

SUPPLEMENTARY MATERIAL

3D Ln-MOFs Featuring Lantern-Shaped Dihelicate Chains: Synthesis, Magnetic and Photophysical Properties

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Crystallographic data and structure refinement parameters for 1-6

Table S1 Crystallographic data and structure refinement parameters for 1-6

identification	Compound 1	Compound 2	Compound 3	Compound 4
formula	C ₁₁ H ₇ N ₃ O ₇ Nd	C ₁₁ H ₇ N ₃ O ₇ Sm	C ₁₁ H ₇ N ₃ O ₇ Eu	C ₁₁ H ₇ N ₃ O ₇ Gd
Mr (g/mol)	437.44	443.55	445.16	450.45
T (K)	293(2)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P21/c	P21/c	P21/c	P21/c
<i>a</i> (Å)	9.7107(8)	9.656(3)	9.7039(13)	9.604(3)
<i>b</i> (Å)	18.1921(16)	18.135(6)	18.125(2)	17.959(5)
<i>c</i> (Å)	7.0968(6)	7.081(2)	7.0937(10)	7.044(2)
α (°)	90	90	90	90
β (°)	104.816(3)	104.846(5)	104.815(3)	104.833(6)
γ (°)	90	90	90	90
<i>Z</i>	4	4	4	4
ρ (g·cm ⁻³)	2.397	2.458	2.451	2.548
μ (mm ⁻¹)	4.329	4.945	5.245	5.694
<i>V</i> (Å ³)	1212.02(18)	1198.6(6)	1206.2(3)	1174.5(6)
<i>F</i> (000)	852	848	852	856
2θ scan range (°)	3.12 to 27.48	3.13 to 25.01	3.13 to 25.01	3.16 to 27.49
<i>R</i> _{int}	0.0262	0.0350	0.0520	0.0299
reflns collected	9441	7589	7620	9066
indep reflns	2779	2111	2123	2686
parameters	200	200	200	199
<i>R</i> ₁ , ω <i>R</i> ₂ [I>2 σ (I)]	0.0257, 0.0476	0.0291, 0.0665	0.0360, 0.0783	0.0306, 0.0468
<i>R</i> ₁ , ω <i>R</i> ₂ [all data]	0.0299,0.0485	0.0323,0.0675	0.0372,0.0786	0.0369,0.0475
God on <i>F</i> ²	1.260	1.285	1.759	1.565
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ ⁻³)	0.511, -0.540	0.453, -0.875	0.855, -1.318	0.614, -0.966

Table S1. (continued)

identification	Compound 5	Compound 6
formula	C ₁₁ H ₇ N ₃ O ₇ Tb	C ₁₁ H ₇ N ₃ O ₇ Dy
Mr (g/mol)	453.12	455.70
T (K)	293(2)	293(2)
crystal system	monoclinic	monoclinic
space group	P21/c	P21/c
<i>a</i> (Å)	9.6284(7)	9.6234(10)
<i>b</i> (Å)	17.9698(13)	17.9128(18)
<i>c</i> (Å)	7.0625(5)	7.0731(7)
α (°)	90	90
β (°)	104.7660(10)	104.720(2)
γ (°)	90	90
<i>Z</i>	4	4
ρ (g·cm ⁻³)	2.547	2.567
μ (mm ⁻¹)	6.032	6.383
<i>V</i> (Å ³)	1181.60(15)	1179.3(2)
F(000)	864	864
2θ scan range (°)	3.15 to 27.48	3.16 to 27.48
<i>R</i> _{int}	0.0286	0.0479
reflns collected	8513	9104
indep reflns	2705	2680
parameters	199	200
<i>R</i> 1, ω R2 [I>2 σ (I)]	0.0317, 0.0562	0.0411, 0.0957
<i>R</i> 1, ω R2 [all data]	0.0383, 0.0673	0.0431, 0.0966
God on F ²	1.307	1.353
$\Delta\rho$ max, $\Delta\rho$ min (eÅ ⁻³)	0.795, -1.036	1.548, -3.382

Selected bonds length and angles for 1-6.

