Supporting Information

Construction of Polyoxometalates from Dynamic Lacunary Polyoxotungstate Building Blocks and Lanthanide Linkers

Lu-Lu Li,[a] Hua-Yan Han,[a] Yong-Hui Wang,*[a] Hua-Qiao Tan,[a] Hong-Ying Zang,*[a] and Yang-Guang Li[a]

Contents

1. Parallel experiments for optimizing the synthetic conditions of compounds 1-5

We carried out a series of parallel experiments in order to explore the various synthetic factors that affect the final quality and yields of the crystalline metal-oxo assemblies. It is found that compound La-1 and Pr-2 can be obtained at pH 4.8-5.2, and the crystals have a better quality at pH 5.0 than other pH parameters. Furthermore, the effects of temperature and time on the final quality and yield of the crystalline products were also studied, indicatingthat the 90 °C reaction temperature and 3 h reaction time are better for compounds **1-2** with higher yield and good quality of single crystal samples. For Compounds **3-5**, the suitable pH range is at pH 6.3-6.7 and the optimum one is pH 6.5. Furthermore, reaction temperature being 90 °C and reaction time being1 h can lead to better quality and higher yield of isolated crystals **3-5**.

Table. S1 Parallel experiments for optimizing the synthetic conditions of compounds **1-5** [a,b,c]

Compounds 1-2				**Compounds 3-5**				
parameter	**isolated crystals**	**Yield(%) based on W**		**parameter**	**isolated crystals**	**Yield(%) based on W**		
T (90 °C) t (3.0 h), pH (4.6)	No	-	-	T (90 °C) t (1.0 h), pH (6.1)	No	-	-	-
T (90 °C) t (3.0 h), pH (4.8)	Yes	24	18	T (90 °C) t (1.0 h), pH (6.3)	Yes	29	15	21
T (90 °C) t (5.0 h), pH (5.0)	Yes	36	30	T (90 °C) t (1.0 h), pH (6.5)	Yes	46	28	37
T (90 °C) t (3.0 h), pH (5.2)	Yes	25	19	T (90 °C) t (1.0 h), pH (6.7)	Yes	31	16	22
T (90 °C) t (3.0 h), pH (5.4)	No	-	-	T (90 °C) t (1.0 h), pH (6.9)	No	-	-	-
T (50 °C) t (3.0 h), pH (5.0)	Yes	28	22	T (50 °C) t (1.0 h), pH (6.5)	Yes	36	20	28
T (70 °C) t (3.0 h), pH (5.0)	Yes	35	29	T (70 °C) t (1.0 h), pH (6.5)	Yes	44	27	35
T (90 °C) t (3.0 h), pH (5.0)	**Yes**	**39**	**32**	**T (90 °C) t (1.0 h), pH (6.5)**	**Yes**	**49**	**32**	**42**
T (30 °C) t (3.0 h), pH (5.0)	Yes	22	16	T (30 °C) t (1.0 h), pH (6.5)	Yes	25	13	19
T (100 °C) t (3.0 h), pH (5.0)	Yes	34	28	T (100 °C)t (1.0 h), pH (6.5)	Yes	42	25	32
T (90 °C) t (1.0 h), pH (5.0)	Yes	19	13	T (90 °C) t (0.2 h), pH (6.5)	Yes	21	11	17
T (90 °C) t (2.0 h), pH (5.0)	Yes	26	20	T (90 °C) t (0.5 h), pH (6.5)	Yes	34	18	25
T (90 °C) t (4.0 h), pH (5.0)	Yes	37	31	T (90 °C) t (3.0 h), pH (6.5)	Yes	47	30	40

[a] T = temperature, t = time, pH means the final pH of the reaction system.

[b] The experimental groups with blue background exhibits the best yield and good quality of crystalline compounds **1-5**

[c] Yes represents the isolation of crystalline compounds **1-5**, and No means an opposite result.

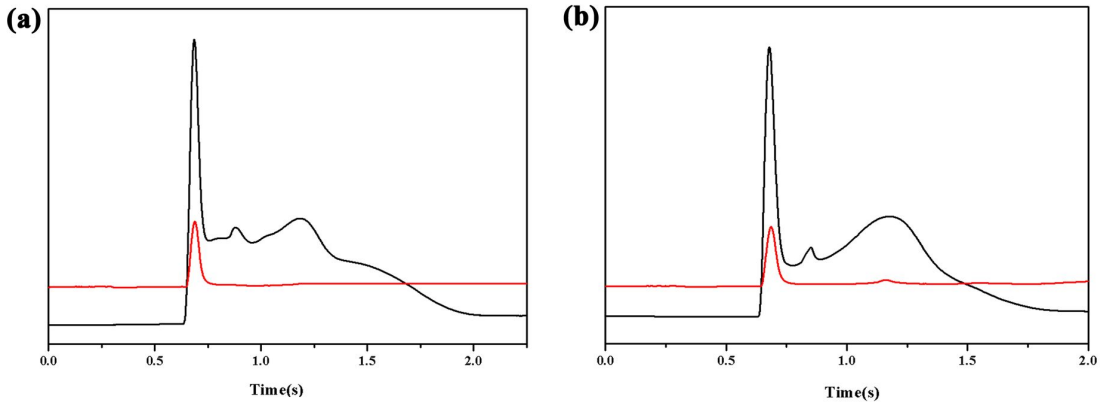

Fig. S1 (a) **La-1** Capillary electrophoresis experiments, red line: isolated crystal of **La-1** (T (90 °C) t (3.0 h), pH (5.0)) dissolved in sodium acetate buffer , black line: optimum synthetic system solution of compound **La-1** (T (90 °C) t (3.0 h), pH (5.0)) dissolved in sodium acetate buffer. (b) Tb-3 Capillary electrophoresis experiments, red line: isolated crystal of **Tb-3** (T (90 °C) t (1.0 h), pH (6.5)) dissolved in sodium acetate buffer, black line: optimum synthetic system solution of **Tb-3** (T (90 °C) t (1.0 h), pH (6.5)) dissolved in sodium acetate buffer. Experimental conditions for capillary electrophoresis: Fused-silica capillaries (50 μm i.d., 365μm o.d., Hebei Yongnian Factory, China) with total length of 50 cm was used. The detection wavelength was set at 200 nm. The running buffer for CE separation was 20 mM sodium acetate buffer (pH 5.9). The separation voltage was set at -25 kV. The sample was hydrodynamically injected into the capillary (10 cm, 10 s).

