Electronic Supplementary Information for Dalton Transactions
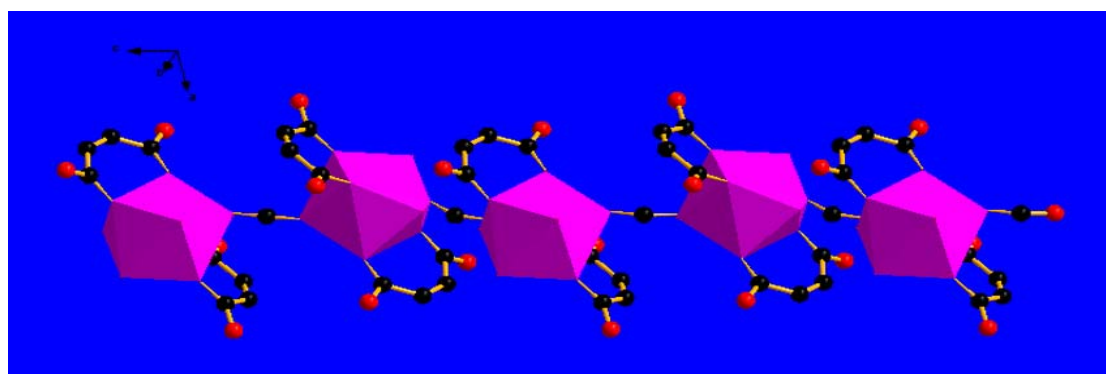
Electronic Supplementary Information for

A series of lanthanide–organic polymers incorporating nitrogen-heterocyclic and aliphatic dicarboxylate mixed –ligands: structures, luminescent and magnetic properties

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Jian Ge Wang, Ng Seik Weng and Xin-Ge Shi

(a)

(b)
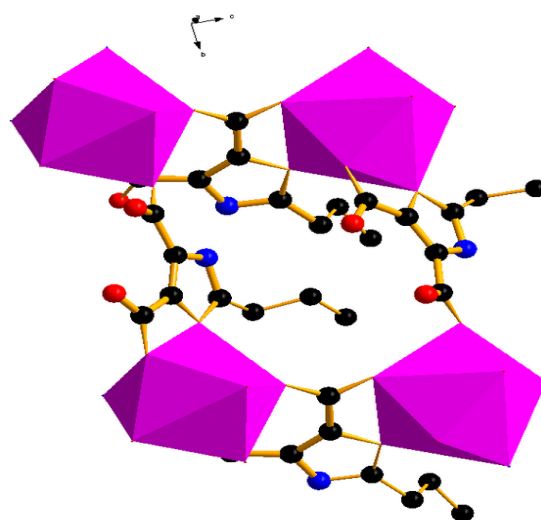
Figure S1. (a) llustration of an individual Sm₄ square lattice motifs linked by the Hpimda ligands viewed approximately down the *ac*-plane in **1**. (b) Polyhedral view of the Sm(2) ions linked by the formate groups to produce an 1D infinite chain.
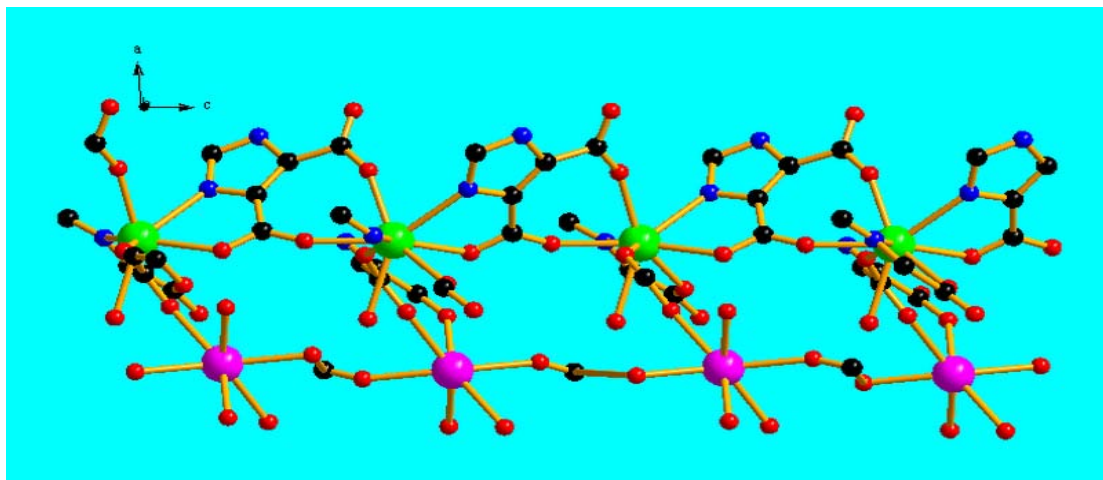
Figure S2. Projective view of the 1D double chain in **1** constructed by the pimda ligand. (Sm (1) green ball, Sm(2) pink ball)
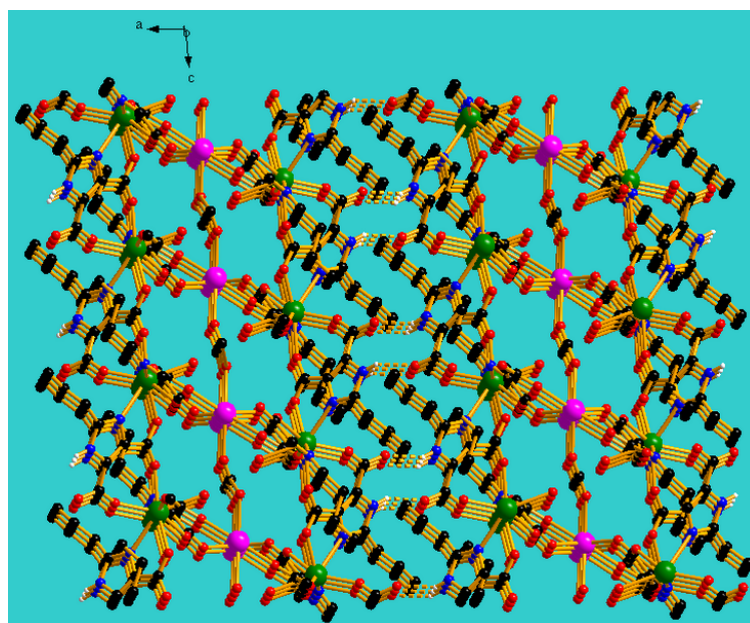