Table S2. Selected bonds length (Å) and angles (°) for complex **1**.

bonds lengths [Å] and angles [°] for complex 1			
Nd(1)-O(1)#1	2.415(2)	O(2)-Nd(1)-O(5)	69.24(8)
Nd(1)-O(3)#2	2.441(2)	O(1)#1-Nd(1)-O(7)	75.67(8)
Nd(1)-O(4)#3	2.450(2)	O(3)#2-Nd(1)-O(7)	128.84(8)
Nd(1)-O(6)	2.457(2)	O(4)#3-Nd(1)-O(7)	70.88(8)
Nd(1)-O(2)	2.459(2)	O(6)-Nd(1)-O(7)	68.26(8)
Nd(1)-O(5)	2.500(2)	O(2)-Nd(1)-O(7)	135.64(9)
Nd(1)-O(7)	2.528(3)	O(5)-Nd(1)-O(7)	123.78(8)
Nd(1)-N(3)#4	2.617(3)	O(1)#1-Nd(1)-N(3)#4	144.94(9)
Nd(1)-O(1)	2.845(2)	O(3)#2-Nd(1)-N(3)#4	142.20(9)
O(1)#1-Nd(1)-O(3)#2	71.52(8)	O(4)#3-Nd(1)-N(3)#4	79.07(8)
O(1)#1-Nd(1)-O(4)#3	76.31(8)	O(6)-Nd(1)-N(3)#4	84.53(8)
O(3)#2-Nd(1)-O(4)#3	133.86(8)	O(2)-Nd(1)-N(3)#4	72.32(8)
O(1)#1-Nd(1)-O(6)	97.96(8)	O(5)-Nd(1)-N(3)#4	72.70(9)
O(3)#2-Nd(1)-O(6)	78.61(8)	O(7)-Nd(1)-N(3)#4	72.89(9)
O(4)#3-Nd(1)-O(6)	138.84(8)	O(1)#1-Nd(1)-O(1)	76.45(8)
O(1)#1-Nd(1)-O(2)	124.16(8)	O(3)#2-Nd(1)-O(1)	73.00(7)
O(3)#2-Nd(1)-O(2)	95.44(8)	O(4)#3-Nd(1)-O(1)	67.88(7)
O(4)#3-Nd(1)-O(2)	76.23(8)	O(6)-Nd(1)-O(1)	151.40(8)
O(6)-Nd(1)-O(2)	133.42(8)	O(2)-Nd(1)-O(1)	48.26(7)
O(1)#1-Nd(1)-O(5)	139.91(8)	O(5)-Nd(1)-O(1)	100.65(7)
O(3)#2-Nd(1)-O(5)	69.53(8)	O(7)-Nd(1)-O(1)	134.37(8)
O(4)#3-Nd(1)-O(5)	140.47(8)	N(3)#4-Nd(1)-O(1)	116.31(8)
O(6)-Nd(1)-O(5)	65.42(7)#		
N(3)#4-Nd(1)-O(1)	116.31(8)		

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

Table S3. Selected bonds length (Å) and angles (°) for complex **2**.

bonds lengths [Å] and angles [°] for complex 2			
O(4)-Sm(1)#1	2.409(4)	O(4)#6-Sm(1)-O(5)	69.99(12)
O(3)-Sm(1)#2	2.421(3)	O(3)#7-Sm(1)-O(5)	139.90(11)
O(2)-Sm(1)#3	2.430(3)	O(6)-Sm(1)-O(5)	66.04(11)
O(1)-Sm(1)#4	2.379(3)	O(2)#8-Sm(1)-O(5)	69.16(11)
O(1)-Sm(1)#3	2.869(3)	O(1)#4-Sm(1)-O(7)	75.21(13)
O(6)-Sm(1)	2.427(3)	O(4)#6-Sm(1)-O(7)	129.65(13)
Sm(1)-O(1)#4	2.379(3)	O(3)#7-Sm(1)-O(7)	70.62(12)
Sm(1)-O(4)#6	2.409(4)	O(6)-Sm(1)-O(7)	68.61(12)
Sm(1)-O(3)#7	2.421(3)	O(2)#8-Sm(1)-O(7)	135.48(13)
Sm(1)-O(2)#8	2.430(3)	O(5)-Sm(1)-O(7)	123.99(12)
Sm(1)-O(5)	2.480(3)	O(1)#4-Sm(1)-N(3)	144.47(13)
Sm(1)-O(7)	2.503(4)	O(4)#6-Sm(1)-N(3)	142.50(13)
Sm(1)-N(3)	2.582(4)	O(3)#7-Sm(1)-N(3)	78.77(12)
Sm(1)-O(1)#8	2.869(3)	O(6)-Sm(1)-N(3)	85.33(12)
O(1)#4-Sm(1)-O(4)#6	71.79(12)	O(2)#8-Sm(1)-N(3)	72.59(13)
O(1)#4-Sm(1)-O(3)#7	76.46(12)	O(5)-Sm(1)-N(3)	72.52(13)
O(4)#6-Sm(1)-O(3)#7	133.42(11)	O(7)-Sm(1)-N(3)	72.74(14)
O(1)#4-Sm(1)-O(6)	97.02(12)	O(1)#4-Sm(1)-O(1)#8	76.70(12)
O(4)#6-Sm(1)-O(6)	78.84(12)	O(4)#6-Sm(1)-O(1)#8	72.43(11)
O(3)#7-Sm(1)-O(6)	139.00(12)	O(3)#7-Sm(1)-O(1)#8	67.67(11)
O(1)#4-Sm(1)-O(2)#8	124.23(11)	O(6)-Sm(1)-O(1)#8	151.14(11)
O(4)#6-Sm(1)-O(2)#8	94.73(13)	O(2)#8-Sm(1)-O(1)#8	48.07(10)
O(3)#7-Sm(1)-O(2)#8	75.96(12)	O(5)-Sm(1)-O(1)#8	100.81(11)
O(6)-Sm(1)-O(2)#8	134.20(11)	O(7)-Sm(1)-O(1)#8	133.86(11)
O(1)#4-Sm(1)-O(5)	140.46(12)	N(3)-Sm(1)-O(1)#8	116.28(11)

