+1,y-1,z; #5, x+1, y, z; #6,x+1,y+1, z. for **5**: #1, x+1,y+1,z; #2, x+1, y, z; #3, x+1,y-1,z; #4, -x+1,-y+1,-z+1; #5, x-1, y, z; #6, x-1,y-1,z. #7 x-1,y+1, z.

Table S2 The Hydrogen bond lengths (Å) and angles (°) for complexes **1** to **4**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Polymer **1**				
O(1W)-H(11)...O(3)#3	0.839(10)	1.931(19)	2.718(3)	156(4)
O(1W)-H(12)...O(7)#5	0.843(10)	2.057(17)	2.861(3)	160(3)
O(2W)-H(22)...O(5)	0.838(10)	2.132(11)	2.969(4)	177(6)
Polymer **2**				
O1(W)-H1(WB)... O(1)	0.747	2.024	152.70	2.709
O(1W)-H(1WB)...O(6)	0.747	2.479	118.24	2.908
O(1W)-H1(WA)... O(7)	0.732	2.137	165.43	2.851
O1W-H1(WA)... O(6)	0.732	2.573	110.15	2.908
O2(W)-H(2WB) ...O(5)	0.811	2.153	170.62	2.956

Polymer **3**				
O(3)-H(3)...O(2)	0.82	1.64	2.431(8)	162.7
Polymer **4**				
O(9)-H(9)...O(8)	0.81(6)	1.64(6)	2.399(5)	155(7)

Symmetry codes for **1**: #1, -x,-y+1,-z; #2, -x+1,-y+1, -z+1; #3, -x,-y,-z+1; #4, -x+1,-y,-z+1; #5, x-1,y,z; for **2**: #1 -x+1,-y,-z+1; #2 -x+1,-y+1,-z ;#3 -x,-y+1, -z; #4 -x,-y,-z; for **3**: #1, -x,-y+1,-z+1; #2, -x,-y+2,-z+1; #3, x-1, y+1,z; #4, -x+1,-y+2,-z+1; #5, x+1, y-1, z; for **4**: #1, x-1, y-1, z; #2, x-1, y, z; #3, -x+1,-y,-z+1; #4, x+1, y-1, z; #5, x+1, y, z.