Electronic Supplementary Information for CrystEngComm

A series of lanthanide–organic polymers incorporating ethyl 4, 5-imidazole-dicarboxylato and formate coligands: structures, luminescent and magnetic properties

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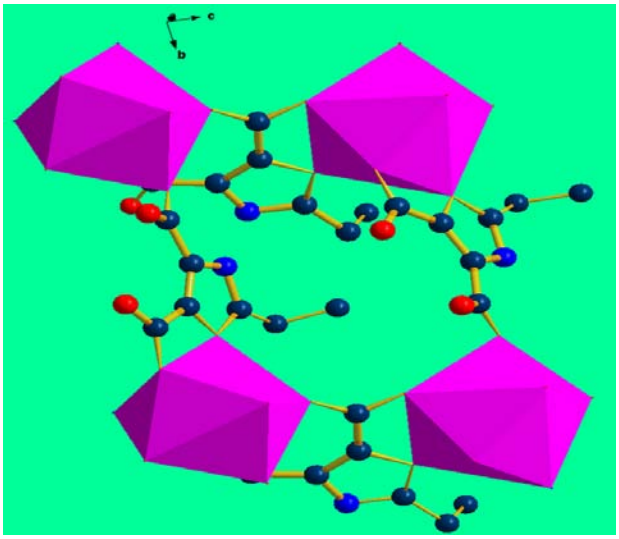
1 Experimental detail

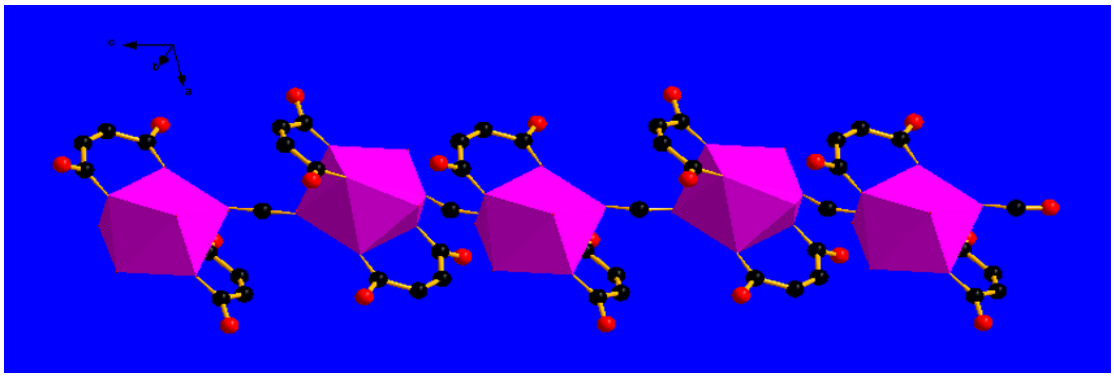
1. 1 Crystallographic data collection and refinement

Single-crystal diffraction data of complexes **1–4** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97), and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97). An empirical absorption correction was applied using the SADABS program. In the structures, the disordered ethyl carbon atoms of Heimda ligand and formate oxygen atoms etc were restrained (except the polymer **4**) in order to obtain reasonable thermal parameters. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms.

2 Additional Figures



(a)



(b)

Figure S1. (a) llustration of an individual Sm_4 square lattice motifs linked by the Hpimda ligands viewed approximately down the *ac*-plane in **1**. (b) Polyhedral view of the Sm(2) ions linked by the formate groups to produce an 1D infinite chain.

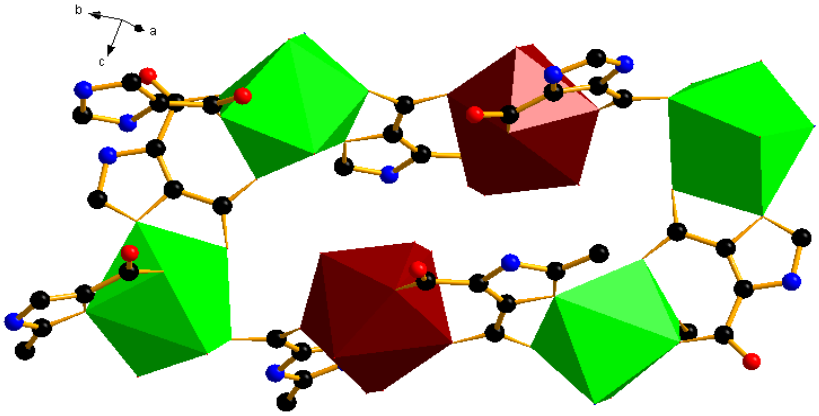


Figure S2. Polyhedral view of an individual Sm_6 hexagon motifs and coordination environment viewed approximately down the *bc* plane in **1**. Color codes: Sm(1) green; Sm(2) purple.