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

Table S4. Selected bonds length (Å) and angles (°) for complex **3**.

bonds lengths [Å] and angles [°] for complex 3			
O(6)-Eu(1)	2.484(4)	O(1)#5-Eu(1)-O(6)	70.11(13)
O(1)-Eu(1)#1	2.399(4)	O(2)#6-Eu(1)-O(6)	139.85(12)
O(2)-Eu(1)#2	2.412(4)	O(3)#7-Eu(1)-O(6)	69.43(13)
O(4)-Eu(1)#3	2.375(4)	O(5)-Eu(1)-O(6)	66.09(12)
O(4)-Eu(1)#4	2.900(4)	O(4)#3-Eu(1)-O(7)	74.88(14)
O(3)-Eu(1)#4	2.421(4)	O(1)#5-Eu(1)-O(7)	129.96(13)
Eu(1)-O(4)#3	2.375(4)	O(2)#6-Eu(1)-O(7)	70.77(13)
Eu(1)-O(1)#5	2.399(4)	O(3)#7-Eu(1)-O(7)	135.65(14)
Eu(1)-O(2)#6	2.412(4)	O(5)-Eu(1)-O(7)	68.59(14)
Eu(1)-O(3)#7	2.421(4)	O(6)-Eu(1)-O(7)	124.07(14)
Eu(1)-O(5)	2.421(4)	O(4)#3-Eu(1)-N(3)	144.15(14)
Eu(1)-O(7)	2.500(4)	O(1)#5-Eu(1)-N(3)	142.65(14)
Eu(1)-N(3)	2.566(5)	O(2)#6-Eu(1)-N(3)	78.81(14)
Eu(1)-O(4)#7	2.900(4)	O(3)#7-Eu(1)-N(3)	72.87(14)
O(4)#3-Eu(1)-O(1)#5	72.09(13)	O(5)-Eu(1)-N(3)	85.40(13)
O(4)#3-Eu(1)-O(2)#6	76.17(13)	O(6)-Eu(1)-N(3)	72.55(14)
O(1)#5-Eu(1)-O(2)#6	132.88(13)	O(7)-Eu(1)-N(3)	72.86(15)
O(4)#3-Eu(1)-O(3)#7	123.85(13)	O(4)#3-Eu(1)-O(4)#7	76.58(13)
O(1)#5-Eu(1)-O(3)#7	94.19(13)	O(1)#5-Eu(1)-O(4)#7	71.98(12)
O(2)#6-Eu(1)-O(3)#7	75.68(13)	O(2)#6-Eu(1)-O(4)#7	67.37(12)
O(4)#3-Eu(1)-O(5)	97.09(13)	O(3)#7-Eu(1)-O(4)#7	47.85(11)
O(1)#5-Eu(1)-O(5)	79.34(13)	O(5)-Eu(1)-O(4)#7	151.23(12)
O(2)#6-Eu(1)-O(5)	139.14(13)	O(6)-Eu(1)-O(4)#7	101.00(12)
O(3)#7-Eu(1)-O(5)	134.56(13)	O(7)-Eu(1)-O(4)#7	133.62(13)
O(4)#3-Eu(1)-O(6)	140.78(13)	N(3)-Eu(1)-O(4)#7	116.30(13)