Figure S3 Side view of the 3D packing diagram of **1** interconnected by the hydrogen bonding interaction along *a* axis. Non hydrogen bonding hydrogen atoms and free water molecules have been omitted for clarity.
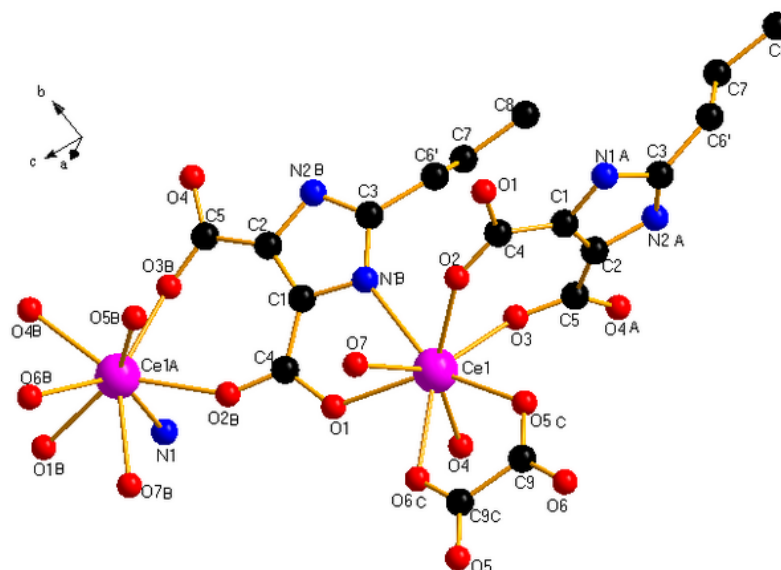
Figure S4. Coordination environments of the Ce(III) ions in complex **6** with the atoms labeling scheme. Symmetry codes follow: A: $x, -y+1/2, z-1/2$. B: $-x+1, y+1/2, -z+1/2$. C: $-1+x, -y+1/2, z-1/2$. D: $x+1, -y, -z$.
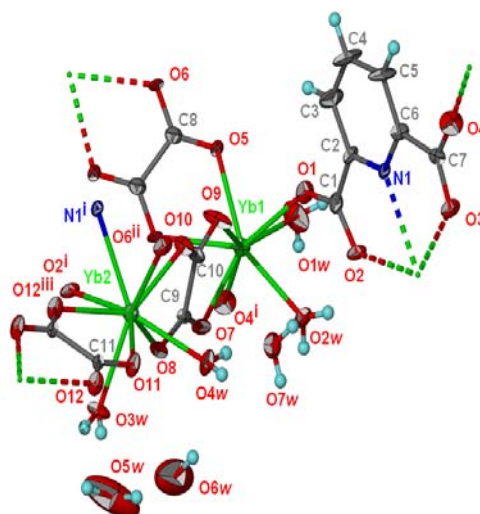