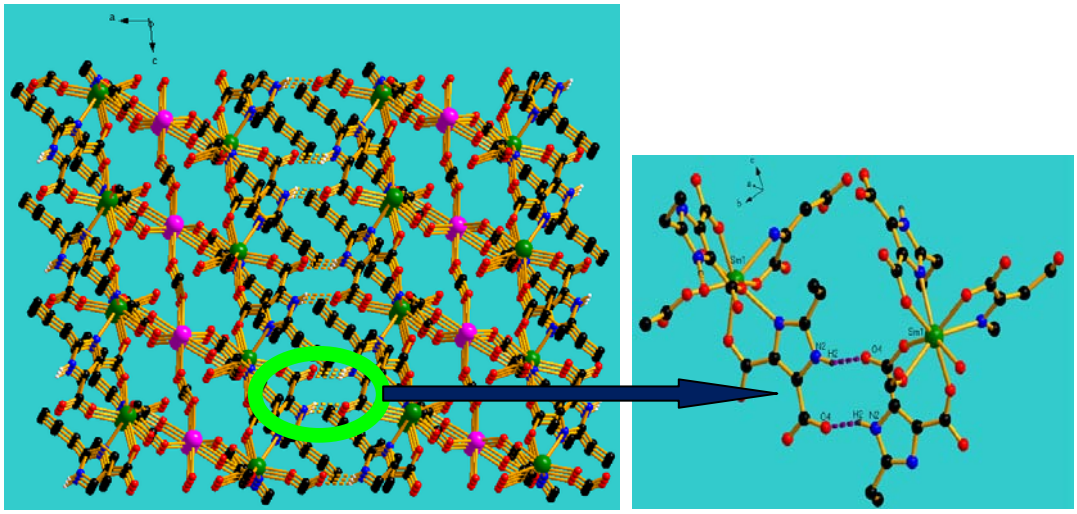


Figure S3. Side view of the 3D packing diagram of **1** interconnected by the hydrogen bonding interaction along *a* axis. Non hydrogen bonding hydrogen atoms and free water molecules have been omitted for clarity.

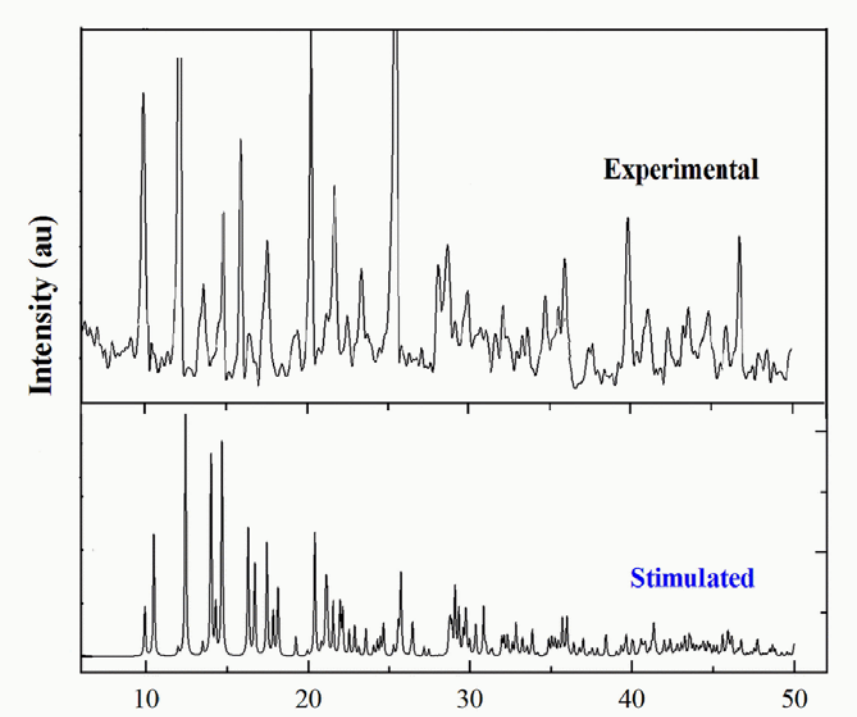


Figure S4 The X-ray powder diffraction diagrams of microcrystalline powders of **1**

