Electronic Supplementary Information (ESI)

$Tb^{III}/3d–Tb^{III}$ clusters derived from 1,4,7–triazacyclononane-based hexadentate ligand with field-induced slow magnetic relaxation and oxygen-sensitive luminescence

He-Rui Wen,[a]* Jia-Li Zhang,[a] Fu-Yong Liang,[a] KaiYang,[a] Sui-Jun Liu,[a]* Jin-Sheng Liao[a] and Cai-Ming Liu[b]

[a]*School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, China.*

[b]*Beijing National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China*

E-mail: wenherui63@163.com (H.-R. Wen), liusuijun147@163.com (S.-J. Liu)

Table S1. Selected bond lengths(Å) and angles(deg) for **1**

Tb1—O3	2.172(2)	Tb1—N2	2.542(3)
Tb1—O4	2.181(2)	Tb1—N3	2.553(3)
Tb1—O2	2.188(2)	Tb1—N1	2.564(2)
Tb1—O1	2.470(3)		
O3—Tb1—O4	112.80(8)	O3—Tb1—O1	80.55(10)
O3—Tb1—O2	117.44(9)	O4—Tb1—O1	82.71(9)
O4—Tb1—O2	118.86(8)	O2—Tb1—O1	73.73(9)
O4—Tb1—N2	87.16(8)	O3—Tb1—N2	141.13(8)
O2—Tb1—N2	74.95(8)	N2—Tb1—N3	69.09(8)
O1—Tb1—N2	136.82(9)	O3—Tb1—N1	83.50(8)
O3—Tb1—N3	75.62(8)	O4—Tb1—N1	75.70(8)
O4—Tb1—N3	142.17(8)	O2—Tb1—N1	140.44(8)
O2—Tb1—N3	83.90(8)	O1—Tb1—N1	145.58(9)
O1—Tb1—N3	134.69(10)	N2—Tb1—N1	69.04(8)
N3—Tb1—N1	68.56(8)		