Capillary electrophoresis Discussion

The capillary electrophoretic method has been used to investigate the POM solution situation. In such measurement, the peak signals originated from the optimum synthetic systems of **1** and **3** were compared with those from the aqueous solution dissolving **1** and **3**, respectively. As shown in Fig. S1， compounds **1** and **3** has a same peak shape to its mother solution indicating that product **1** and **3** were the main POM product of each solution system. The different peak intensities were caused by different concentration of product in mother liquor and the corresponding dissolved crystals in solution. Some other small peaks were also observed but those peaks were very weak compared with main peak of the product, which made it hard to be isolated from mother liquor as solid crystals. Based on the above experiment, we can envision that **La-1** and **Tb-3** are main species in the optimum synthetic solution system, respectively.

The technique of capillary electrophoresis was designed to separate species based on their charge to size ratio in the interior of a small capillary filled with an electrolyte under electronic field and monitored by a UV-vis detector. The electrophoretic migration mobility (μ_p) of an analyte toward the electrode of opposite charge is:

$$\mu_{\mathrm{p}} = \frac{v_p}{E} \qquad (1)$$

where v_p and μ_p are the electrophoretic velocity and mobility, and E is the electric field strength. The electrophoretic mobility is proportional to the ionic charge to size ratio of a sample. The velocity of migration of an analyte in capillary electrophoresis is also dependent upon the rate of electroosmotic flow (EOF) of the buffer solution. The apparent mobility (μ) of an analyte in an electric field is the resultant of its electrophoretic mobility and EOF as:

$$\mu = \mu_p + \mu_{eof} = \frac{v_p + v_{eof}}{E} \qquad (2)$$

Where v_{eof} and μ_{eof} are the electroosmotic velosity and mobility. The apparent migration time (t_m) of an analyte, *i.e.* how long an ion takes to travel through a certain distance (*L*, from the capillary inlet to detection window) under a definite electric field is defined as:

$$t_m = \frac{L}{\mu \cdot E} = \frac{L}{(\mu_p + \mu_{eof}) \cdot E} \quad (3)$$

2. Additional structural figures for compounds 1-5

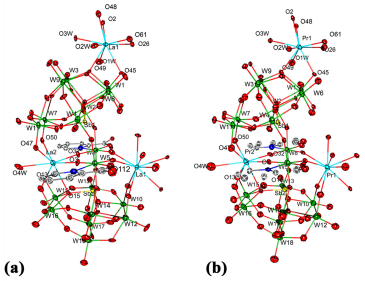

Fig. S2. The ORTEP diagram of the basic structural units of **(a) La-1** and **(b) Pr-2** with thermal ellipsoids at 30% probability displacement. All H atoms, counter cations and lattice water molecules are omitted for clarity.

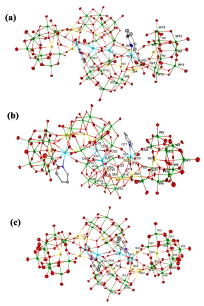

Fig.S3. The ORTEP diagram of the basic structural unit of **(a) Tb-3**, **(b) Dy-4** and **(c) Ho-5** with thermal ellipsoids at 30% probability displacement. H atoms, counter-cations and lattice water molecules are omitted for clarity

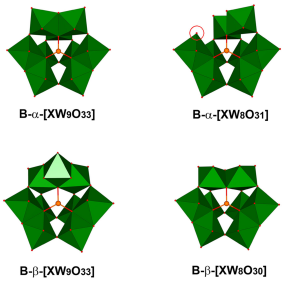

Fig. S4 Polyhedral view of the four types of lacunary POM units mentioned in compounds **1-5**

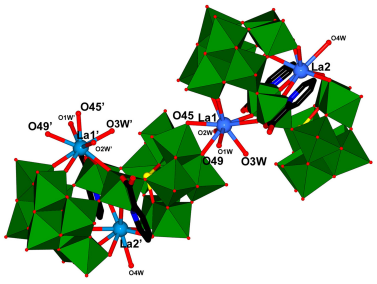

Fig. S5 The connection mode between two adjacent polyoxoanion units in **1**

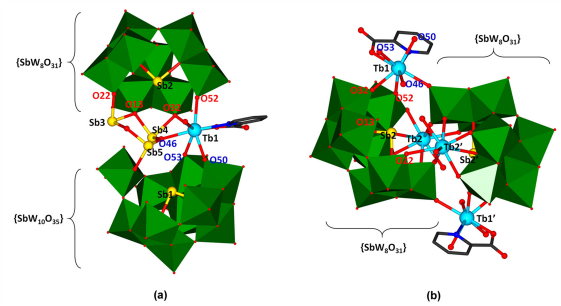

Fig. S6 The connection modes **(a)** between adjacent $\{SbW_8O_{31}\}$ and $\{SbW_{10}O_{35}\}$ units and **(b)** between two adjacent $\{SbW_8O_{31}\}$ units in **3**

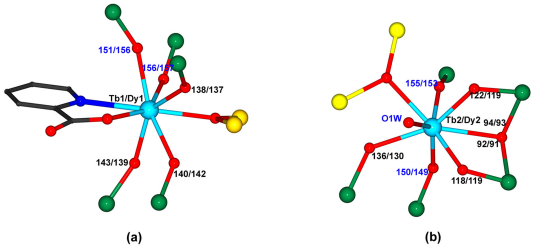

Fig. S7 Coordination environments of potential luminescent Tb1/Dy1 centers **(a)** and Tb2/Dy2 centers **(b)** in **Tb-3** and **Dy-4.** The bond angles of Ln-O-W are shown in the Figure. Blue ball, Ln; Green ball, W; Yellow ball, Sb; Red ball, O; Deep blue ball, N; Black ball, C.