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

Table S5. Selected bonds length (Å) and angles (°) for complex **4**.

bonds lengths [Å] and angles [°] for complex 4			
Gd(1)-O(4)#1	2.336(3)	O(5)-Gd(1)-O(6)	66.56(9)
Gd(1)-O(1)	2.371(3)	O(4)#1-Gd(1)-O(7)	75.04(9)
Gd(1)-O(2)#2	2.386(3)	O(1)-Gd(1)-O(7)	130.07(9)
Gd(1)-O(3)#3	2.391(2)	O(2)#2-Gd(1)-O(7)	71.20(9)
Gd(1)-O(5)	2.391(3)	O(3)#3-Gd(1)-O(7)	136.18(9)
Gd(1)-O(6)	2.453(3)	O(5)-Gd(1)-O(7)	68.15(9)
Gd(1)-O(7)	2.473(3)	O(6)-Gd(1)-O(7)	123.79(9)
Gd(1)-N(9)#4	2.542(3)	O(4)#1-Gd(1)-N(9)#4	143.91(10)
Gd(1)-O(4)#3	2.894(3)	O(1)-Gd(1)-N(9)#4	142.79(10)
O(4)#1-Gd(1)-O(1)	72.14(10)	O(2)#2-Gd(1)-N(9)#4	78.69(9)
O(4)#1-Gd(1)-O(2)#2	76.37(9)	O(3)#3-Gd(1)-N(9)#4	73.46(9)
O(1)-Gd(1)-O(2)#2	132.80(9)	O(5)-Gd(1)-N(9)#4	85.59(9)
O(4)#1-Gd(1)-O(3)#3	123.85(9)	O(6)-Gd(1)-N(9)#4	72.59(10)
O(1)-Gd(1)-O(3)#3	93.58(9)	O(7)-Gd(1)-N(9)#4	72.45(10)
O(2)#2-Gd(1)-O(3)#3	75.83(9)	O(4)#1-Gd(1)-O(4)#3	76.56(9)
O(4)#1-Gd(1)-O(5)	96.59(9)	O(1)-Gd(1)-O(4)#3	71.80(8)
O(1)-Gd(1)-O(5)	79.37(9)	O(2)#2-Gd(1)-O(4)#3	67.25(8)
O(2)#2-Gd(1)-O(5)	139.16(9)	O(3)#3-Gd(1)-O(4)#3	47.79(8)
O(3)#3-Gd(1)-O(5)	134.80(9)	O(5)-Gd(1)-O(4)#3	151.12(8)
O(4)#1-Gd(1)-O(6)	140.91(9)	O(6)-Gd(1)-O(4)#3	101.02(8)
O(1)-Gd(1)-O(6)	70.21(9)	O(7)-Gd(1)-O(4)#3	133.87(9)
O(2)#2-Gd(1)-O(6)	139.49(9)	N(9)#4-Gd(1)-O(4)#3	116.59(9)
O(3)#3-Gd(1)-O(6)	69.05(9)		

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

Table S6. Selected bonds length (Å) and angles (°) for complex **5**.