Table S2. Selected bond lengths(Å) and angles(deg) for **2**

Tb1—O1$^{\#1}$	2.171 (5)	Tb1—N1$^{\#1}$	2.509 (7)
Tb1—O1	2.171 (5)	Tb1—N1	2.509 (7)
Tb1—O1$^{\#2}$	2.171 (5)	Tb1—O1W$^{\#2}$	2.58 (7)
Tb1—O1W$^{\#3}$	2.37 (7)	Tb1—O1W$^{\#1}$	2.58 (7)
Tb1—O1W$^{\#4}$	2.37 (7)	Tb1—O1W	2.58 (7)
Tb1—O1W$^{\#5}$	2.37 (7)	O1W—Tb1$^{\#3}$	2.37 (7)
Tb1—N1$^{\#2}$	2.509 (7)		
O1$^{\#1}$—Tb1—O1	114.85 (13)	O1$^{\#2}$—Tb1—O1W$^{\#4}$	77 (4)
O1$^{\#1}$—Tb1—O1$^{\#2}$	114.84 (13)	O1W$^{\#3}$—Tb1—O1W$^{\#4}$	25.4 (13)
O1—Tb1—O1$^{\#2}$	114.85 (13)	O1$^{\#1}$—Tb1—O1W$^{\#5}$	89 (2)
O1$^{\#1}$—Tb1—O1W$^{\#3}$	77 (4)	O1—Tb1—O1W$^{\#5}$	77 (4)
O1—Tb1—O1W$^{\#3}$	64 (2)	O1$^{\#2}$—Tb1—O1W$^{\#5}$	64 (2)
O1$^{\#2}$—Tb1—O1W$^{\#3}$	89 (2)	O1W$^{\#3}$—Tb1—O1W$^{\#5}$	25.4 (13)
O1$^{\#1}$—Tb1—O1W$^{\#4}$	64 (2)	O1W$^{\#4}$—Tb1—O1W$^{\#5}$	25.4 (13)
O1—Tb1—O1W$^{\#4}$	89 (2)		
O1$^{\#1}$—Tb1—N1$^{\#2}$	144.5 (2)	N1$^{\#1}$—Tb1—N1	70.5 (3)
O1—Tb1—N1$^{\#2}$	86.0 (2)	O1$^{\#1}$—Tb1—O1W$^{\#2}$	65 (2)
O1$^{\#2}$—Tb1—N1$^{\#2}$	76.8 (2)	O1—Tb1—O1W$^{\#2}$	77 (4)
O1W$^{\#3}$—Tb1—N1$^{\#2}$	138 (4)	O1$^{\#2}$—Tb1—O1W$^{\#2}$	88 (2)
O1W$^{\#4}$—Tb1—N1$^{\#2}$	149 (3)	O1W$^{\#3}$—Tb1—O1W$^{\#2}$	14.0 (6)
O1W$^{\#5}$—Tb1—N1$^{\#2}$	124.4 (15)	O1W$^{\#4}$—Tb1—O1W$^{\#2}$	14.0 (6)
O1$^{\#1}$—Tb1—N1$^{\#1}$	76.8 (2)	O1W$^{\#5}$—Tb1—O1W$^{\#2}$	28.2 (13)
O1—Tb1—N1$^{\#1}$	144.5 (2)	N1$^{\#2}$—Tb1—O1W$^{\#2}$	150 (2)
O1$^{\#2}$—Tb1—N1$^{\#1}$	86.0 (2)	N1$^{\#1}$—Tb1—O1W$^{\#2}$	135 (4)
O1W$^{\#3}$—Tb1—N1$^{\#1}$	149 (3)	N1—Tb1—O1W$^{\#2}$	127 (2)
O1W$^{\#4}$—Tb1—N1$^{\#1}$	124.4 (15)	O1$^{\#1}$—Tb1—O1W$^{\#1}$	88 (2)
O1W$^{\#5}$—Tb1—N1$^{\#1}$	138 (4)	O1—Tb1—O1W$^{\#1}$	65 (2)
N1$^{\#2}$—Tb1—N1$^{\#1}$	70.5 (3)	O1$^{\#2}$—Tb1—O1W$^{\#1}$	77 (4)
O1$^{\#1}$—Tb1—N1	86.0 (2)	O1W$^{\#3}$—Tb1—O1W$^{\#1}$	14.0 (6)
O1—Tb1—N1	76.8 (2)	O1W$^{\#4}$—Tb1—O1W$^{\#1}$	28.2 (13)
O1$^{\#2}$—Tb1—N1	144.5 (2)	O1W$^{\#5}$—Tb1—O1W$^{\#1}$	14.0 (6)
O1W$^{\#3}$—Tb1—N1	124.4 (14)	N1$^{\#2}$—Tb1—O1W$^{\#1}$	127 (2)
O1W$^{\#4}$—Tb1—N1	138 (4)	N1$^{\#1}$—Tb1—O1W$^{\#1}$	150 (2)
O1W$^{\#5}$—Tb1—N1	149 (3)	N1—Tb1—O1W$^{\#1}$	135 (4)
N1$^{\#2}$—Tb1—N1	70.5 (3)		
O1W$^{\#2}$—Tb1—O1W$^{\#1}$	23.3 (14)	O1W$^{\#5}$—Tb1—O1W	14.0 (6)
O1$^{\#1}$—Tb1—O1W	77 (4)	N1$^{\#2}$—Tb1—O1W	135 (4)
O1—Tb1—O1W	88 (2)	N1$^{\#1}$—Tb1—O1W	127 (2)
O1$^{\#2}$—Tb1—O1W	65 (2)	N1—Tb1—O1W	150 (2)
O1W$^{\#3}$—Tb1—O1W	28.2 (13)	O1W$^{\#2}$—Tb1—O1W	23.3 (14)
O1W$^{\#4}$—Tb1—O1W	14.0 (6)	O1W$^{\#1}$—Tb1—O1W	23.3 (14)

Symmetry codes: (#1) -x+y, -x+1, z; (#2) -y+1, x-y+1, z; (#3) -x+2/3, -y+4/3, -z+1/3; (#4) x-y+2/3, x+1/3, -z+1/3; (#5) y-1/3, -x+y+1/3, -z+1/3.