Figure S5. Coordination environments of the Yb(III) ions in complex **7** with the atoms labeling scheme. Symmetry codes follow: #1 x+1, y+1, z; #2 -x+1, -y+2, -z; #3 x+1, y, z.
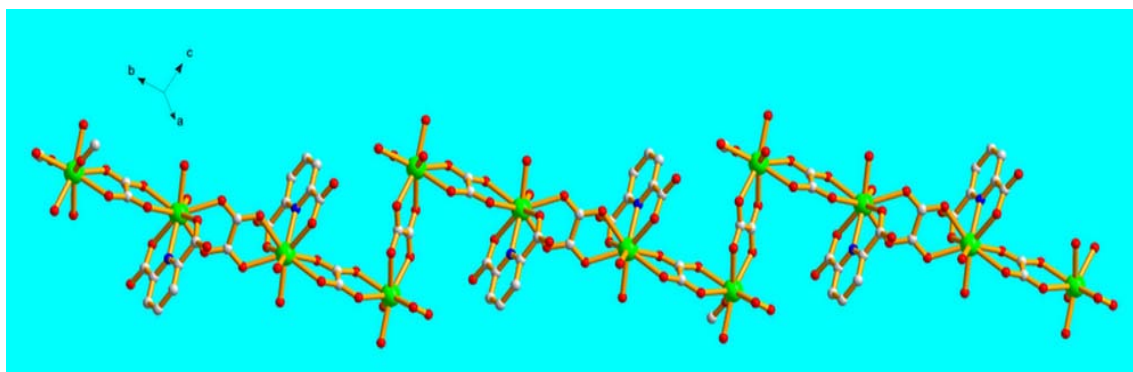
Figure S6. Ball-and-stick representation of the Yb(III) ions linked by the oxalate ligands resulting in an infinite zigzag alternate chain in the complex **7**
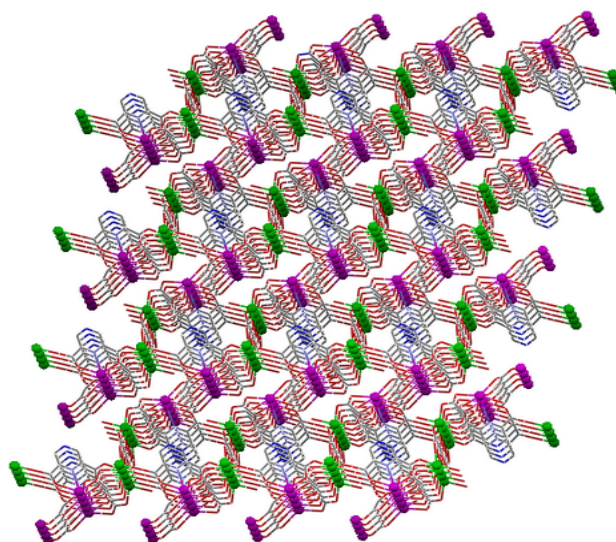

Figure S7 The 3D packing diagram of **7** viewed along the *a b* plane. The guest water molecules have been omitted for clarity.
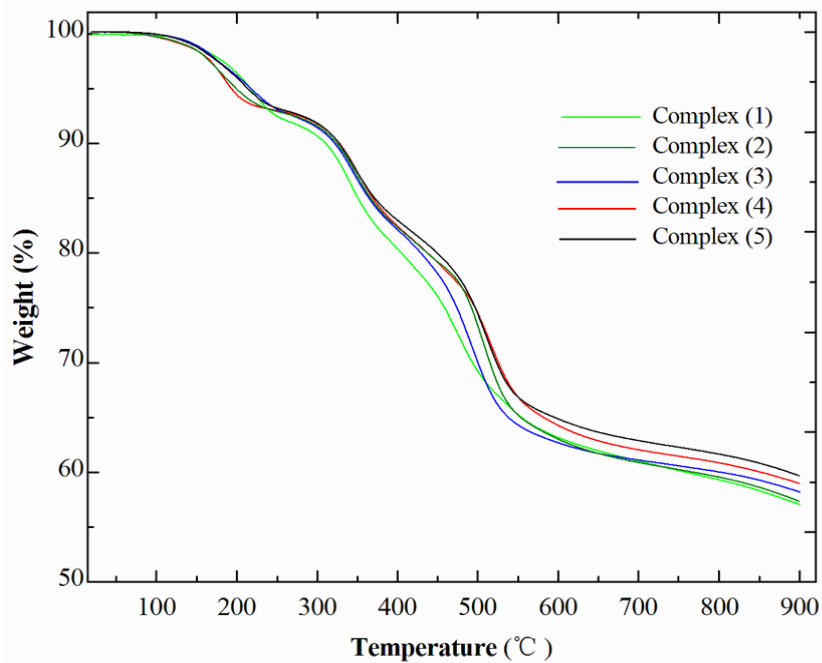
Figure S8 (a). The TGA diagrams of complexes **1, 2**, **3**, **4** and **5**
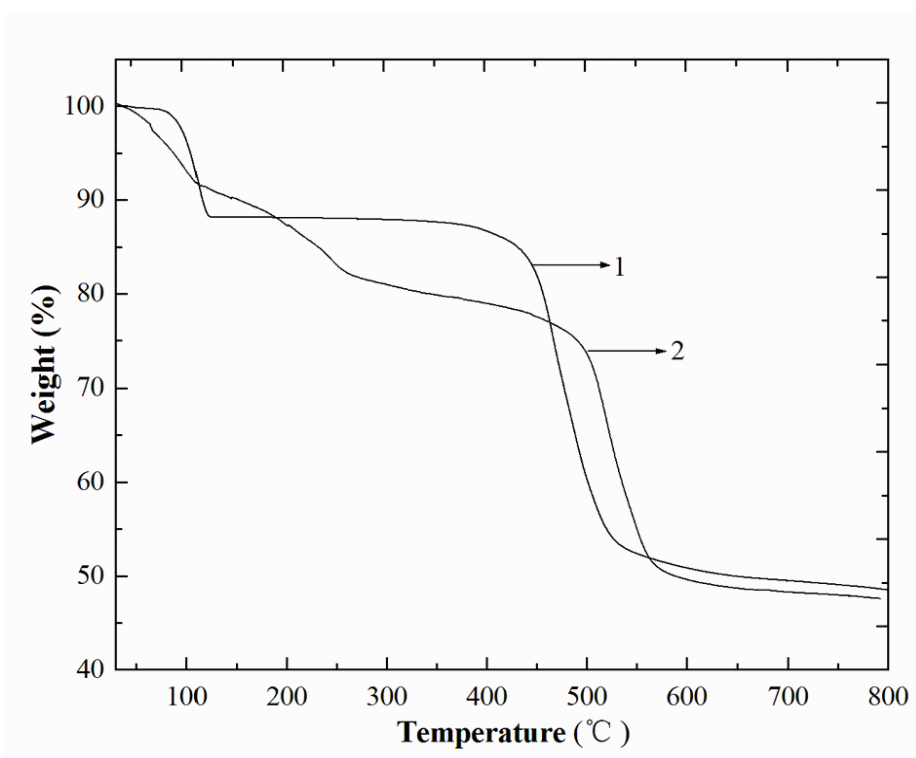