3. Selected bond lengths and angles for compounds La1 - Ho-5

Table S2. Selected bond lengths (Å) and angles (°) for **La-1**

W(1)-O(45)	1.732(19)	W(1)-O(53)	2.22(2)	W(4)-O(57)	2.29(2)
W(2)-O(11)	1.71(2)	W(2)-O(53)	2.308(18)	W(5)-O(2)	1.65(2)
W(3)-O(53)	2.325(18)	W(3)-O(39)	1.77(2)	W(5)-O(111)	2.14(3)
W(4)-O(35)	1.718(19)	W(11)-O(25)	1.70(2)	W(6)-O(23)	1.73(2)
W(7)-O(50)	1.71(2)	W(11)-O(41)	2.317(19)	W(16)-O(18)	1.76(2)
W(7)-O(41)	2.24(2)	W(12)-O(26)	1.72(2)	W(16)-O(15)	2.26(2)
W(8)-O(48)	1.71(2)	W(12)-O(30)	2.25(2)	W(17)-O(62)	1.76(2)
W(8)-O(211)	2.23(2)	W(13)-O(5)	1.74(2)	W(17)-O(24)	2.28(2)
W(9)-O(42)	1.74(2)	W(13)-O(24)	2.31(2)	W(18)-O(63)	1.73(2)
W(9)-O(57)	2.34(2)	W(14)-O(8)	1.66(3)	W(18)-O(30)	2.27(2)
W(10)-O(38)	1.72(3)	W(14)-O(30)	2.28(2)	W(10)-O(24)	2.19(3)
Sb(1)-O(41)	1.90(2)	W(15)-O(60)	1.75(2)	W(15)-O(15)	2.24(2)
Sb(1)-O(53)	1.999(18)	Sb(2)-O(24)	2.04(2)	La(1)-O(3W)	2.56(2)
Sb(2)-O(15)	2.00(2)	La(1)-O(61)	2.41(2)	La(1)-O(49)	2.59(2)
La(1)-O(26)	2.56(2)	La(1)-O(2)	2.74(2)	La(1)-O(48)	2.60(2)
La(1)-O(2W)	2.67(2)	La(1)-O(45)	2.648(18)	La(1)-O(1W)	2.62(2)
La(2)-O(47)	2.46(2)	La(2)-O(32)#1	2.47(2)	La(2)-O(12)#1	2.47(2)
La(2)-O(41)	3.02(2)	La(2)-O(50)	2.50(2)	La(2)-O(13)#1	2.53(3)
La(1)-O(2)	2.74(2)	La(2)-O(3)#1	2.55(2)	La(2)-O(15)#1	2.75(2)
La(2)-O(4W)	2.80(3)	O(11)-W(2)-O(56)	100.9(9)	O(45)-W(1)-O(54)	105.4(9)
O(2)-W(5)-O(3)	106.3(10)	O(39)-W(3)-O(22)	102.5(10)	O(35)-W(4)-O(17)	97.9(10)
O(48)-W(8)-O(32)	104.0(10)	O(23)-W(6)-O(29)	107.0(12)	O(50)-W(7)-O(40)	99.5(10)
O(26)-W(12)-O(14)	104.5(12)	O(42)-W(9)-O(33)	105.5(11)	O(38)-W(10)-O(61)	101.8(12)
O(60)-W(15)-O(13)	97.9(12)	O(5)-W(13)-O(7)	103.2(11)	O(8)-W(14)-O(21)	103.9(12)
O(63)-W(18)-O(30)	165.4(11)	O(28)-W(16)-O(15)	85.7(9)	O(62)-W(17)-O(16)	101.5(12)
O(61)-La(1)-O(26)	68.5(7)	O(41)-Sb(1)-O(57)	97.6(8)	O(15)-Sb(2)-O(24)	96.8(9)
O(15)#1-La(2)-O(41)	140.5(6)	O(48)-La(1)-O(45)	147.9(6)	O(47)-La(2)-O(41)	61.2(6)

Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y+1/2,-z+2.

Table S3. Selected bond lengths (Å) and angles (°) for **Pr-2**

W(1)-O(54)	1.75(3)	W(2)-O(56)	1.93(3)	W(9)-O(42)	1.71(3)
W(2)-O(53)	2.32(3)	W(9)-O(57)	2.24(4)	W(10)-O(38)	1.68(4)
W(3)-O(39)	1.72(3)	W(10)-O(24)	2.24(4)	W(14)-O(8)	1.67(4)
W(3)-O(53)	2.28(3)	W(11)-O(41)	2.26(3)	W(12)-O(30)	2.26(3)
W(4)-O(35)	1.65(3)	W(12)-O(14)	1.69(4)	W(13)-O(5)	1.69(4)
W(4)-O(57)	2.22(3)	W(18)-O(30)	2.24(4)	W(15)-O(60)	1.65(5)
W(5)-O(2)	1.71(3)	Sb(1)-O(41)	1.96(3)	W(13)-O(24)	2.17(4)
W(5)-O(111)	2.16(3)	W(17)-O(24)	2.31(4)	Sb(1)-O(57)	2.07(3)
W(6)-O(23)	1.63(4)	W(18)-O(28)	1.70(4)	Sb(2)-O(15)	1.96(3)
W(6)-O(57)	2.26(4)	W(16)-O(15)	2.27(3)	Sb(2)-O(24)	2.06(4)
W(7)-O(40)	1.70(3)	W(17)-O(62)	1.68(4)	Pr(1)-O(1W)	2.45(4)
W(7)-O(41)	2.26(3)	W(16)-O(18)	1.71(5)	Pr(1)-O(2W)	2.66(4)
W(8)-O(211)	2.06(4)	W(15)-O(15)	2.29(3)	Pr(1)-O(48)	2.55(3)
W(14)-O(30)	2.29(3)	Pr(1)-O(61)	2.51(3)	Pr(1)-O(3W)	2.56(3)
Pr(1)-O(26)	2.46(4)	Pr(1)-O(49)	2.58(4)	Pr(2)-O(3)#1	2.41(3)
Pr(1)-O(2)	2.63(3)	Pr(1)-O(45)	2.58(3)	Pr(2)-O(41)	2.87(3)
Pr(2)-O(47)	2.41(4)	Pr(2)-O(32)#1	2.43(4)	Pr(2)-O(50)	2.45(4)
Pr(2)-O(12)#1	2.50(4)	Pr(2)-O(15)#1	2.71(3)	Pr(2)-O(4W)	2.85(5)
Pr(2)-O(13)#1	2.46(5)	O(58)-W(3)-O(53)	76.7(11)	O(54)-W(1)-O(45)	103.4(15)
O(39)-W(3)-O(22)	103.8(17)	O(23)-W(6)-O(17)	97.4(16)	O(11)-W(2)-O(58)	97.8(16)
O(2)-W(5)-O(3)	105.8(13)	O(42)-W(9)-O(33)	103.9(15)	O(35)-W(4)-O(17)	99.1(16)
O(48)-W(8)-O(20)	94.7(13)	O(14)-W(12)-O(10)	95.1(19)	O(40)-W(7)-O(46)	100.1(16)
O(47)-W(11)-O(33)	165.7(17)	O(13)-W(15)-O(19)	97.5(17)	O(61)-W(10)-O(16)	158.5(18)
O(4)-W(14)-O(34)	85.5(19)	O(4)-W(18)-O(30)	74.4(16)	O(20)-W(13)-O(7)	92.8(18)
O(16)-W(17)-O(24)	71.2(17)	O(1W)-Pr(1)-O(26)	76.3(15)	O(34)-W(16)-O(19)	154.0(17)
O(30)-Sb(2)-O(24)	96.8(14)	O(3)#1-Pr(2)-W(15)#1	114.8(8)	O(41)-Sb(1)-O(57)	95.6(14)
O(12)#1-Pr(2)-O(15)#1	62.3(12)	O(1W)-Pr(1)-O(48)	138.0(12)		

Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y+1/2,-z+2

Table S4. Selected bond lengths (Å) and angles (°) for **Tb-3**

W(1)-O(4)	1.719(18)	W(1)-O(7)	2.225(16)	W(2)-O(7)	2.368(15)
W(3)-O(7)	2.415(16)	W(2)-O(5)	1.761(19)	W(3)-O(3)	1.711(14)
W(4)-O(16)	1.767(15)	W(4)-O(25)	2.242(14)	W(5)-O(8)	2.240(15)
W(6)-O(15)	2.263(15)	W(5)-O(10)	1.728(16)	W(6)-O(44)	1.732(17)
W(7)-O(66)	1.731(16)	W(7)-O(39)	2.274(15)	W(8)-O(17)	2.292(14)
W(9)-O(62)	1.708(16)	W(8)-O(28)	1.750(14)	W(9)-O(17)	2.313(15)
W(10)-O(17)	2.265(16)	W(11)-O(40)	2.281(16)	W(10)-O(27)	1.721(16)
W(11)-O(45)	1.700(17)	W(12)-O(68)	1.751(16)	W(12)-O(39)	2.361(15)
W(13)-O(25)	2.341(16)	W(14)-O(39)	2.239(15)	W(13)-O(63)	1.697(16)
W(14)-O(55)	1.753(16)	W(15)-O(51)	1.694(15)	W(15)-O(40)	2.253(15)
W(16)-O(38)	1.685(14)	W(16)-O(25)	2.295(15)	W(17)-O(40)	2.287(16)
W(18)-O(56)	1.742(15)	W(17)-O(34)	1.713(15)	W(18)-O(15)	2.229(13)
Sb(1)-O(39)	1.982(14)	Sb(1)-O(7)	1.946(17)	Sb(2)-O(25)	2.023(14)
Sb(2)-O(15)	1.949(15)	Sb(3)-O(22)	2.175(15)	Sb(3)-O(12)	1.999(14)
O(16)-W(4)-O(42)	100.8(7)	Sb(4)-O(46)	2.003(13)	Sb(4)-O(32)	2.247(15)
Tb(1)-O(52)	2.300(15)	Sb(5)-O(8)	2.033(17)	Sb(5)-O(12)	1.956(14)
Tb(1)-O(46)	2.453(14)	Tb(1)-O(42)#2	2.326(14)	Tb(1)-O(72)	2.331(15)
Tb(1)-O(50)	2.310(16)	Tb(1)-O(53)	2.416(16)	Tb(1)-O(32)	2.347(14)
Tb(1)-N(1)	2.578(14)	Tb(2)-O(57)	2.304(15)	Tb(2)-O(22)#2	2.450(14)
Tb(2)-O(16)	2.305(15)	Tb(2)-O(12)#2	2.482(15)	Tb(2)-O(1W)	2.464(18)
Tb(2)-O(26)	2.322(14)	Tb(2)-O(15)	2.687(15)	Tb(2)-O(20)#2	2.303(15)
O(16)-W(4)-O(24)	162.4(6)	O(10)-W(5)-O(36)	169.3(7)	O(70)-W(5)-O(8)	77.4(6)
O(18)-W(6)-O(15)	74.0(6)	O(66)-W(7)-O(39)	165.2(6)	O(60)-W(7)-O(39)	73.7(6)
O(14)-W(8)-O(35)	81.5(7)	O(28)-W(8)-O(17)	168.9(6)	O(65)-W(9)-O(61)	91.2(7)
O(62)-W(9)-O(17)	167.3(7)	O(27)-W(10)-O(35)	99.4(7)	O(54)-W(11)-O(40)	72.7(6)
O(33)-W(13)-O(61)	160.9(6)	O(23)-W(14)-O(58)	160.6(7)	O(68)-W(12)-O(58)	101.9(8)
O(36)-W(15)-O(54)	154.6(6)	O(54)-W(15)-O(40)	73.1(6)	O(31)-W(16)-O(25)	74.6(6)
O(49)-W(17)-O(41)	157.4(6)	O(56)-W(18)-O(18)	94.7(7)	O(52)-Tb(1)-O(42)#2	71.1(5)
O(42)#2-Tb(1)-O(72)	148.7(5)	O(57)-Tb(2)-O(1W)	73.0(6)	O(22)#2-Tb(2)-O(15)	147.7(5)
O(7)-Sb(1)-O(40)	90.3(7)	O(40)-Sb(1)-O(39)	89.0(6)	O(15)-Sb(2)-O(25)	96.2(6)
O(12)-Sb(3)-O(70)	84.9(6)	O(70)-Sb(3)-O(22)	153.5(6)	O(46)-Sb(4)-O(32)	76.7(5)
O(70)-Sb(4)-O(32)	145.1(6)	O(46)-Sb(5)-O(8)	93.6(6)	O(3)-W(1)-O(7)	64.5(6)
O(47)-W(1)-O(1)	156.9(7)	O(1)-W(2)-O(29)	155.9(7)	O(1)-W(2)-O(64)	85.6(8)
O(3)-W(3)-O(7)	65.8(6)	O(59)-W(3)-O(2)	158.5(8)		