Table S3. Selected bond lengths(Å) and angles(deg) for **3**

Tb1—O3	2.250(4)	Zn1—N2	2.111(7)
Tb1—O1	2.292(5)	Zn1—N1	2.124(6)
Tb1—O2	2.281(5)	Zn1—N3	2.129(5)
Zn1—O1	2.170(5)	Zn1—O2	2.136(5)
Zn1—O3	2.145(5)		
O3—Tb1—O3$^{\#1}$	180.0(3)	O3—Tb1—O2	76.34(16)
O3—Tb1—O1$^{\#1}$	103.60(17)	O3$^{\#1}$—Tb1—O2	103.66(16)
O3$^{\#1}$—Tb1—O1$^{\#1}$	76.40(17)	O1$^{\#1}$—Tb1—O2	104.59(19)
O3—Tb1—O1	76.40(17)	O1—Tb1—O2	75.41(19)
O3$^{\#1}$—Tb1—O1	103.60(17)	O3—Tb1—O2$^{\#1}$	103.66(16)
O1$^{\#1}$—Tb1—O1	180.0(2)	O3$^{\#1}$—Tb1—O2$^{\#1}$	76.34(16)
O1—Tb1—O2$^{\#1}$	104.59(19)	O1$^{\#1}$—Tb1—O2$^{\#1}$	75.41(19)
O2—Tb1—O2$^{\#1}$	180.000(1)	N2—Zn1—N1	84.6(2)
N2—Zn1—O2	90.8(2)	N2—Zn1—N3	83.5(2)
N1—Zn1—O2	105.0(2)	N1—Zn1—N3	83.3(2)
N2—Zn1—O3	104.9(2)	N3—Zn1—O2	169.5(2)
N3—Zn1—O3	91.2(2)	N1—Zn1—O3	168.5(2)
O2—Zn1—O3	81.72(18)	Zn1—O1—Tb1	84.95(19)
N2—Zn1—O1	169.08(18)	Zn1—O3—Tb1	86.59(15)
N1—Zn1—O1	90.5(2)	Zn2—O5—Tb2	85.4(2)
N3—Zn1—O1	105.6(2)	Zn2—O4—Tb2	85.9(2)
O2—Zn1—O1	81.00(19)	Zn2—O6—Tb2	85.92(16)
O3—Zn1—O1	81.23(19)	Zn1—O2—Tb1	86.03(18)
O4—Tb2—O4$^{\#2}$	180.00(8)	N5—Zn2—O6	104.5(2)
O4—Tb2—O6	75.51(18)	N4—Zn2—O6	169.7(3)
O4$^{\#2}$—Tb2—O6	104.49(18)	O5—Zn2—O6	81.6(2)
O4—Tb2—O6$^{\#2}$	104.49(18)	N6—Zn2—O4	103.3(2)
O4$^{\#2}$—Tb2—O6$^{\#2}$	75.51(18)	N5—Zn2—O4	171.3(2)
O6—Tb2—O6$^{\#2}$	180.000(1)	N4—Zn2—O4	90.2(2)
O4—Tb2—O5	76.4(2)	O5—Zn2—O4	82.5(2)
O4$^{\#2}$—Tb2—O5	103.6(2)	O6—Zn2—O4	80.91(19)
O6—Tb2—O5	75.76(19)	N6—Zn2—N5	83.6(3)
O6$^{\#2}$—Tb2—O5	104.24(19)	N6—Zn2—N4	85.7(3)
O4—Tb2—O5$^{\#2}$	103.6(2)	N5—Zn2—N4	85.0(3)
O4$^{\#2}$—Tb2—O5$^{\#2}$	76.4(2)	N6—Zn2—O5	170.1(2)
O6—Tb2—O5$^{\#2}$	104.24(19)	N5—Zn2—O5	91.5(3)
O6$^{\#2}$—Tb2—O5$^{\#2}$	75.76(19)	N4—Zn2—O5	102.5(2)
O5—Tb2—O5$^{\#2}$	180.000(1)	N6—Zn2—O6	91.3(2)

Symmetry codes:(#1) $-x+1, -y+1, -z$;(#2) $-x, -y+1, -z+1$.