Figure S8 (b). The TGA diagrams of complexes **6** (1) and **7** (2)
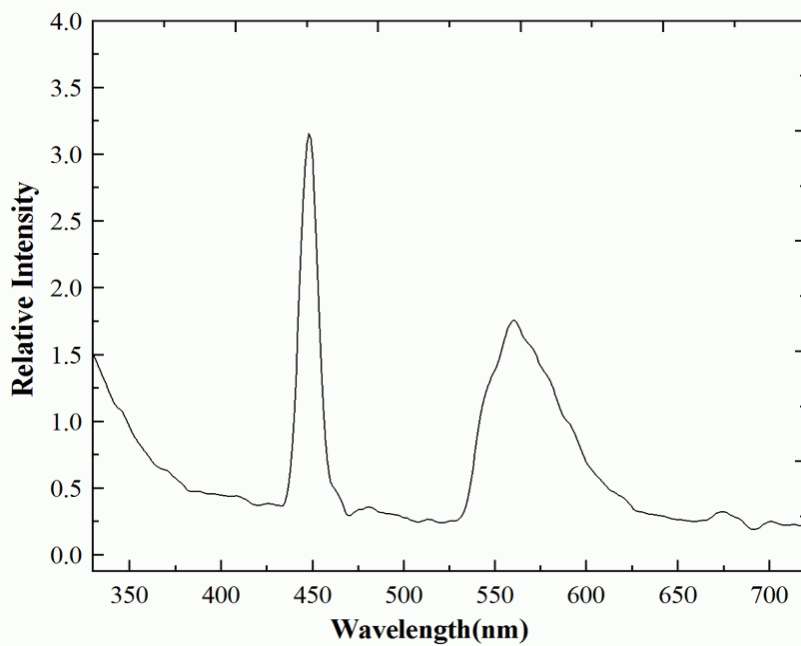
Figure S9 (a)
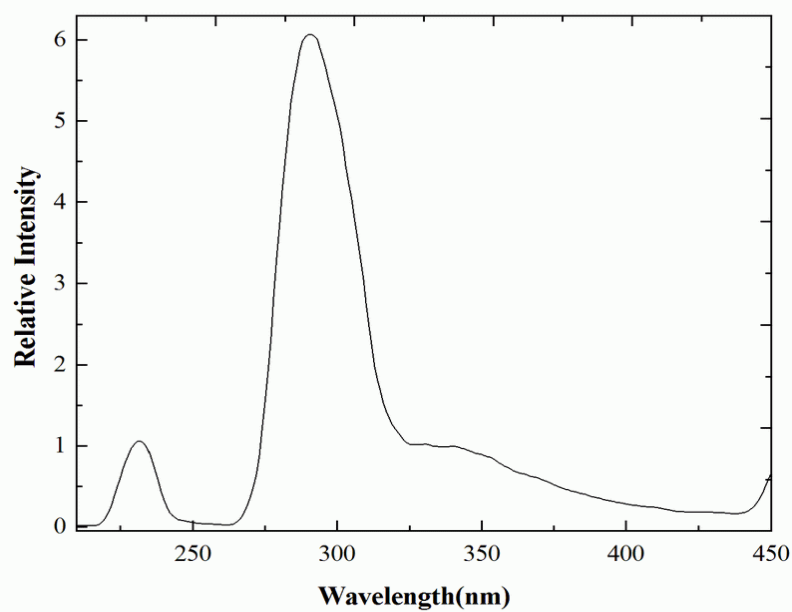
Figure S9 (b)