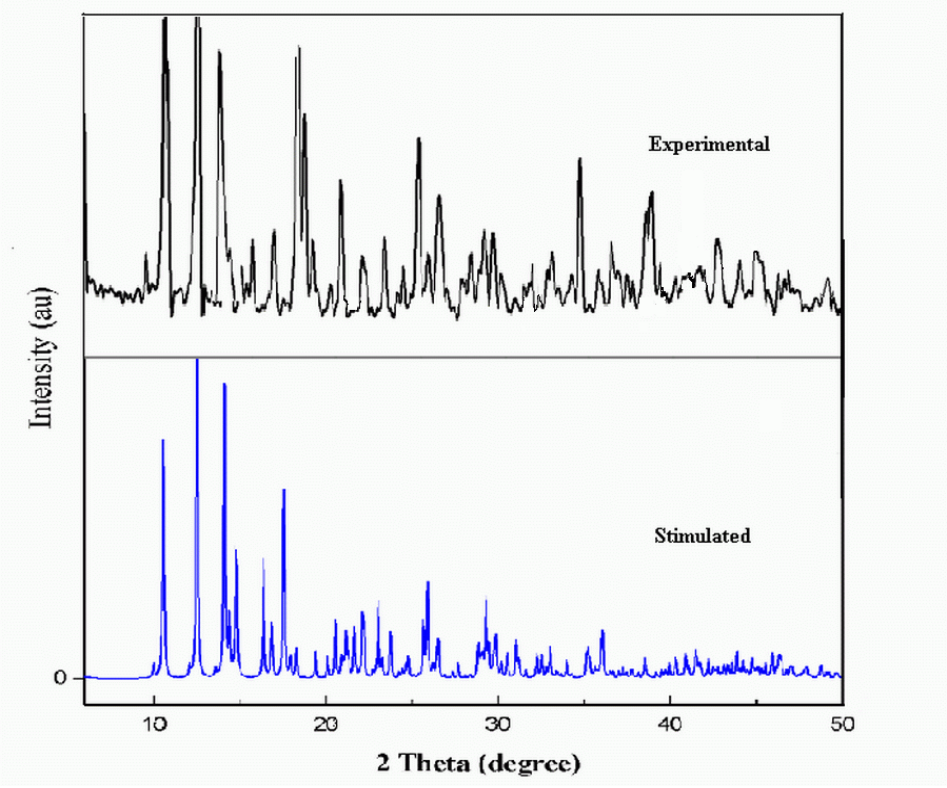


Figure S5 The X-ray powder diffraction diagrams of microcrystalline powders of **2**