Table S4. Selected bond lengths(Å) and angles(deg) for **4**

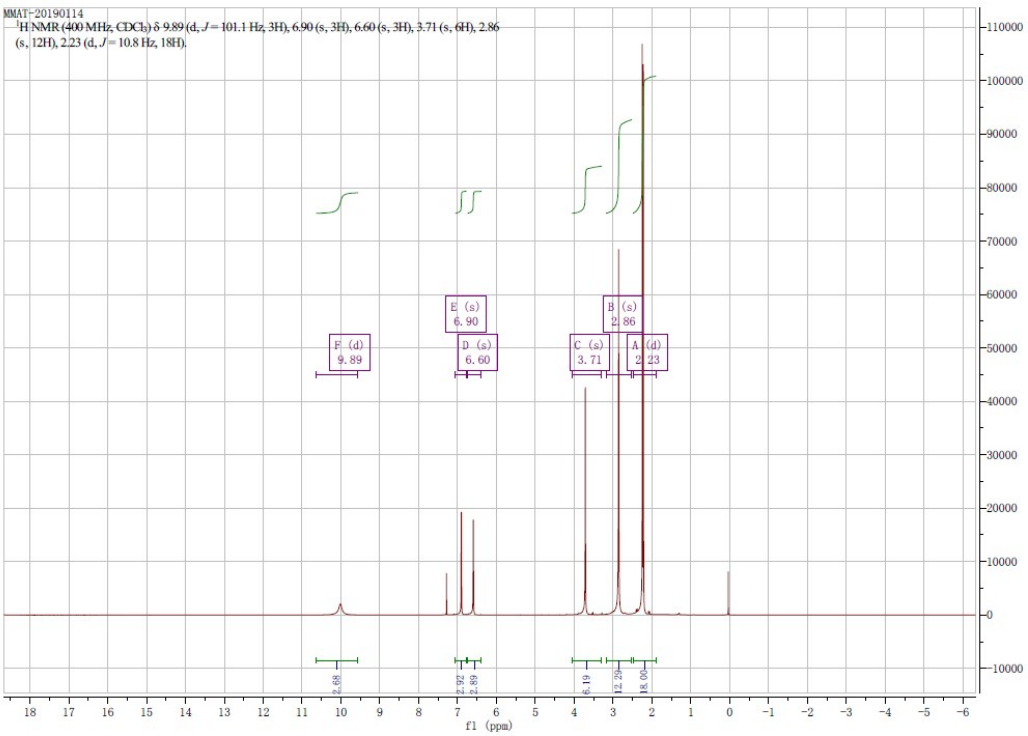
Tb1—O3	2.268(4)	Tb2—O4	2.288(5)
Tb1—O2	2.272(4)	Tb2—O5	2.297(5)