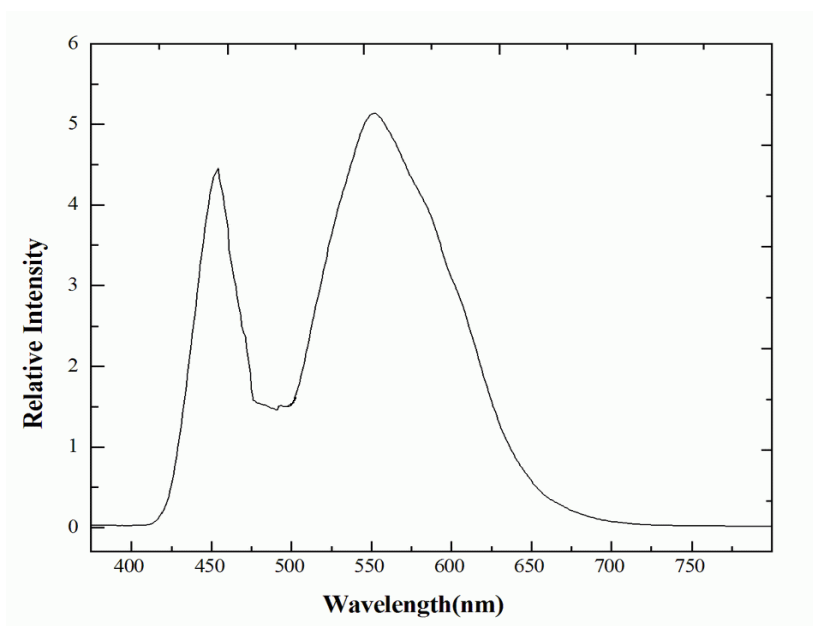
Figure S9 (c)
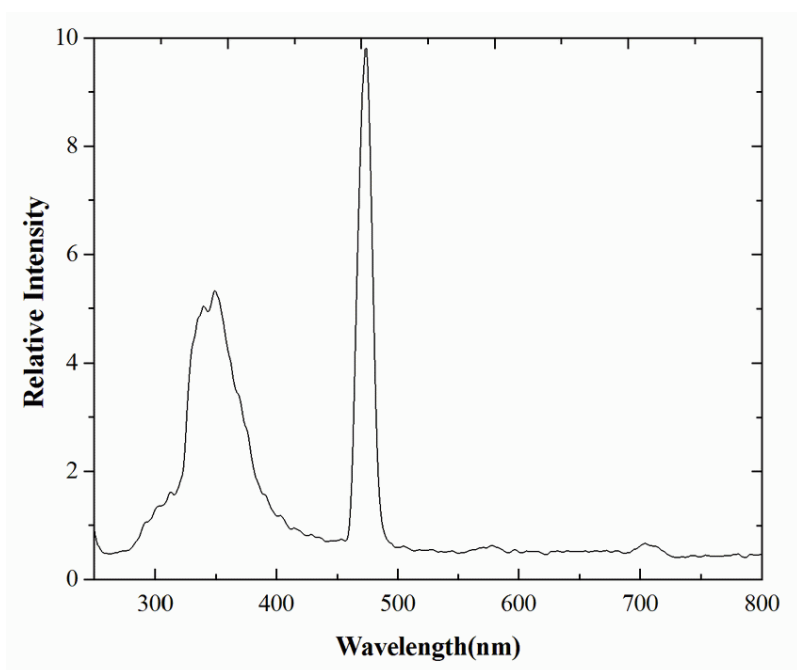
Figure S9 (d)
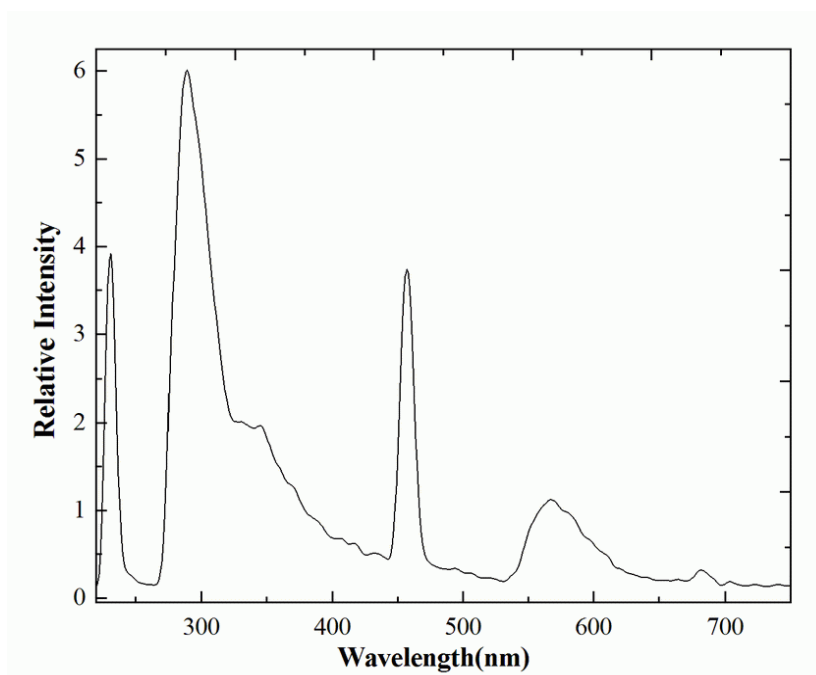
Figure S9 (e)