bonds lengths [Å] and angles [°] for complex 5			
O(5)-Tb(1)	2.393(4)	O(3)#7-Tb(1)-O(5)	139.57(13)
O(1)-Tb(1)#2	2.327(4)	O(2)#8-Tb(1)-O(5)	135.51(13)
O(4)-Tb(1)#3	2.366(4)	O(1)#2-Tb(1)-O(6)	140.88(13)
O(2)-Tb(1)#4	2.383(4)	O(4)#6-Tb(1)-O(6)	70.08(13)
O(3)-Tb(1)#5	2.373(4)	O(3)#7-Tb(1)-O(6)	139.20(13)
b(1)-O(1)#2	2.327(4)	O(2)#8-Tb(1)-O(6)	68.96(13)
Tb(1)-O(4)#6	2.366(4)	O(5)-Tb(1)-O(6)	67.22(12)
Tb(1)-O(3)#7	2.373(4)	O(1)#2-Tb(1)-O(7)	74.83(14)
Tb(1)-O(2)#8	2.383(4)	O(4)#6-Tb(1)-O(7)	130.81(13)
Tb(1)-O(6)	2.445(4)	O(3)#7-Tb(1)-O(7)	71.42(13)
Tb(1)-O(7)	2.480(4)	O(2)#8-Tb(1)-O(7)	136.54(14)
Tb(1)-N(3)	2.536(5)	O(5)-Tb(1)-O(7)	68.30(13)
O(1)#2-Tb(1)-O(4)#6	72.31(14)	O(6)-Tb(1)-O(7)	124.38(13)
O(1)#2-Tb(1)-O(3)#7	76.37(13)	O(1)#2-Tb(1)-N(3)	143.85(15)
O(4)#6-Tb(1)-O(3)#7	131.92(13)	O(4)#6-Tb(1)-N(3)	142.82(14)
O(1)#2-Tb(1)-O(2)#8	123.35(13)	O(3)#7-Tb(1)-N(3)	78.92(14)
O(4)#6-Tb(1)-O(2)#8	92.38(14)	O(2)#8-Tb(1)-N(3)	74.16(14)
O(3)#7-Tb(1)-O(2)#8	75.51(14)	O(5)-Tb(1)-N(3)	85.96(14)
O(1)#2-Tb(1)-O(5)	96.07(13)	O(6)-Tb(1)-N(3)	72.74(14)
O(4)#6-Tb(1)-O(5)	79.89(13)#	O(7)-Tb(1)-N(3)	72.49(15)

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

Table S7. Selected bonds length (Å) and angles (°) for complex **6**.

bonds lengths [Å] and angles [°] for complex 6			
O(7)-Dy(1)	2.437(5)	O(3)#7-Dy(1)-O(5)	139.78(16)
O(4)-Dy(1)#2	2.350(5)	O(2)#8-Dy(1)-O(5)	135.92(16)
O(3)-Dy(1)#3	2.360(5)	O(1)#5-Dy(1)-O(7)	141.14(16)
O(2)-Dy(1)#4	2.372(4)	O(4)#6-Dy(1)-O(7)	70.30(16)
O(1)-Dy(1)#5	2.306(4)	O(3)#7-Dy(1)-O(7)	139.07(15)
Dy(1)-O(1)#5	2.306(4)	O(2)#8-Dy(1)-O(7)	69.20(16)
Dy(1)-O(4)#6	2.350(5)	O(5)-Dy(1)-O(7)	67.24(15)
Dy(1)-O(3)#7	2.360(5)	O(1)#5-Dy(1)-O(6)	74.41(17)
Dy(1)-O(2)#8	2.372(4)	O(4)#6-Dy(1)-O(6)	131.30(17)
Dy(1)-O(5)	2.377(4)	O(3)#7-Dy(1)-O(6)	71.51(16)
Dy(1)-O(6)	2.461(5)	O(2)#8-Dy(1)-O(6)	136.89(18)
Dy(1)-N(3)	2.509(5)	O(5)-Dy(1)-O(6)	68.40(17)
O(1)#5-Dy(1)-O(4)#6	72.60(17)	O(7)-Dy(1)-O(6)	124.26(16)
O(1)#5-Dy(1)-O(3)#7	76.43(16)	O(1)#5-Dy(1)-N(3)	143.74(18)
O(4)#6-Dy(1)-O(3)#7	131.43(15)	O(4)#6-Dy(1)-N(3)	142.73(18)
O(1)#5-Dy(1)-O(2)#8	123.23(16)	O(3)#7-Dy(1)-N(3)	78.95(17)
O(4)#6-Dy(1)-O(2)#8	91.46(17)	O(2)#8-Dy(1)-N(3)	74.46(17)
O(3)#7-Dy(1)-O(2)#8	75.39(17)	O(5)-Dy(1)-N(3)	86.36(17)
O(1)#5-Dy(1)-O(5)	95.58(16)	O(7)-Dy(1)-N(3)	72.44(17)
O(4)#6-Dy(1)-O(5)	80.26(16)#	O(6)-Dy(1)-N(3)	72.75(18)

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

Crystal structure

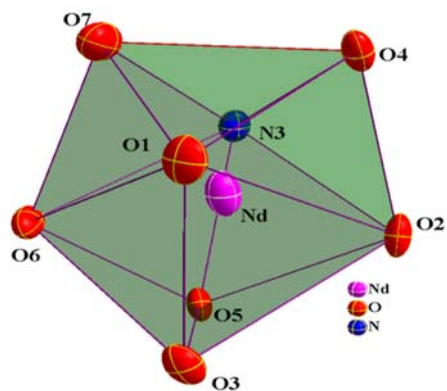


Figure S1. The D_{2d} symmetry polyhedral of Nd(III) ions in **1** (All of H-atoms are omitted for clarity).