Symmetry transformations used to generate equivalent atoms: #2 -x,-y+1,-z+1

Table S5. Selected bond lengths (Å) and angles (°) for **Dy-4**

W(1)-O(71)	1.76(2)	W(1)-O(46)	2.424(15)	W(2)-O(46)	2.313(14)
W(3)-O(46)	2.243(13)	W(2)-O(66)	1.65(2)	W(3)-O(67)	1.759(18)
W(4)-O(57)	1.696(18)	W(4)-O(22)	2.366(15)	W(6)-O(61)	1.713(18)
W(5)-O(22)	2.230(14)	W(5)-O(51)	1.716(15)	W(6)-O(47)	2.295(14)
W(7)-O(58)	2.304(14)	W(8)-O(47)	2.199(14)	W(7)-O(52)	1.696(18)
W(8)-O(62)	1.735(14)	W(9)-O(63)	1.744(15)	W(10)-O(18)	2.243(12)
W(9)-O(22)	2.281(15)	W(11)-O(37)	1.720(15)	W(11)-O(47)	2.287(14)
W(10)-O(1)	1.761(13)	W(12)-O(27)	2.249(13)	W(12)-O(17)#2	1.738(15)
W(13)-O(23)	2.321(14)	W(13)-O(40)	1.727(15)	W(15)-O(27)	2.343(13)
W(14)-O(39)	1.715(13)	W(14)-O(23)	2.302(13)	W(16)-O(34)	1.752(15)
W(16)-O(27)	2.329(12)	W(15)-O(56)	1.739(15)	W(17)-O(18)	2.285(13)
W(17)-O(55)	1.781(14)	W(18)-O(9)	1.721(15)	W(18)-O(23)	2.279(14)
Sb(1)-O(22)	1.961(15)	Sb(2)-O(18)	1.948(12)	Sb(2)-O(27)	1.993(14)
Sb(3)-O(58)	2.013(14)	Sb(4)-O(11)	2.006(13)	Sb(3)-O(11)	1.939(13)
Sb(4)-O(7)	2.238(13)	Sb(5)-O(2)#2	1.972(13)	Sb(5)-O(7)	2.206(14)
Dy(1)-O(72)	2.261(12)	Dy(1)-O(11)	2.493(14)	Dy(1)-O(14)	2.373(13)
Dy(1)-O(21)	2.312(14)	Dy(1)-N(1)	2.520(11)	Dy(1)-O(28)	2.333(16)
Dy(1)-O(17)	2.334(14)	Dy(1)-O(25)	2.430(14)	Dy(1)-O(11)	2.493(14)
Dy(2)-O(32)	2.298(12)	Dy(2)-O(36)	2.348(13)	Dy(2)-O(38)#2	2.422(11)
Dy(2)-O(2)	2.499(13)	Dy(2)-O(1W)	2.503(15)	Dy(2)-O(41)#2	2.278(15)
Dy(2)-O(18)	2.661(11)	Dy(2)-O(42)	2.300(14)	O(43)-W(1)-O(69)	87.3(7)
O(29)-W(1)-O(46)	72.0(6)	O(71)-W(1)-O(43)	103.0(10)	O(35)-W(3)-O(60)	91.2(8)
O(67)-W(3)-O(46)	166.0(7)	O(29)-W(2)-O(19)	163.0(7)	O(54)-W(4)-O(43)	158.6(7)
O(51)-W(5)-O(22)	168.0(7)	O(54)-W(4)-O(45)	88.5(7)	O(61)-W(6)-O(47)	168.7(7)
O(52)-W(7)-O(58)	86.1(7)	O(33)-W(6)-O(10)	89.3(7)	O(30)-W(8)-O(50)	95.3(6)
O(62)-W(8)-O(47)	168.2(6)	O(49)-W(7)-O(58)	172.1(7)	O(1)-W(10)-O(15)	100.2(6)
O(15)-W(10)-O(44)	85.9(6)	O(28)-W(9)-O(13)	91.2(6)	O(13)-W(11)-O(50)	157.8(6)
O(41)-W(12)-O(31)	159.6(6)	O(37)-W(11)-O(25)	105.6(7)	O(39)-W(14)-O(23)	169.1(6)
O(3)-W(15)-O(27)	76.0(5)	O(41)-W(12)-O(31)	159.6(6)	O(72)-W(17)-O(15)	154.6(5)
O(4)-W(18)-O(6)	82.8(6)	O(31)-W(16)-O(20)	90.8(6)	O(18)-Sb(2)-O(27)	94.0(5)
O(11)-Sb(3)-O(2)#2	94.1(6)	O(22)-Sb(1)-O(46)	94.7(6)	O(11)-Sb(4)-O(16)	89.9(5)
O(72)-Dy(1)-O(21)	83.1(5)	O(16)-Sb(4)-O(7)	69.4(5)	O(21)-Dy(1)-N(1)	65.8(4)
O(11)-Dy(1)-N(1)	150.4(4)	O(72)-Dy(1)-O(25)	139.0(4)	O(41)#2-Dy(2)-O(1W)	138.6(5)
O(41)#2-Dy(2)-O(38)#2	78.0(5)				