Figure S9. Photoemission spectra of the complexes **1Sm** (a), **3Gd** (b), **4Dy**(c),) **5Ho** (d) and **6Ce**

(e) in methanolic suspension state

Magnetic Properties of the **1**

Fitting of the complex **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

$$E(J) = \lambda[J(J+1) - {}^{35}/_4]/2$$

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:

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

with $\chi(J)$ being given by *eq* 1 and **E(J)** by eq (S0). X_M may be expanded as:

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

$$x = J/kT \qquad\qquad\qquad Eq\,(1)$$

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 2 was assigned as a molecular field approximation

$$\chi = \frac{\chi'}{1-(2zj'/Ng^2\beta^2)\chi'} \qquad\qquad eq\,(2)$$
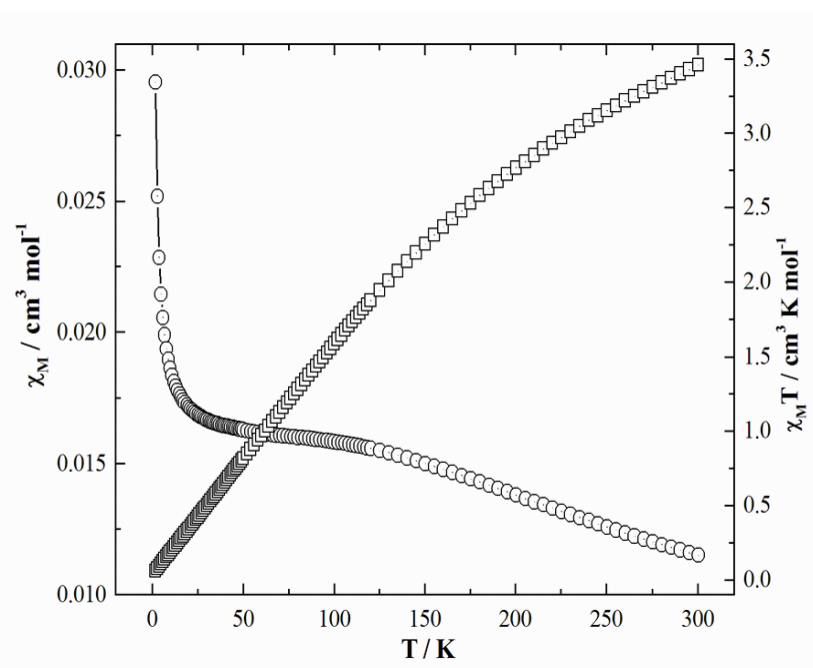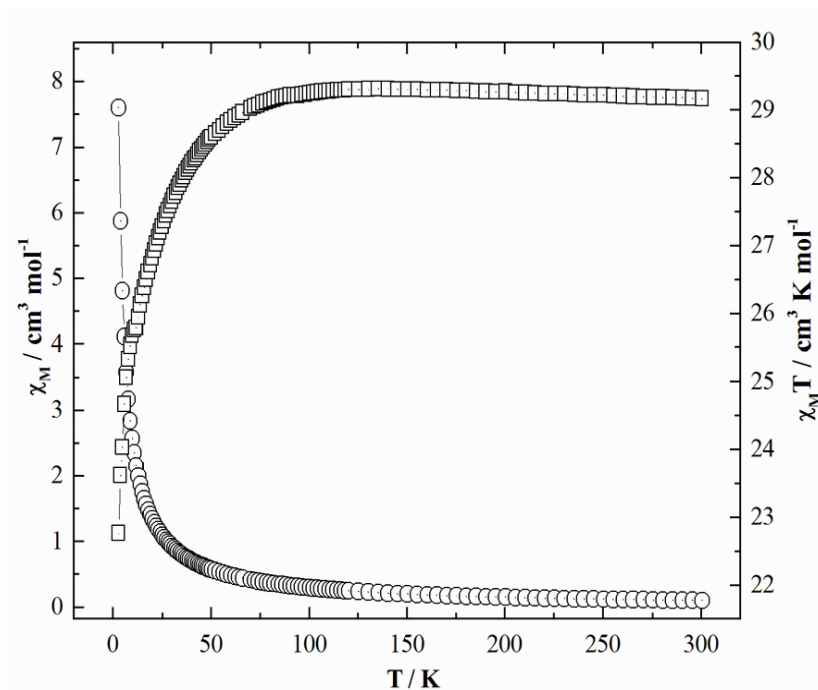
Figure. S10 (a)