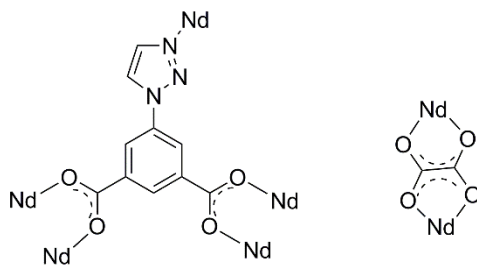


Figure S2. Bridging Nd(III) modes of tia^{2-} and $C_2O_4^{2-}$.

Absorption spectra

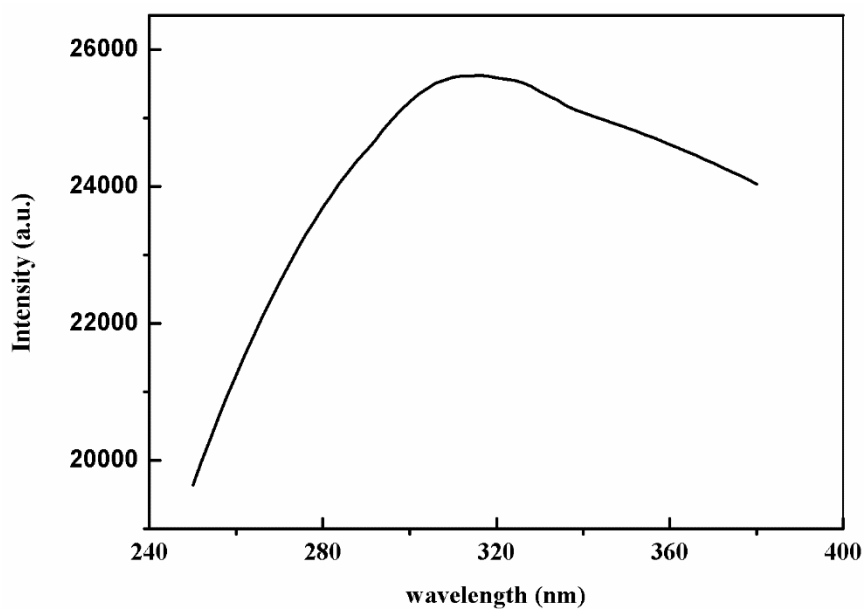


Figure S3. Absorption spectra of 1

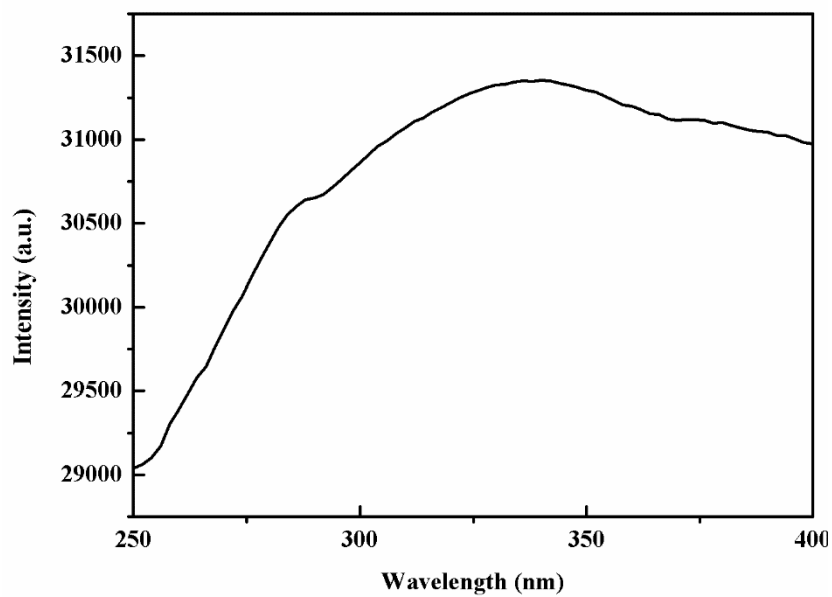


Figure S4. Absorption spectra of 2

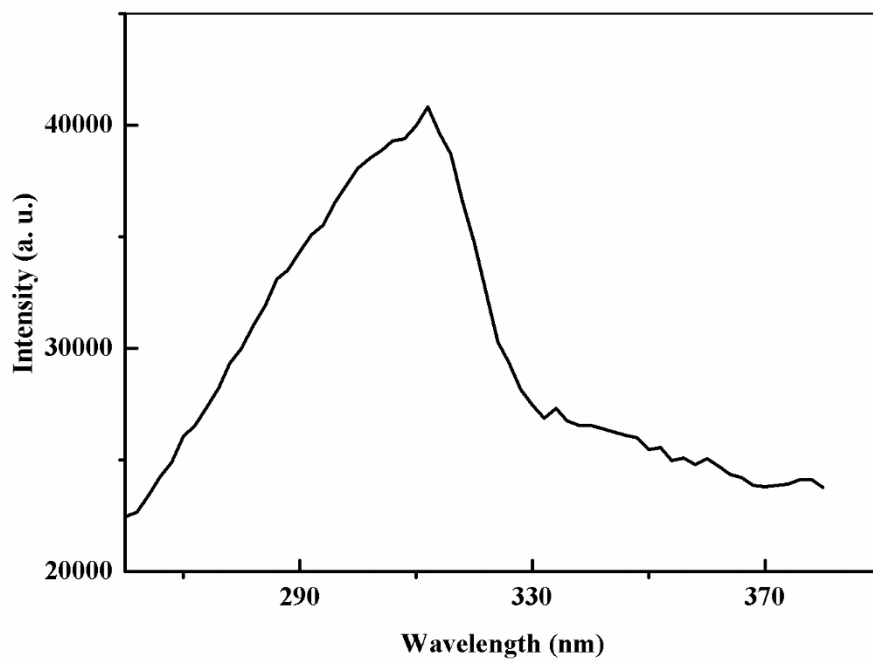