Tb1—O1	2.282(4)	Tb2—O4$^{\#2}$	2.288(5)
Tb2—O6	2.279(5)	Ni2—N4	2.059(7)
Ni1—N2	2.070(5)	Ni2—N6	2.074(6)
Ni1—N3	2.074(5)	Ni2—N5	2.075(5)
Ni1—N1	2.084(5)	Ni2—O5	2.113(5)
Ni1—O1	2.105(4)	Ni2—O6$^{\#2}$	2.124(4)
Ni1—O3$^{\#1}$	2.128(4)	Ni2—O4	2.125(5)
Ni1—O2	2.138(4)		
O3$^{\#1}$—Tb1—O3	180.00(17)	Ni2—O4—Tb2	85.66(16)
O3$^{\#1}$—Tb1—O2	75.74(15)	Ni2—O5—Tb2	85.69(17)
O3—Tb1—O2	104.26(15)	N2—Ni1—N3	85.2(2)
O3$^{\#1}$—Tb1—O2$^{\#1}$	104.26(15)	N2—Ni1—N1	84.6(2)
O3—Tb1—O2$^{\#1}$	75.74(15)	N3—Ni1—N1	85.1(2)
O2—Tb1—O2$^{\#1}$	180.0(2)	N2—Ni1—O1	92.23(19)
O3$^{\#1}$—Tb1—O1	75.15(15)	Ni1—O1—Tb1	86.55(14)
O3—Tb1—O1	104.85(15)	Ni1—O2—Tb1	86.02(15)
O2—Tb1—O1	74.53(15)	Ni1$^{\#1}$—O3—Tb1	86.36(14)
O2$^{\#1}$—Tb1—O1	105.47(15)	O2—Tb1—O1$^{\#1}$	105.47(15)
O3$^{\#1}$—Tb1—O1$^{\#1}$	104.85(15)	O2$^{\#1}$—Tb1—O1$^{\#1}$	74.53(15)
O3—Tb1—O1$^{\#1}$	75.15(15)	O1—Tb1—O1$^{\#1}$	180.0
N3—Ni1—O1	101.75(18)	N3—Ni1—O3$^{\#1}$	172.27(19)
N1—Ni1—O1	172.22(19)	N2—Ni1—O3$^{\#1}$	101.57(19)
N1—Ni1—O3$^{\#1}$	91.73(18)	N4—Ni2—N6	85.0(3)
O1—Ni1—O3$^{\#1}$	81.93(16)	N4—Ni2—N5	85.7(2)
N2—Ni1—O2	172.18(19)	N6—Ni2—N5	86.0(2)
N3—Ni1—O2	92.23(18)	N4—Ni2—O5	173.0(2)
N1—Ni1—O2	102.55(18)	N6—Ni2—O5	92.0(2)
O1—Ni1—O2	81.07(16)	N5—Ni2—O5	100.3(2)
O3$^{\#1}$—Ni1—O2	81.57(16)	N4—Ni2—O6$^{\#2}$	92.9(2)
O6—Tb2—O6$^{\#2}$	180.0(2)	N6—Ni2—O6$^{\#2}$	101.7(2)
O6—Tb2—O4$^{\#2}$	75.01(17)	N5—Ni2—O6$^{\#2}$	172.0(2)
O6$^{\#2}$—Tb2—O4$^{\#2}$	104.99(17)	O5—Ni2—O6$^{\#2}$	81.61(18)
O6—Tb2—O4	104.99(17)	N4—Ni2—O4	99.9(2)
O6$^{\#2}$—Tb2—O4	75.01(17)	N6—Ni2—O4	174.0(2)
O4$^{\#2}$—Tb2—O4	180.00(8)	N5—Ni2—O4	90.8(2)
O6—Tb2—O5$^{\#2}$	74.45(17)	O5—Ni2—O4	83.61(19)
O6$^{\#2}$—Tb2—O5$^{\#2}$	105.55(17)	O6$^{\#2}$—Ni2—O4	81.76(18)
O4$^{\#2}$—Tb2—O5$^{\#2}$	76.06(17)	Ni2$^{\#2}$—O6—Tb2	85.90(15)
O4—Tb2—O5$^{\#2}$	103.94(17)	O4—Tb2—O5	76.06(17)
O6—Tb2—O5	105.55(17)	O5$^{\#2}$—Tb2—O5	180.0(2)
O6$^{\#2}$—Tb2—O5	74.45(17)	O4$^{\#2}$—Tb2—O5	103.94(17)