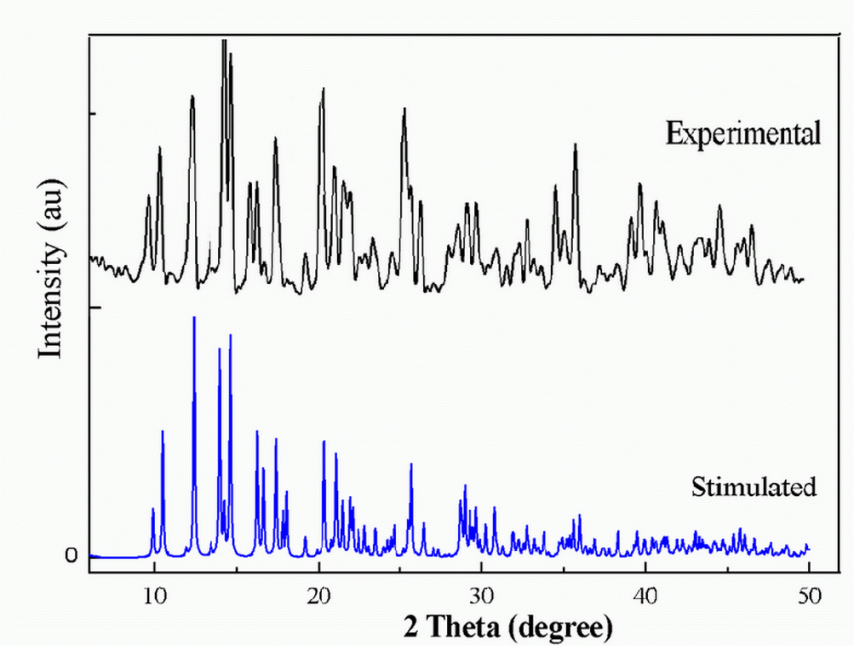


Figure S6 The X-ray powder diffraction diagrams of polymer **3**

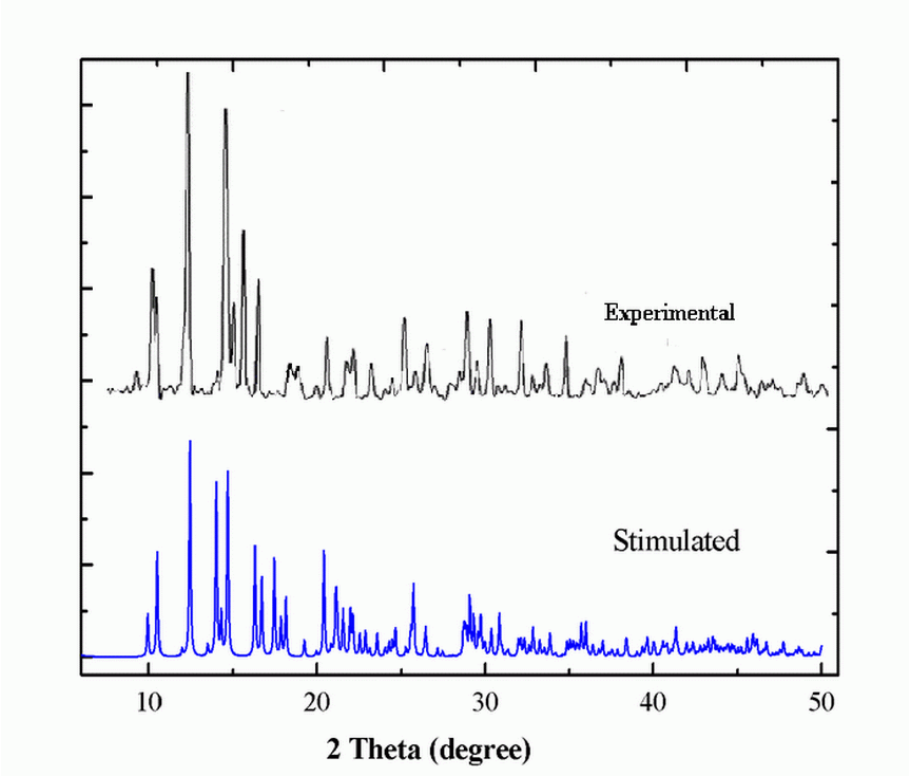


Figure S7 The X-ray powder diffraction diagrams of polymers microcrystalline powders **4**