Figure S5. Absorption spectra of 3

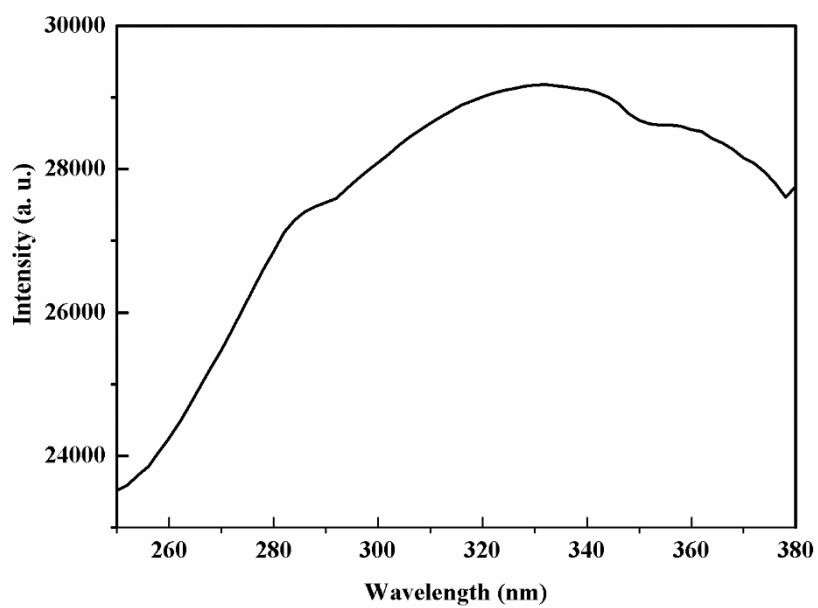


Figure S6. Absorption spectra of 5

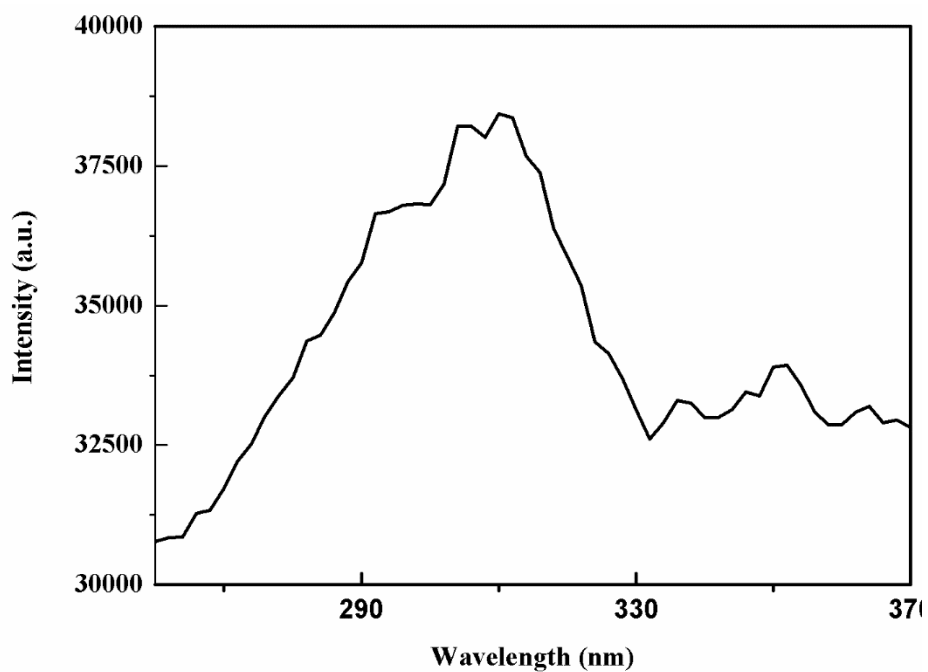


Figure S7. Absorption spectra of 6

Temperature dependence of ac susceptibility for 5 and 6

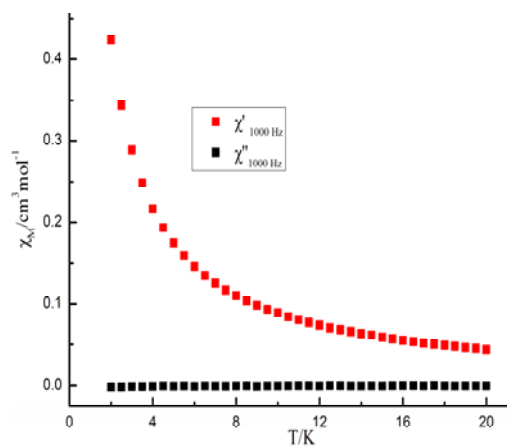


Figure S8. Temperature dependence of ac susceptibility at various frequencies of 5.