Symmetry transformations used to generate equivalent atoms: #2 -x,-y,-z+2

Table S6 Selected bond lengths (Å) and angles (°) for **Ho-5**

W(1)-O(22)	1.689(19)	W(1)-O(19)	2.269(18)	W(2)-O(19)	2.31(2)
W(3)-O(45)	2.228(16)	W(2)-O(5)	1.69(2)	W(3)-O(7)	1.68(3)
W(4)-O(4)	1.76(2)	W(4)-O(45)	2.366(19)	W(5)-O(19)	2.353(19)
W(6)-O(37)	2.303(16)	W(5)-O(1)	1.79(3)	W(6)-O(8)	1.75(2)
W(7)-O(32)	1.72(2)	W(7)-O(45)	2.307(18)	W(9)-O(26)	2.287(16)
W(10)-O(63)	2.277(15)	W(8)-O(42)	1.709(15)	W(10)-O(59)	1.739(16)
W(11)-O(27)	1.743(15)	W(11)-O(53)	2.246(14)	W(12)-O(58)	1.707(15)
W(12)-O(37)	2.253(16)	W(13)-O(69)	2.299(14)	W(14)-O(69)	2.289(15)
W(13)-O(40)	1.742(18)	W(14)-O(30)	1.752(15)	W(15)-O(36)	1.736(15)
W(15)-O(63)	2.310(15)	W(16)-O(53)	2.208(15)	W(17)-O(51)	1.703(16)
W(16)-O(25)	1.739(15)	W(17)-O(63)	2.242(15)	W(18)-O(69)	2.363(14)
W(18)-O(43)	1.714(17)	Sb(1)-O(45)	1.955(19)	Sb(1)-O(19)	2.000(18)
Sb(2)-O(63)	2.031(14)	Sb(3)-O(26)	2.008(15)	Sb(2)-O(69)	1.981(15)
Sb(3)-O(35)	1.978(15)	Sb(4)-O(35)	1.987(14)	Sb(4)-O(34)	2.546(15)
Sb(5)-O(65)	1.962(14)	Sb(5)-Ho(2)	3.5837(18)	Ho(1)-O(39)	2.228(16)
Ho(1)-O(34)	2.442(15)	Ho(1)-N(1)	2.552(19)	Ho(1)-O(67)	2.338(14)
Ho(1)-O(38)	2.299(16)	Ho(1)-O(111)	2.328(17)	Ho(1)-O(30)#1	2.300(15)
Ho(1)-O(35)	2.435(14)	Ho(2)-O(60)#1	2.252(15)	Ho(2)-O(49)#1	2.304(15)
Ho(2)-O(68)	2.270(14)	Ho(2)-O(52)	2.405(17)	Ho(2)-O(54)	2.420(14)
Ho(2)-O(65)	2.511(14)	O(22)-W(1)-O(2)	108.3(10)	Ho(2)-O(64)#1	2.246(15)
Ho(2)-O(53)#1	2.646(15)	O(6)-W(2)-O(10)	79.5(10)	O(22)-W(1)-O(15)	155.1(8)
O(15)-W(2)-O(6)	155.8(9)	O(24)-W(4)-O(45)	73.9(7)	O(21)-W(3)-O(24)	80.4(9)
O(24)-W(4)-O(41)	154.0(8)	O(16)-W(6)-O(37)	71.9(6)	O(1)-W(5)-O(19)	171.7(9)
O(8)-W(6)-O(37)	169.4(8)	O(20)-W(8)-O(37)	72.1(7)	O(23)-W(7)-O(45)	72.1(7)
O(33)-W(8)-O(29)	154.4(7)	O(48)-W(10)-O(31)	160.0(6)	O(18)-W(9)-O(26)	172.8(8)
O(28)-W(9)-O(26)	78.2(6)	O(58)-W(12)-O(17)	107.7(7)	O(49)-W(11)-O(48)	166.2(6)
O(50)-W(11)-O(48)	81.2(7)	O(60)-W(14)-O(68)	98.3(7)	O(34)-W(12)-O(16)	161.8(7)
O(56)-W(13)-O(62)	89.6(7)	O(46)-W(15)-O(63)	73.1(6)	O(30)-W(14)-O(69)	159.9(6)
O(50)-W(13)-O(62)	155.7(7)	O(57)-W(17)-O(46)	160.1(7)	O(31)-W(15)-O(61)	156.2(6)
O(39)-W(16)-O(57)	79.5(6)	O(62)-W(18)-O(69)	73.0(6)	O(57)-W(17)-O(55)	93.6(7)
O(70)-W(18)-O(71)	158.3(6)	O(67)-Sb(4)-O(47)	146.5(5)	O(37)-Sb(1)-O(19)	91.0(7)
O(35)-Sb(3)-O(65)	95.3(6)	O(39)-Ho(1)-O(38)	147.1(6)	O(35)-Sb(4)-O(34)	71.6(6)
O(61)-Sb(5)-O(47)	73.9(6)	O(35)-Ho(1)-N(1)	148.7(5)	O(67)-Ho(1)-O(34)	69.1(5)
O(38)-Ho(1)-N(1)	72.6(6)	O(38)-Ho(1)-N(1)	72.6(6)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z

Table S7 Selected bond lengths of Na-O and distances of Na…Na (Å) in compound **La-1**

O(111)-Na(1)	2.91(5)	Na(1)-Na(2)#2	3.97(6)
Na(1)-O(29)#2	2.95(5)	Na(1)-Na(6)	4.11(6)
Na(2)-O(7W)	2.41(6)	Na(2)-O(6W)#1	2.94(6)

O(6W)-Na(2)#2	2.94(6)	Na(2)-O(39)#1	2.94(5)
O(29)-Na(2)	2.99(5)	O(38)-Na(2)	2.86(5)
Na(2)-Na(7)#1	3.01(6)	Na(3)-Na(7)	3.42(6)
O(33)-Na(3)	2.91(4)	Na(4)-O(9W)	2.85(7)
Na(3)-Na(5)	3.80(6)	O(2W)-Na(4)	2.91(4)
O(23)-Na(4)	2.86(4)	O(25)-Na(5)	3.01(5)
O(31)-Na(4)	2.73(4)	O(21)-Na(6)	2.95(5)
Na(5)-O(5)#4	2.72(5)	O(17W)-Na(7)#1	2.97(7)
Na(5)-O(16W)	2.81(8)	O(40)-Na(7)	2.97(5)
O(1W)-Na(6)	2.95(5)	Na(7)-Na(2)#2	3.01(6)

Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y+1/2,-z+2; #2 x-1/2,-y+1/2,-z+2; #4 -x+1,y+1/2,-z+3/2

Table S8 Selected bond lengths of Na-O and distances of Na…Na (Å) in compound **Pr-2**

O(33)-Na(1)	2.94(6)	O(40)-Na(2)	3.01(7)
O(29)-Na(3)	2.79(9)	Na(3)-O(111)#1	2.89(10)
O(111)-Na(3)#2	2.89(10)	O(38)-Na(4)	2.55(9)
Na(4)-O(39)#1	2.86(8)	O(31)-Na(5)	2.85(8)
O(2W)-Na(5)	2.92(7)	Na(2)-Na(4)#2	3.00(10)
Na(1)-Na(2)	3.33(8)	Na(4)-Na(2)#1	3.00(10)

Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y+1/2,-z+2; #2 x-1/2,-y+1/2,-z+2

Table S9 Selected bond lengths of Na-O and distances of Na…Na (Å) in compound **Tb-3**

Na(1)-O(31)#7	2.87(3)	O(19)-Na(1)	2.76(3)
Na(1)-O(5W)#7	2.98(3)	Na(2)-O(57)#2	2.84(3)
Na(2)-O(6W)	2.73(3)	O(38)-Na(2)	3.01(3)
Na(2)-O(1W)#2	2.93(3)	O(26)-Na(3)	2.71(3)
Na(2)-Na(5)#2	4.08(3)	Na(4)-O(10W)#4	2.28(4)
Na(3)-O(13W)#8	2.45(4)	Na(4)-O(22W)	2.43(5)
O(51)-Na(4)	2.42(3)	O(9)-Na(4)	2.33(3)
Na(4)-O(9W)	2.68(5)	Na(5)-O(23W)	2.66(5)
Na(4)-O(4)#9	2.68(3)	Na(5)-Na(2)#2	4.08(3)
O(56)-Na(5)	2.73(3)	Na(6)-O(2W)#1	3.00(3)
Na(5)-O(10)#8	2.75(3)	Na(5)-O(15W)	2.83(5)
O(58)-Na(6)	2.77(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x-1/2,y-1/2,-z+3/2; #2 -x,-y+1,-z+1; #7 x-1/2,-y+3/2,z+1/2; #8 x-1,y,z; #9 -x+1/2,y+1/2,-z+3/2