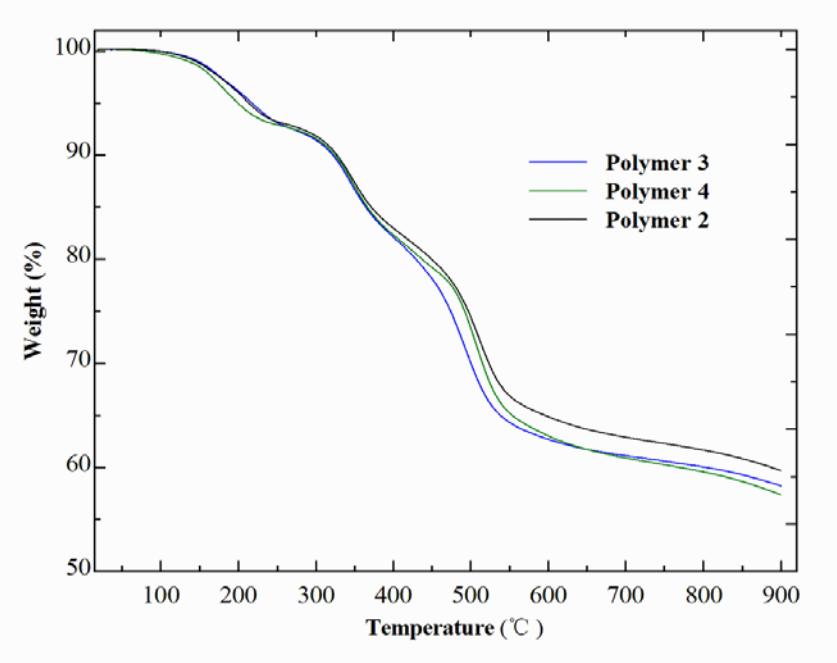


Figure S8. The TGA analysis diagrams of complexes **2**, **3** and **4**

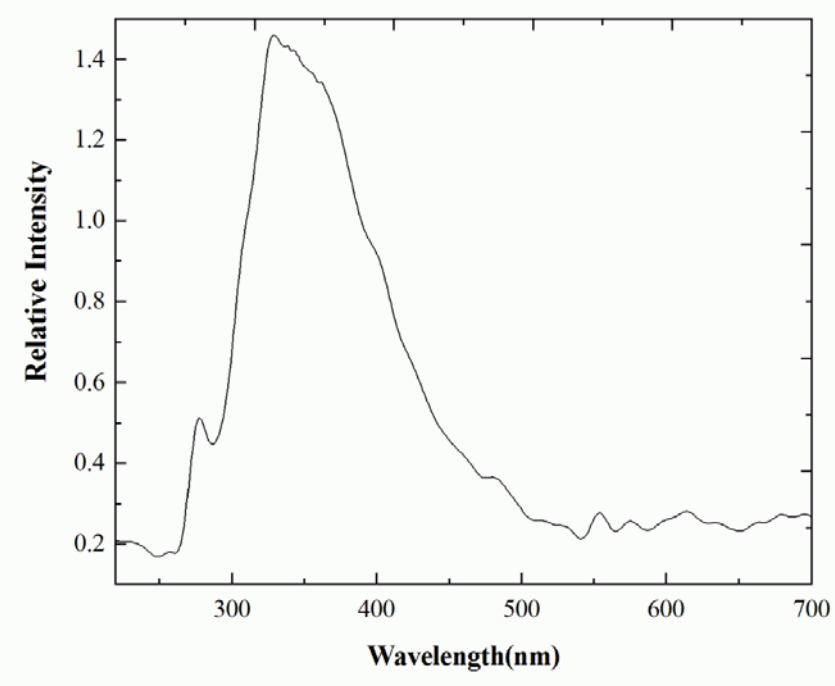


Figure S9. Photoemission spectrum of the free H_3eimda ligand in methanolic suspension state

3 Magnetic Properties

Fitting of the polymer **1** based on Sm^{3+} ion and equation S1

1 Sm. 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:

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

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

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

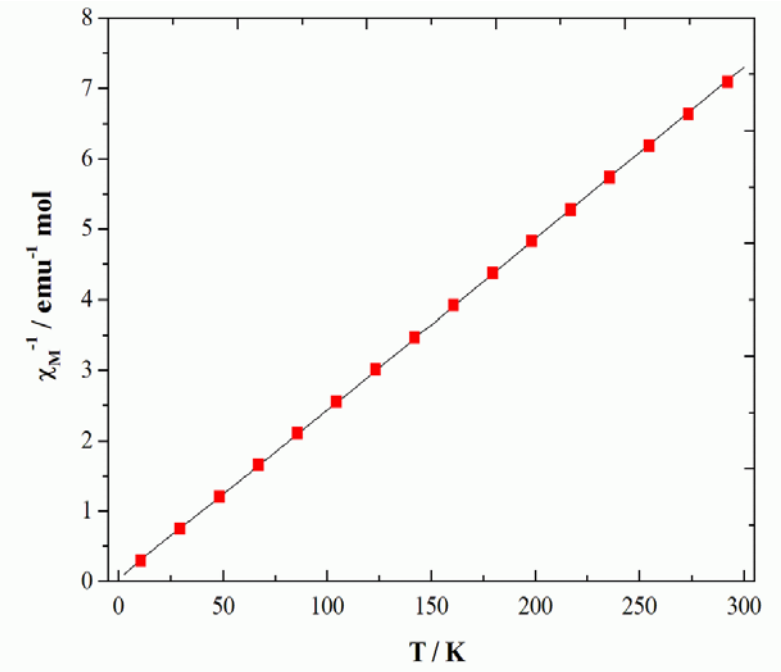


Figure S10 Temperature dependence of the inverse susceptibility for polymer **3** between 2 and 300 K.

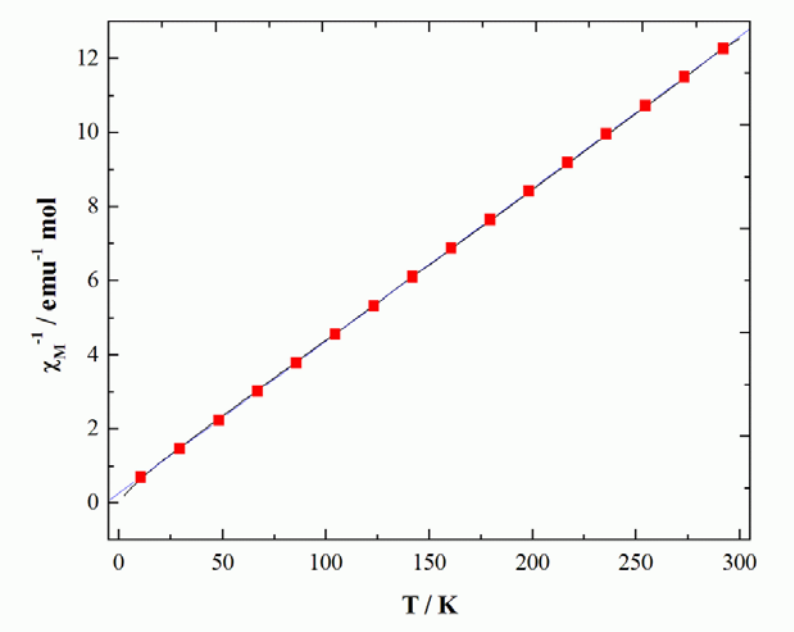


Figure S11 Temperature dependence of the inverse susceptibility for polymer **4** between 2 and 300 K.