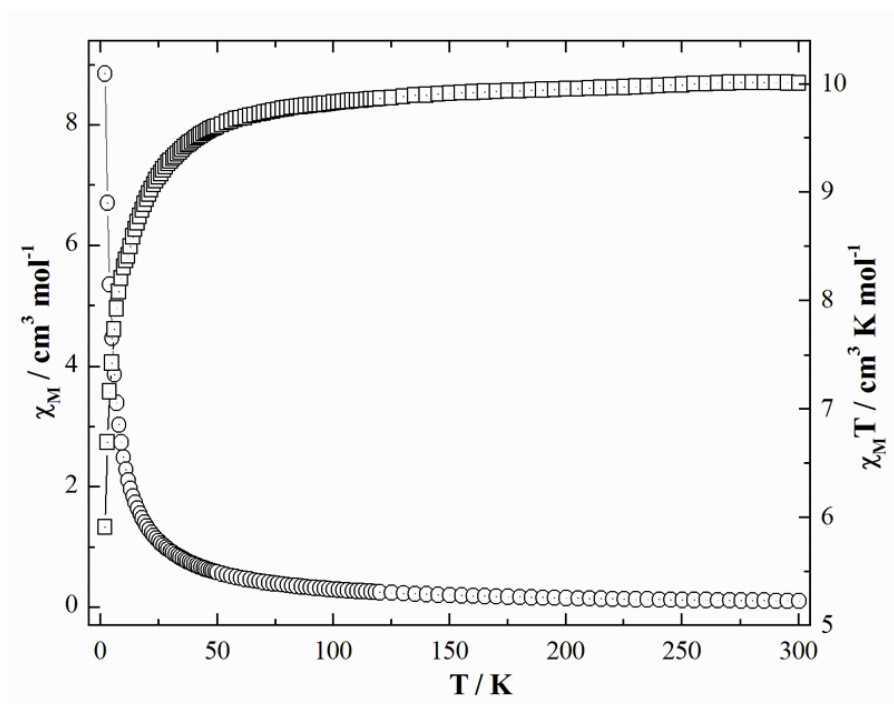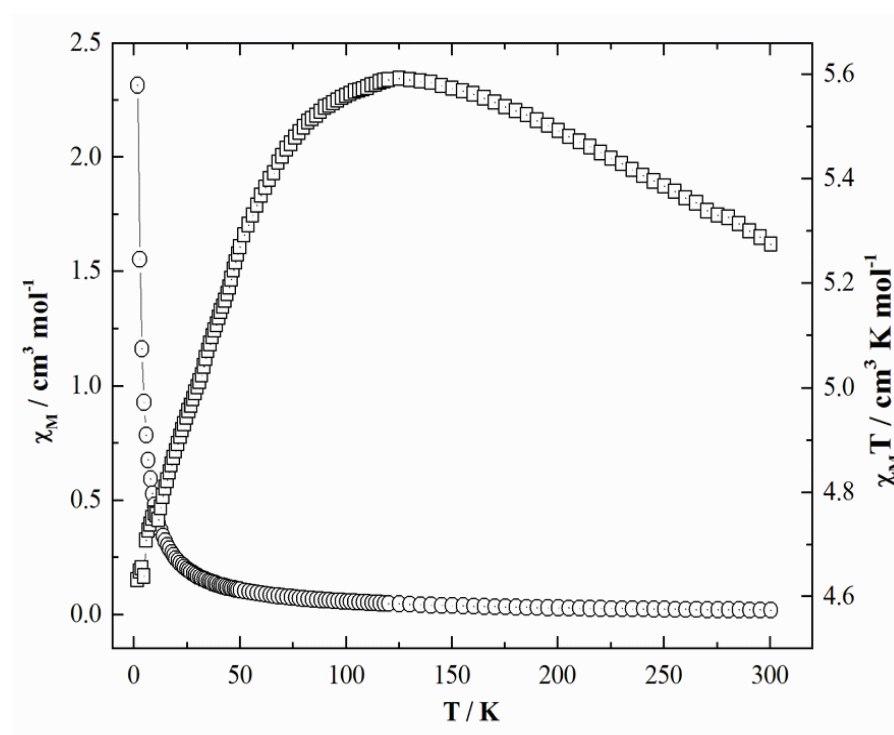**Figure. S10** (b)

Figure. S10 (c)

(d)

Figure. S10 .Temperature dependence of $\chi_M T$ ($\square$) and χ_M (O) for **2**(a). **4**(b), **5**(c), **7**(d) between 2 and 300 K.

Table S1   Selected bond lengths [Å] and angles [°] for complexes **1**–**7**

Complex **1**					
Sm(1)-O(3)#2	2.331(3)	Sm(1)-N(3)	2.604(3)	Sm(2)-O(11)#4	2.440(3)
Sm(1)-O(2)#2	2.353(3)	Sm(1)-N(1)	2.620(3)	Sm(2)-O(11)	2.440(3)
Sm(1)-O(1)	2.387(3)	Sm(2)-O(6)#4	2.321(3)	Sm(2)-O(9')#4	2.459(6)
Sm(1)-O(8)#3	2.413(3)	Sm(2)-O(6)	2.321(3)	O(2)-Sm(1)#5	2.353(3)
Sm(1)-O(5)	2.432(3)	Sm(2)-O(7)#4	2.413(3)	O(3)-Sm(1)#5	2.331(3)
Sm(1)-O(10)	2.485(4)	Sm(2)-O(9)#4	2.417(8)	O(8)-Sm(1)#6	2.413(3)

Complex **2**					
Eu(1)-O(3)#2	2.319(6)	Eu(1)-N(3)	2.583(8)	Eu(2)-O(7)	2.404(6)
Eu(1)-O(2)#2	2.352(6)	Eu(1)-N(1)	2.612(7)	Eu(2)-O(9')#4	2.425(11)
Eu(1)-O(1)	2.369(6)	Eu(2)-O(6)#4	2.321(7)	Eu(2)-O(11)#4	2.427(7)
Eu(1)-O(8)#3	2.390(6)	Eu(2)-O(6)	2.321(7)	Eu(2)-O(11)	2.427(7)
Eu(1)-O(5)	2.424(6)	Eu(2)-O(9)#4	2.395(14)	O(2)-Eu(1)#5	2.352(6)
Eu(1)-O(10)	2.468(8)	Eu(2)-O(7)#4	2.404(6)	O(8)-Eu(1)#6	2.390(6)