Table S10 Selected bond lengths of Na-O and distances of Na…Na (Å) in compound **Dy-4**

Na(1)-O(4W)#3	2.43(3)	O(70)-Na(1)	2.67(2)
Na(1)-O(2W)#3	2.45(2)	O(9)-Na(1)	2.509(18)
Na(1)-O(37)#3	2.88(2)	O(21)-Na(1)	2.453(16)
O(37)-Na(1)	2.365(18)	Na(1)-Na(1)#3	3.65(2)

Na(1)-Na(7)#3	3.67(3)	O(35)-Na(2)	2.57(2)
Na(2)-O(11W)	2.32(4)	Na(2)-O(3W)#2	2.49(3)
Na(2)-O(5W)#2	2.36(3)	Na(2)-O(6W)	2.50(5)
Na(2)-O(8W)	2.42(3)	O(31)-Na(3)	2.74(3)
Na(2)-Na(6)#1	3.59(3)	Na(3)-Na(6)#6	3.89(3)
Na(3)-O(64)#2	2.89(3)	O(1W)-Na(4)	2.77(3)
O(64)-Na(3)#2	2.89(3)	O(1W)-Na(5)#2	2.78(3)
Na(4)-O(56)#7	2.84(3)	O(52)-Na(5)	2.70(3)
O(42)-Na(4)	2.76(3)	Na(6)-O(51)#1	2.52(4)
Na(5)-O(67)#5	2.72(3)	Na(6)-Na(6)#1	3.55(7)
Na(5)-O(1W)#2	2.78(3)	Na(6)-Na(2)#1	3.59(3)
Na(5)-O(5W)#2	2.89(3)	O(51)-Na(6)	2.31(3)
Na(6)-O(9W)	2.44(5)	Na(7)-O(9)#3	2.46(3)
Na(6)-O(6W)#1	2.48(5)	Na(7)-Na(1)#3	3.67(3)
Na(6)-O(8W)#1	2.51(4)	Na(6)-Na(3)#8	3.89(3)
Na(7)-O(4W)	2.29(4)	Na(7)-O(16W)#3	2.27(5)
Na(7)-O(13W)#3	2.32(5)		

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

Table S11 Selected bond lengths of Na-O and distances of Na…Na (Å) in compound **Ho-5**

Na(1)-O(1W)	2.39(2)	O(58)-Na(1)	2.449(18)
Na(1)-O(2W)	2.42(2)	O(52)-Na(5)#1	2.78(6)
Na(1)-O(58)#3	2.739(18)	O(111)-Na(1)	2.428(18)
O(51)-Na(1)	2.57(2)	O(112)-Na(1)	2.682(18)
Na(1)-Na(3)	3.734(14)	Na(1)-Na(1)#3	3.677(18)
Na(1)-Na(2)	3.744(14)	Na(2)-O(8W)	2.38(4)
Na(2)-O(9W)	2.20(4)	Na(2)-O(3W)	2.44(2)
Na(2)-O(1W)	2.37(2)	Na(2)-O(7W)	2.44(3)
O(112)-Na(2)	2.31(2)	Na(2)-Na(3)	3.718(17)
Na(3)-O(10W)	2.32(3)	Na(3)-O(4W)	2.46(3)
Na(3)-O(2W)	2.437(19)	Na(3)-O(3W)	2.65(2)
O(25)-Na(3)	2.397(19)	O(112)-Na(3)	2.39(2)
Na(4)-O(16W)#1	2.87(6)	O(11)-Na(4)	2.72(5)
O(52)-Na(4)	2.68(5)	O(43)-Na(5)#2	2.76(6)
Na(5)-O(43)#4	2.76(6)	O(64)-Na(5)	2.79(5)
Na(5)-Na(5)#5	3.50(10)	Na(5)-O(52)#1	2.78(6)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z; #2 x+1,y,z; #3 -x,-y,-z; #4 x-1,y,z; #5 -x-1,-y+1,-z

4. Additional physical measurements for compounds 1-5

4.1 FT-IR spectra of compounds 1-5

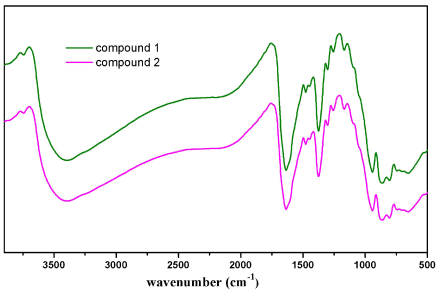

Fig S8. FT-IR spectrum for compound **1**, **2** at room temperature

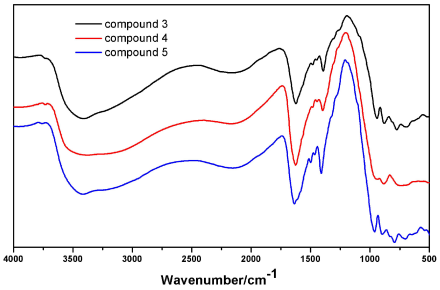

Fig S9. FT-IR spectrum for compound **3-5** at room temperature

FT-IR spectra

In the FT-IR spectra of compounds **1** and **2**: the features in the range of 1000-600 cm^{-1} are ascribed to the vibrations ν(Sb−O_a), ν(W−O_d), ν(W− O_b− W), and ν(W− O_c− W) in polyoxoanion framework. The broad band around 3391(s)cm^{-1} can be regarded as features of the lattice and coordinated water molecules. The peaks at close to 1634(s)cm^{-1} can be attributed to the vibration of carboxy group, and the vibration of pyridyl can be observed at 1478 (m), 1446(m), 1379(s), 1301(m), 1259(m), 1170(m).