4 Additional Tables

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

Polymer **1**					
Sm(1)-O(6)#1	2.305(2)□	Sm(2)-O(10)#3	2.431(3)□	Sm(1)-N(3)	2.600(3)□
Sm(1)-O(7)#1	2.349(2)□	O(7)-Sm(1)#7	2.349(2)□	Sm(2)-O(2)#3	2.319(3)□
Sm(1)-O(8)	2.381(2)□	Sm(1)-O(9)	2.465(3)□	Sm(1)-N(1)	2.590(3)□
Sm(1)-O(4)#2	2.393(2)□	Sm(2)-O(12)	2.480(8)	Sm(2)-O(3)#3	2.421(2)□
Sm(1)-O(1)	2.411(2)□	O(6)-Sm(1)#7	2.305(2)	O(7)-Sm(1)#7	2.349(2)
O(6)#1-Sm(1)-O(7)#1	75.29(9)□	O(2)#3-Sm(2)-O(3)	145.33(9)□	O(4)#2-Sm(1)-N(1)	151.70(9)□
O(6)#1-Sm(1)-O(8)	107.33(9)□	O(2)-Sm(2)-O(3)	75.81(9)	O(1)-Sm(1)-N(1)	64.87(8)□
O(7)#1-Sm(1)-O(8)	150.79(8)□	O(2)-Sm(2)-O(10)	146.72(9)	O(9)-Sm(1)-N(1)	97.64(11)□
O(8)-Sm(1)-O(1)	73.93(8)□	O(7)#1-Sm(1)-O(1)	121.32(8)□	O(6)#1-Sm(1)-N(3)	73.14(9)□
O(4)#2-Sm(1)-O(1)	132.68(8)□	O(3)-Sm(2)-O(10)	76.79(10)	O(7)#1-Sm(1)-N(3)	139.34(9)□
O(8)-Sm(1)-O(4)#2	75.24(8)□	O(1)-Sm(1)-N(3)	75.85(9)□	O(8)-Sm(1)-N(3)	65.10(8)□
O(6)#1-Sm(1)-O(1)	144.48(9)□	O(3)-Sm(2)-O(12)	128.6(2)□	O(4)#2-Sm(1)-N(3)	120.71(9)□
Polymer **2**					
Dy(1)-O(6)#1	2.270(3)□	Dy(2)-O(10)	2.382(3)□	Dy(1)-N(3)	2.573(3)□
Dy(1)-O(7)#1	2.318(3)□	Dy(2)-O(3)	2.389(3)□	Dy(2)-O(2)	2.279(3)□
Dy(1)-O(8)	2.346(3)□	Dy(2)-O(12)#3	2.443(9)□	Dy(2)-O(12)	2.443(9)
Dy(1)-O(4)#2	2.357(3)□	Dy(2)-O(2)#3	2.279(3)□	Dy(2)-O(12')#4	2.363(11)□
Dy(1)-O(1)	2.378(3)□	O(4)-Dy(1)#6	2.357(3)□	O(7)-Dy(1)#7	2.318(3)
Dy(1)-O(9)	2.414(3)□	O(6)-Dy(1)#7	2.270(3)□	Dy(1)-N(1)	2.548(3)□
O(7)#1-Dy(1)-N(1)	74.61(10)□	O(6)#1-Dy(1)-O(8)	106.88(11)	O(3)-Dy(2)-O(12)#3	75.9(2)□
O(9)-Dy(1)-N(1)	97.65(13)□	O(7)#1-Dy(1)-O(8)	150.38(10)	O(2)#3-Dy(2)-O(12)	73.7(2)□
O(6)#1-Dy(1)-N(3)	72.76(11)□	O(6)#1-Dy(1)-O(1)	144.63(11)	O(2)-Dy(2)-O(12)	69.4(2)□
O(8)-Dy(1)-N(3)	66.02(10)□	O(7)#1-Dy(1)-O(1)	121.38(10)	O(12')#4-Dy(2)-O(12)	14.8(2)□
O(4)#2-Dy(1)-N(3)	121.33(11)	O(8)-Dy(1)-O(1)	73.45(10)□	O(10)-Dy(2)-O(12)	143.6(2)□
O(1)-Dy(1)-N(3)	75.63(11)□	O(4)#2-Dy(1)-O(1)	132.27(10)	O(3)#3-Dy(2)-O(12)	75.9(2)□
Polymer **3**					
O(12')-Ho(2)#1	2.359(6)□	Ho(1)-O(1)	2.390(3)□	Ho(2)-O(12')#1	2.359(6)□
Ho(1)-O(6)#2	2.282(3)□	Ho(1)-O(9)	2.418(4)□	Ho(2)-O(10)#4	2.397(3)□
Ho(1)-O(7)#2	2.327(3)□	Ho(1)-N(1)	2.551(4)□	Ho(2)-O(10)	2.397(3)□
Ho(1)-O(8)	2.349(3)□	Ho(1)-N(3)	2.566(4)□	Ho(2)-O(3)#4	2.398(3)□