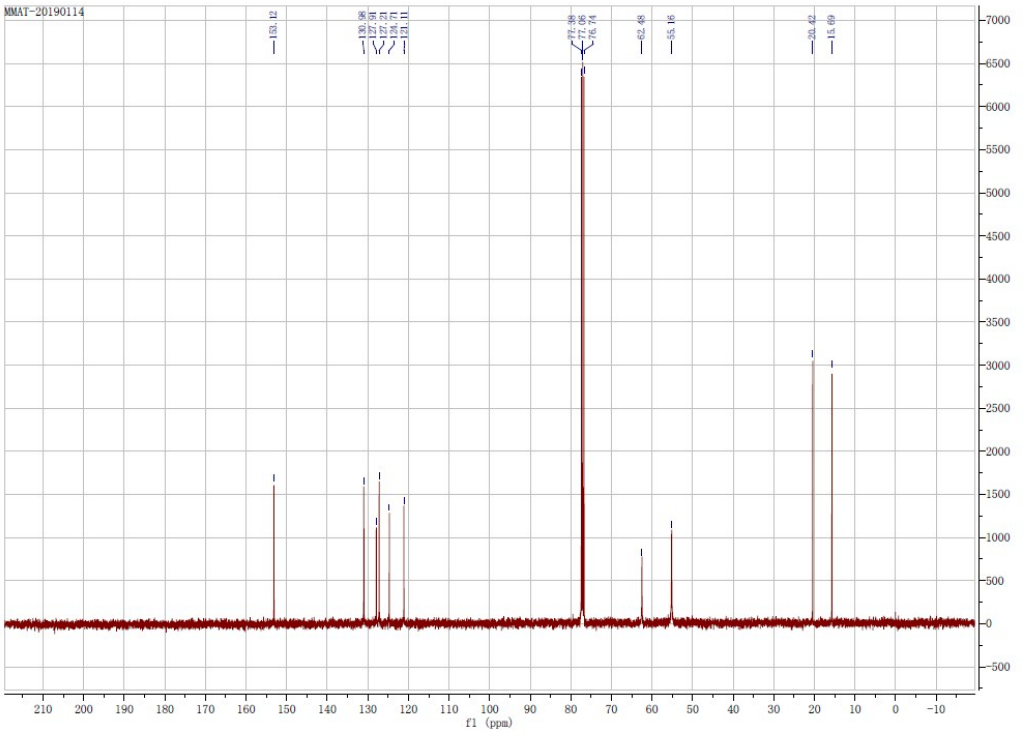
Symmetry codes:(#1) −x, −y+1, −z;(#2) −x+1, −y+1, −z+1.

Table S5. SHAPE analysis of the Tb/Zn/Ni ions in complex**1**–**4**

Complex	Metal Ions	Label	Shape	Symmetry	Distortion(τ)
1	Tb	HP-7	Heptagon	D_{7h}	32.986
		HPY-7	Hexagonal pyramid	C_{6v}	20.545
		PBPY-7	Pentagonal bipyramid	D_{5h}	8.399
		COC-7	**Capped octahedron**	**C_{3v}**	**1.126**
		CTPR-7	Capped trigonal prism	C_{2v}	2.259
		JPBPY-7	Johnson pentagonal bipyramid J13	D_{5h}	11.241
		JETPY-7	Johnson elongated triangular pyramid J7	C_{3v}	13.69
2	Tb	HP-7	Heptagon	D_{7h}	34.195
		HPY-7	Hexagonal pyramid	C_{6v}	20.904
		PBPY-7	Pentagonal bipyramid	D_{5h}	9.059
		COC-7	**Capped octahedron**	**C_{3v}**	**0.869**
		CTPR-7	Capped trigonal prism	C_{2v}	2.671
		JPBPY-7	Johnson pentagonal bipyramid J13	D_{5h}	12.087
		JETPY-7	Johnson elongated triangular pyramid J7	C_{3v}	13.708
3	Tb	HP-6	Hexagon	D_{6h}	29.187
		PPY-6	Pentagonal pyramid	C_{5v}	29.09
		OC-6	**Octahedron**	**O_h**	**2.668**
		TPR-6	Trigonal prism	D_{3h}	14.294
		JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	31.802
3	Zn	HP-6	Hexagon	D_{6h}	31.378
		PPY-6	Pentagonal pyramid	C_{5v}	24.742
		OC-6	**Octahedron**	**O_h**	**1.41**
		TPR-6	Trigonal prism	D_{3h}	9.703
		JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	28.359
4	Tb	HP-6	Hexagon	D_{6h}	28.975
		PPY-6	Pentagonal pyramid	C_{5v}	29.181
		OC-6	**Octahedron**	**O_h**	**3.002**
		TPR-6	Trigonal prism	D_{3h}	14.291
		JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	31.880
4	Ni	HP-6	Hexagon	D_{6h}	31.237
		PPY-6	Pentagonal pyramid	C_{5v}	25.958
		OC-6	**Octahedron**	**O_h**	**0.899**
		TPR-6	Trigonal prism	D_{3h}	11.354
		JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	29.523



(a)



(b)

Fig. S1. (a) ^{1}H NMR (400 MHz, $CDCl_3$) : δ 9.89 (d, J = 101.1 Hz, 3H), 6.90 (s, 3H), 6.60 (s, 3H), 3.71 (s, 6H), 2.86 (s, 12H), 2.23 (d, J = 10.8 Hz, 18H); (b) ^{13}C (^{1}H) NMR (101 MHz, $CDCl_3$): δ 15.69 (Me_a), 20.42 (Me_b), 55.16 (TACN, ring CH_2), 62.48 (benzylic,CH_2), 121.11, 124.71, 127.21, 127.91, 130.98, 153.13 (phenyl C′s).