In the FT-IR spectrum of compounds **3-5**: The FT-IR spectrum of compound **3**, **4,** and **5** are similar to compound **1** and **2.** The features in the range of 1000-600 cm^{-1} are ascribed to the vibrations ν(Sb−O_a), ν(W−O_d), ν(W− O_b− W), and ν(W− O_c− W) in polyoxoanion framework. And the broad band around 3420(s)cm^{-1} can be regarded as features of the lattice and coordinated water molecules. The peaks at close to 1621(s)cm^{-1} can be attributed to the vibration of carboxy group, and the vibration of pyridyl can be observed at 1581 (m), 1466(w), 1414(s), 961(s).

4.2 TG analysis of compounds 1-5

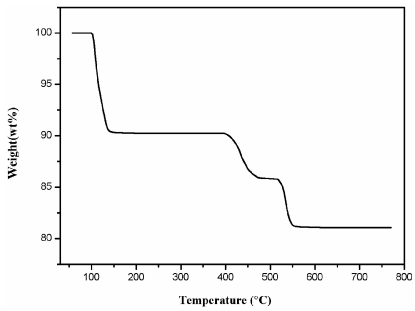

Fig S10. TG curve of compound **1**

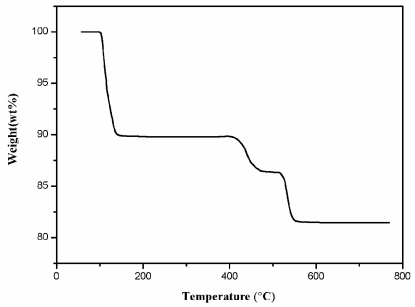

Fig S11. TG curve of compound **2**

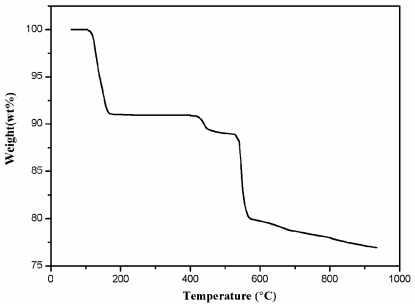

Fig S12. TG curve of compound **3**

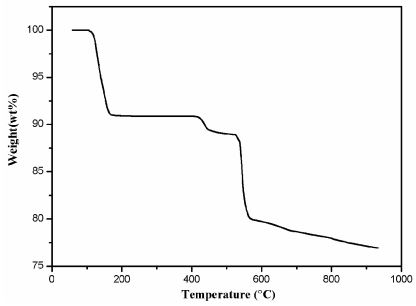

Fig S13. TG curve of compound **4**

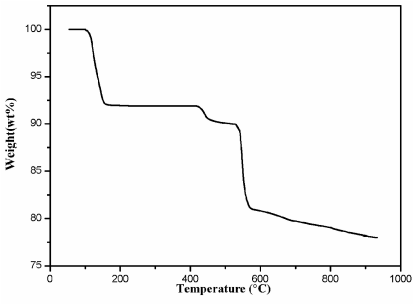

Fig S14. TG curve of compound **5**

TG analysis

TG analyses were performed on a Pyris Diamond TG instrument in flowing N_2 with a heating rate of 10°C min^{-1}. The TG curve of compound **1** shows a total weight loss of 19.24% in accordance with the calculated value of 19.15%, which can be divided into three steps. 9.90% loss of the total weight from 100 to 191°C was attributed to the loss of all crystalline and coordinated water molecules (calc. 9.92%). The weight loss of 4.21% from 389 to 511°C corresponds to the decomposition and loss of pyridine carboxylic acid ligands(calc. 4.20%). 5.13% loss of the total weight from 512 to 570°C corresponds to the loss of Sb_2O_3(calc. 5.02%). The thermal gravimetric (TG) curve of compound **2** is similar to that of compound **1**. 6.72% loss of the total weight from 100 to 163°C was attributed to the loss of all crystalline and coordinated water molecules (calc. 6.76%). The weight loss of 4.34% from 400 to 492 °C corresponds to the decomposition and loss of pyridine carboxylic acid ligands(calc. 4.36%). 5.20% loss of the total weight from 511 to 580°C corresponds to the loss of Sb_2O_3(calc. 5.21%).

As for compound **3**, the total weight loss was 23.20% agree with the calculated value 23.06%. And three steps follow: First, 9.45% loss of the total weight at 100-189°C belong to the loss of all crystalline and coordinated water molecules (calc. 9.40%). Second, 2.00% loss of the total at 391-522°C was ascribed to decomposition and loss of pyridine carboxylic acid ligands(calc. 1.96%). The last, 11.75% loss of the total was resulted to the sublimation of Sb_2O_3(calc. 11.70%). The thermal gravimetric (TG) curve of compound **4**, **5** is similar to that of **3**. The first, the TGA curves of **4**, **5** show weight loss of 9.15% 8.05% in the range of 100-196°C 100-190°C which are assigned to all crystalline and coordinated water molecules loss(calc. 9.14%, 8.09%) respectively. In the second region, The TG curve of compound **4**, **5** show weight loss of 1.94% 2.00% in the range of 412-521°C 417-524°C which are assigned to decomposition and loss of pyridine carboxylic acid ligands loss(calc. 1.97%, 1.99%). The last, 11.78%, 11.93% loss of the total was resulted to the sublimation of Sb_2O_3(calc. 11.74%, 11.90%).

4.3 Powder X-ray diffractions of compounds Tb-3 and Dy-4

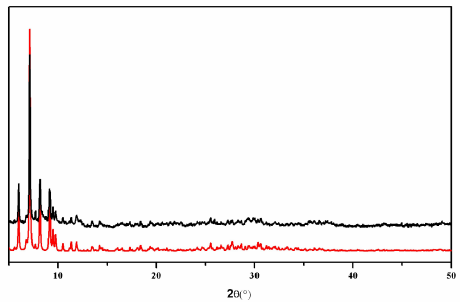

Fig S15. Experimental powder X-ray diffraction pattern of **Tb-3** (red) and simulated PXRD pattern (from the single-crystal X-ray diffraction data) of Tb-**3** (black).

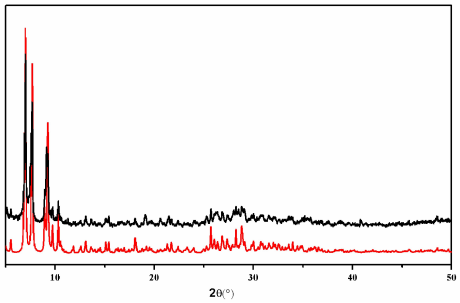

Fig S16. Experimental powder X-ray diffraction pattern of **Dy-4** (red) and simulated PXRD pattern (from the single-crystal X-ray diffraction data) of **Dy-4** (black).