Ho(1)-O(4)#3	2.374(3)□	Ho(2)-O(2)#4	2.290(3)□	Ho(2)-O(12)#4	2.409(6)
O(6)#2-Ho(1)-O(7)#2	75.88(11)□	O(4)#3-Ho(1)-O(1)	132.47(10)	O(8)-Ho(1)-N(3)	65.85(11)□
O(6)#2-Ho(1)-O(8)	107.03(11)	O(6)#2-Ho(1)-N(1)	94.19(12)□	O(4)#3-Ho(1)-N(3)	121.26(11)
O(7)#2-Ho(1)-O(8)	150.64(10)	O(7)#2-Ho(1)-N(1)	74.62(10)□	O(1)-Ho(1)-N(3)	75.55(12)□
O(6)#2-Ho(1)-O(4)#3	78.79(12)□	O(8)-Ho(1)-N(1)	132.87(10)	O(9)-Ho(1)-N(3)	142.62(12)
O(7)#2-Ho(1)-O(4)#3	76.74(10)□	O(4)#3-Ho(1)-N(1)	151.36(11)	N(1)-Ho(1)-N(3)	81.87(11)□
O(8)-Ho(1)-O(4)#3	75.30(10)□	O(1)-Ho(1)-N(1)	65.69(11)□	O(2)#4-Ho(2)-O(2)	91.42(17)□
O(6)#2-Ho(1)-O(1)	144.70(11)	O(9)-Ho(1)-N(1)	97.88(12)□	O(2)-Ho(2)-O(10)	146.65(11)
O(7)#2-Ho(1)-O(1)	121.55(10)	O(6)#2-Ho(1)-N(3)	72.97(12)□	O(8)-Ho(1)-N(3)	65.85(11)□
O(8)-Ho(1)-O(1)	73.33(10)□	O(7)#2-Ho(1)-N(3)	139.09(11)	O(2)#4-Ho(2)-O(2)	91.42(17)□
Polymer **4**					
Er(1)-O(2)#1	2.256(3)	Er(1)-O(3)#1	2.381(3)	Er(2)-O(4)#5	2.336(3)
Er(1)-O(2)	2.256(3)	Er(1)-O(3)	2.381(3)	Er(2)-O(1)	2.366(3)
Er(1)-O(1W)	2.359(4)	Er(2)-O(7)#4	2.251(3)	Er(2)-N(1)	2.521(3)
Er(1)-O(10)#2	2.359(13)	Er(2)-O(6)#4	2.305(3)	Er(2)-N(3)	2.553(4)
Er(1)-O(10)#3	2.359(13)	Er(2)-O(5)	2.319(3)	O(4)-Er(2)#6	2.336(3)
O(10)-Er(1)#2	2.359(13)	O(7)-Er(2)#7	2.251(3)	O(6)-Er(2)#7	2.305(3)
O(2)#1-Er(1)-O(2)	90.8(2)	O(2)-Er(1)-O(9)	69.2(3)	O(1W)#1-Er(1)-O(9)	81.9(3)
O(2)-Er(1)-O(1W)	147.03(12)	O(1W)-Er(1)-O(3)	76.12(13)	O(3)#1-Er(1)-O(9)	76.0(3)
O(2)#1-Er(1)-O(10)#2	85.1(3)	O(10)#3-Er(1)-O(3)	69.5(3)	O(2)-Er(1)-O(9)#1	73.4(3)
O(2)-Er(1)-O(10)#2	77.1(3)	O(3)#1-Er(1)-O(3)	129.94(15)	O(3)-Er(1)-O(9)#1	76.0(3)
O(2)-Er(1)-O(3)#1	145.12(12)	O(2)#1-Er(1)-O(9)	73.4(3)	O(9)-Er(1)-O(9)#1	125.7(4)

Symmetry transformations used to generate equivalent atoms for **1**: #1 x,-y,z-1/2 ; #2 x,y-1,z ; #3 -x+1,y,-z+1/2 ;#4 -x+1,-y+1,-z+1; #5 x,-y+1,z-1/2; #6 x,y+1,z ; #7 x,-y,z+1/2. for **2**: #1 -x+1,-y+1,-z+1. #2 x ,-y, z-1/2. #3 x, y-1,z. #4 -x+1,y,-z+1/2. #5 x,-y+1,z-1/2. #6 x, y+1,z #7 x,-y, z+1/2. for **3**: #1 -x+1,-y+1,-z+1. #2 x,-y,z-1/2. #3 x, y-1, z. #4 -x+1 , y,-z+1/2 #5 x,-y+1, z-1/2. #6 x, y+1, z. #7 x,-y, z+1/2. for **4**: #1 -x+1,y,-z+1/2 #2 -x+1,-y+1,-z+1 #3 x,- y+1, z-1/2. #4 x, -y, z-1/2. #5 x, y-1, z. #6 x, y+1, z #7 x,-y, z+1/2. #8 -x+1, y+1,-z+1/2 . #9 -x+3/2,-y+1/2,-z+1