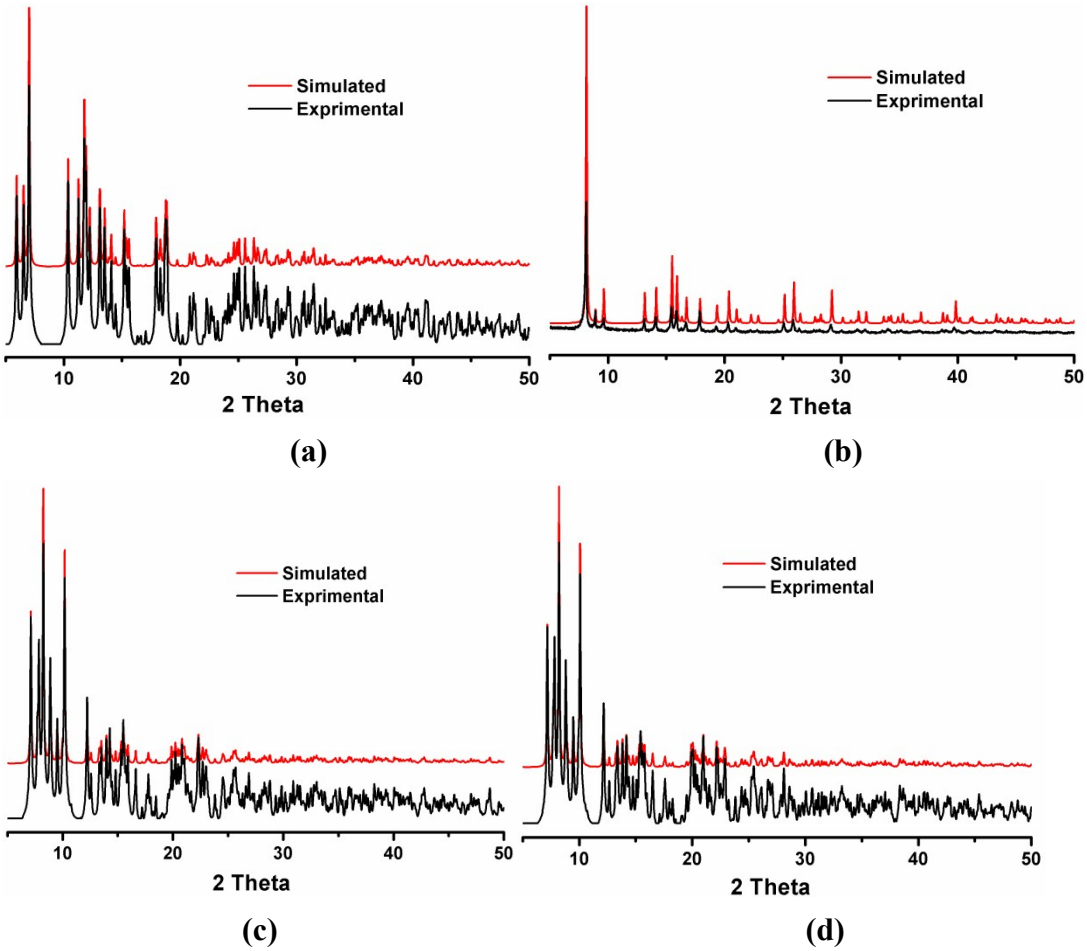


Fig. S2. The PXRD patterns of complexes **1** (a), **2** (b), **3** (c) and **4** (d).