Complex**3**					
O(9)-Gd(2)	2.445(5)	Gd(1)-N(3)	2.578(3)	Gd(2)-O(11)#4	2.417(3)
Gd(1)-O(3)#2	2.313(2)	Gd(1)-N(1)	2.596(3)	Gd(2)-O(11)	2.417(3)
Gd(1)-O(2)#2	2.347(2)	Gd(2)-O(6)#4	2.303(3)	Gd(2)-O(9')#4	2.445(5)
Gd(1)-O(1)	2.369(2)	Gd(2)-O(6)	2.303(3)	O(1)-C(4)	1.276(4)
Gd(1)-O(8)#3	2.392(2)	Gd(2)-O(7)	2.402(3)	O(2)-C(4)	1.244(4)
Gd(1)-O(5)	2.425(2)	Gd(2)-O(7)#4	2.402(3)	O(2)-Gd(1)#5	2.347(2)
Gd(1)-O(10)	2.454(3)	Gd(2)-O(9)#4	2.404(7)	O(3)-Gd(1)#5	2.313(2)

Complex **4**					
O(9)-Dy(2)	2.365(7)	Dy(1)-O(10)	2.418(3)	Dy(2)-O(7)	2.380(3)
Dy(1)-O(3)#2	2.287(3)	Dy(1)-N(3)	2.554(3)	O(8)-Dy(1)#6	2.370(3)
Dy(1)-O(2)#2	2.320(3)	Dy(1)-N(1)	2.576(3)	Dy(2)-O(9')#4	2.413(6)
Dy(1)-O(1)	2.344(3)	Dy(2)-O(6)	2.280(3)	O(3)-Dy(1)#5	2.287(3)
Dy(1)-O(8)#3	2.370(3)	Dy(2)-O(9)#4	2.365(7)	Dy(2)-O(7)#4	2.380(3)
Dy(1)-O(5)	2.399(3)	Dy(2)-O(11)	2.379(3)	O(2)-Dy(1)#5	2.320(3)

Complex **5**					
O(9)-Ho(2)	2.350(6)	Ho(1)-O(10)	2.390(3)	Ho(2)-O(11)	2.369(3)
O(9')-Ho(2)	2.387(5)	Ho(1)-N(3)	2.534(3)	Ho(2)-O(7)#4	2.372(3)
Ho(1)-O(3)#2	2.274(3)	Ho(1)-N(1)	2.561(3)	Ho(2)-O(9')#4	2.387(5)
Ho(1)-O(2)#2	2.315(3)	Ho(2)-O(6)	2.256(3)	O(2)-Ho(1)#5	2.315(3)
Ho(1)-O(1)	2.332(2)	Ho(2)-O(9)#4	2.350(6)	O(3)-Ho(1)#5	2.274(3)
Ho(1)-O(5)	2.390(3)	Ho(2)-O(11)#4	2.369(3)	O(8)-Ho(1)#6	2.352(2)

Complex **6**					
Ce(1)-O(3)#1	2.252(5)	Ce(1)-O(5)	2.354(5)	O(6)-Ce(1)#3	2.393(5)
Ce(1)-O(2)#1	2.295(5)	Ce(1)-O(6)#3	2.393(5)	O(2)-Ce(1)#4	2.295(5)
Ce(1)-O(4)#2	2.314(5)	Ce(1)-O(7)	2.395(6)	O(3)-Ce(1)#4	2.252(5)
Ce(1)-O(1)	2.326(5)	Ce(1)-N(1)	2.514(6)	O(4)-Ce(1)#5	2.314(5)
Complex **7**					
Yb(1)-O(4)#1	2.298(5)	Yb(2)-O(15)	2.412(5)	Yb(2)-N(1)#3	2.538(5)
Yb(1)-O(14)	2.359(5)	Yb(2)-O(16)	2.415(5)	O(2)-Yb(2)#5	2.432(5)
Yb(1)-O(8)	2.365(5)	Yb(2)-O(7)	2.425(5)	O(3)-Yb(2)#5	2.432(5)
Yb(1)-O(1)	2.389(5)	Yb(2)-O(2)#3	2.432(5)	O(4)-Yb(1)#6	2.298(5)
Yb(1)-O(10)	2.406(5)	Yb(2)-O(3)#3	2.432(5)	O(9)-Yb(1)#2	2.458(5)
Yb(1)-O(5)	2.443(5)	Yb(2)-O(12)#4	2.453(5)	O(12)-Yb(2)#4	2.453(5)
Yb(1)-O(9)#2	2.458(5)	Yb(2)-O(11)	2.453(5)	N(1)-Yb(2)#5	2.538(5)
Yb(1)-O(13)	2.460(5)	Yb(2)-O(6)	2.533(5)		

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