Table S2 The Hydrogen bond lengths (Å) and angles (°) for polymers **1**, **2**, **3** and **4**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)□
Polymer **1**				
N(4)-H(4A)...O(5)#8	0.86	1.91	2.740(6)	163□
N(4)-H(4A)...O(5B)#8	0.86	1.96	2.781(15)	160□
O(11)-H(11B)...O(9)#3	0.82	2.23	2.715(5)	118□
O(11)-H(11A)...O(1)	0.82	2.20	2.957(5)	152□
O(10)-H(10A)...O(8)#10	0.82	2.05	2.853(4)	165□
O(9)-H(9D)...O(11)#3	0.82	1.92	2.715(5)	162□
O(9)-H(9D)...O(11)#3	0.82	1.92	2.715(5)	162□
O(9)-H(9B)...O(11)#1	0.83	2.30	3.116(5)	169
Polymer **2**				
O(9)-H(9B)...O(11)#1	0.82	2.27	3.077(6)	169□
O(9)-H(9D)...O(11)#3	0.82	1.92	2.707(5)	161□
O(9)-H(9D)...O(11)#3	0.82	1.92	2.707(5)	161□
O(10)-H(10A)...O(8)#8	0.82	2.05	2.848(4)	165□
O(11)-H(11A)...O(1)	0.82	2.18	2.925(5)	152□
O(11)-H(11B)...O(9)#3	0.82	2.22	2.707(5)	118□
N(4)-H(4A)...O(5B)#10	0.86	1.95	2.78(2)	160□
N(4)-H(4A)...O(5)#10	0.86	1.92	2.752(7)	164
Polymer **3**				
O(9)-H(9B)...O(11)#1	0.82	2.29	3.094(6)	169
O(9)-H(9D)...O(11)#3	0.82	1.92	2.706(5)	161
O(9)-H(9C)...O(3)#2	0.82	2.30	3.055(5)	154
O(9)-H(9D)...O(11)#3	0.82	1.92	2.706(5)	161
O(10)-H(10A)...O(8)#8	0.82	2.06	2.861(5)	165
O(11)-H(11A)...O(1)	0.82	2.17	2.925(5)	152
O(11)-H(11B)...O(9)#3	0.82	2.22	2.706(5)	118
O(11)-H(11C)...O(12)	0.82	2.42	3.119(1)	143
N(4)-H(4A)...O(5B)#10	0.86	1.95	2.773(2)	161
Polymer **4**				
O(9)-H(9D)...O(11)#3	0.82	1.92	2.708(6)	161.3
O(10)-H(10A)...O(8)#8	0.82	2.06	2.857(5)	165.5
O(11)-H(11A)...O(1)	0.82	2.15	2.899(6)	151.8
O(11)-H(11B)...O(9)#3	0.82	2.22	2.708(6)	118.8
N(4)-H(4A)...O(5B)#10	0.86	1.94	2.76(3)	158.8
N(4)-H(4A)...O(5)#10	0.86	1.91	2.751(9)	164.9

Symmetry transformations used to generate equivalent atoms for **1**: #1 x,-y,z-1/2; #2 x,y-1,z; #3 -x+1,y,-z+1/2; #4 -x+1,-y+1,-z+1 #5 x,-y+1,z-1/2 #6 x,y+1,z; #7 x,-y,z+1/2; #8 -x+3/2,-y+1/2,-z+1 #9 -x+1,-y+1,-z; #10 -x+1,y+1,-z+1/2. for **2**: #1 x,-y,z-1/2; #2 x,y-1,z; #3 -x+1,y,-z+1/2; #4 -x+1,-y+1,-z+1; #5 x,-y+1,z-1/2; #6 x,y+1,z ; #7 x,-y,z+1/2. for **3**: #1 x,-y,z-1/2 #2 x,y-1,z #3 -x+1,y,-z+1/2. #4 -x+1,-y+1,-z+1 #5 x,-y+1,z-1/2 #6 x,y+1,z #7 x,-y,z+1/2 #8 -x+1,y+1,-z+1/2 #9 -x+1,-y+1,-z #10 -x+3/2,-y+1/2,-z+1. for **4**: #1 x,-y,z-1/2; #2 x,y-1,z;#3 -x+1,y,-z+1/2; #4 -x+1,-y+1,-z+1; #5 x,-y+1,z-1/2; #6 x,y+1,z; #7 x,-y,z+1/2 #8 -x+1,y+1,-z+1/2. #9 -x+1, -y+1,-z. #10 -x+3/2,-y+1/2,-z+1