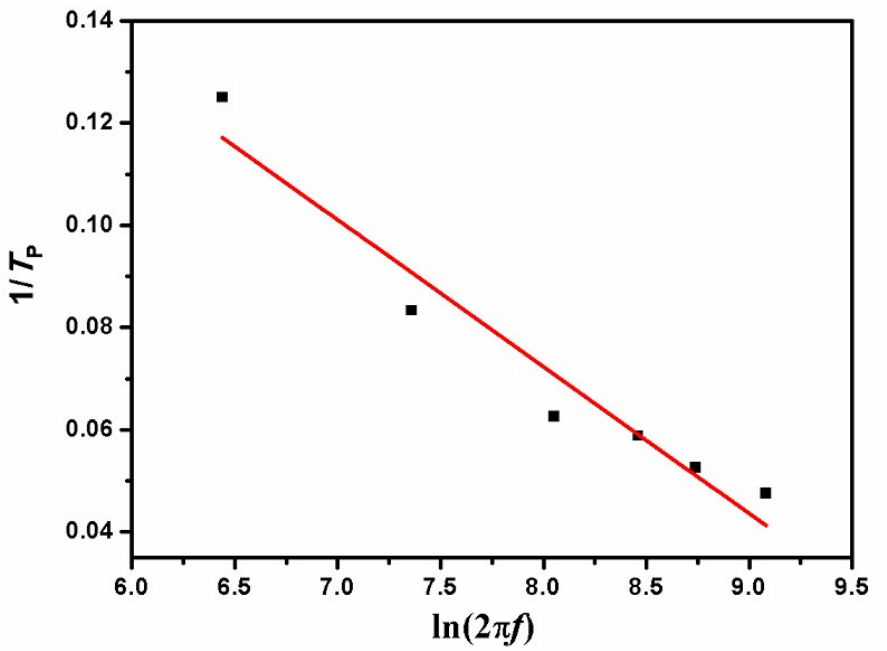


Fig. S3. The least-squares fit for **3** of the experimental data to the Arrhénius equation.

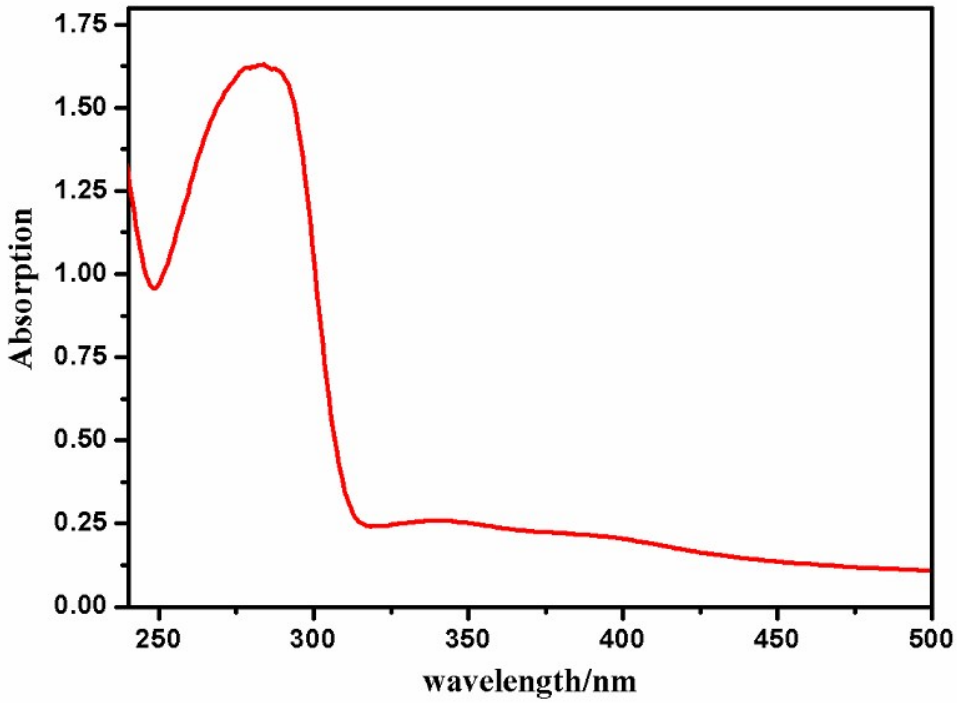


Fig. S4. The UV spectrum of H_3L.