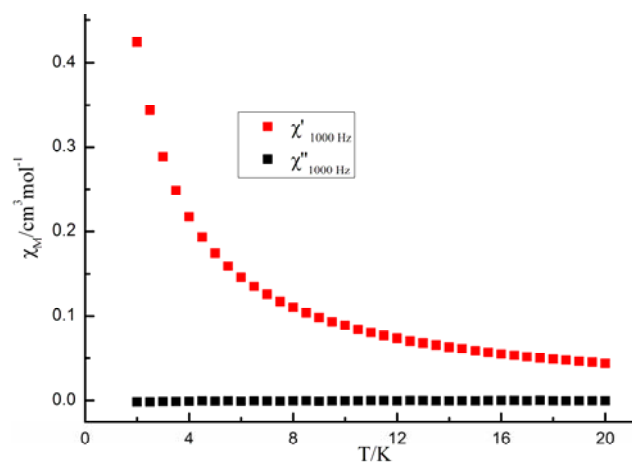


Figure S9. Temperature dependence of ac susceptibility at various frequencies of **6**.

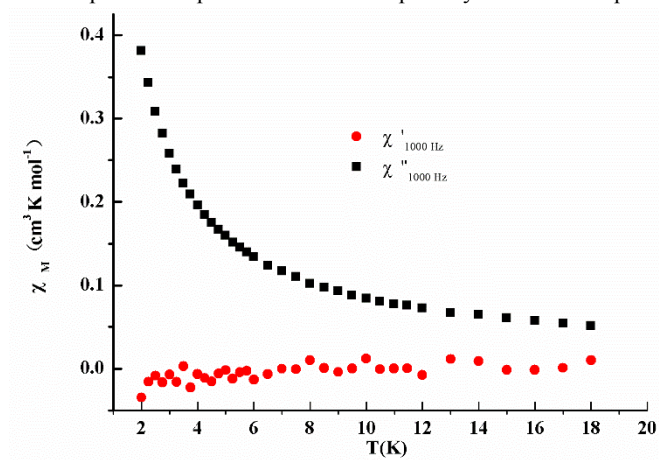


Figure S10. Temperature dependence of ac susceptibility at various frequencies of **6** under 1000 Oe applied magnetic field.