Electronic Supplementary Information (ESI)

$[Ln_4@Ln_4]$ matryoshka tetrahedron: A novel secondary building unit

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Contents

Experimental Section

1. Materials and Methods.

All chemicals purchased were of analytical grade and used as received unless noted otherwise. 2,2'-Dimethoxy-4,4'-biphenyldicarboxylic acid (H_2L) was synthesized following the method provided by our group.[1] $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Eu, Gd, Dy), *N,N*'-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Elemental

analyses (C, H, N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectra were recorded in the range 4000-400 cm^{-1} using KBr pellets on a Bruker Vector 22 FT-IR spectrophotometer. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449C thermal analyzer under nitrogen atmosphere at a heating rate of 10°C min^{-1}. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer with Cu K_α radiation (λ = 1.5406 Å). Fluorescence spectroscopy data for **1** were recorded on a Perkin-Elmer LS-55 spectrophotometer. Temperature-dependent magnetic measurements for **2** and **3** were carried out on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic correction was made with Pascal's constants.[2]

2. Syntheses of MOFs 1-3.

2.1 Synthesis of $[Eu_2(\mu_3\text{-}OH)L_{2.5}(H_2O)_2]\cdot 0.5DMF$ (**1**).

The mixture of $Eu(NO_3)_3\cdot 6H_2O$ (0.0446 g, 0.1 mmol), H_2L (0.0377 g, 0.125 mmol), DMF (2.4 mL), and H_2O (5.6 mL) was heated in a 25 mL capacity stainless-steel reactor lined with Teflon at 135°C for 2 days and then cooled to room temperature. Colorless block crystals of **1** were obtained. Yield, 66.3% (37.9 mg) based on Eu(III). FT-IR (KBr, cm^{-1}): 3604(m), 3339(b, m), 2934(w), 1667(m), 1587(s), 1531(s), 1416(vs), 1243(m), 1037(m), 781(s). Anal. Calcd for $C_{41.5}H_{37.5}Eu_2N_{0.5}O_{18.5}$ (%): C, 43.60; H, 3.31; N, 0.61. Found: C, 43.28; H, 3.56; N, 0.81.

2.2 Synthesis of $[Gd_2(\mu_3\text{-}OH)L_{2.5}(H_2O)_2]\cdot 0.5DMF$ (**2**).

The procedure was the same as that for **1** except that $Eu(NO_3)_3\cdot 6H_2O$ was replaced by $Gd(NO_3)_3\cdot 6H_2O$ (0.0451 g, 0.1 mmol). Colorless block crystals of **2** were obtained. Yield, 74.5% (43.0 mg) based on Gd(III). FT-IR (KBr, cm^{-1}): 3608(m), 3337(b, m), 2934(w), 1668(m), 1588(s), 1546(s), 1420(vs), 1243(m), 1037(m), 781(s). Anal. Calcd for $C_{41.5}H_{37.5}Gd_2N_{0.5}O_{18.5}$ (%): C, 43.20; H, 3.28; N, 0.61. Found: C, 43.38; H, 3.56; N, 0.73.

2.3 Synthesis of $[Dy_2(\mu_3\text{-}OH)L_{2.5}(H_2O)_2]\cdot 0.5DMF$ (**3**).

The procedure was the same as that for **1** except that $Eu(NO_3)_3\cdot 6H_2O$ was replaced by $Dy(NO_3)_3\cdot 6H_2O$ (0.0457 g, 0.1 mmol). Colorless block crystals of **3** were obtained. Yield, 70.8% (41.2 mg) based on Dy(III). FT-IR (KBr, cm^{-1}): 3611(m), 3346(b, m), 2931(w), 1668(m), 1589(s), 1547(s), 1420(vs), 1243(m), 1037(m), 780(s). Anal. Calcd for $C_{41.5}H_{37.5}Dy_2N_{0.5}O_{18.5}$ (%): C, 42.81; H, 3.25; N, 0.60. Found: C, 43.18; H, 3.56; N, 0.78.

3. Crystal Structure Determination.

Diffraction data for **1-3** were collected on a Bruker Smart APEX II CCD diffractometer with

graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The diffraction data of **1** were collected at room temperature, and **2** and **3** were collected at 150 K. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, were placed on calculated positions (C-H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms. The crystal data and structure refinement of **1-3** are summarized in Table S1. Selected bond lengths of **1-3** are listed in Table S2. Selected bond angles of **1-3** are listed in Table S3. Crystallographic data for MOFs **1-3** have been deposited with the Cambridge Crystallograhic Data Centre as supplementary publications CCDC-976994 (**1**), 998558 (**2**) and 998559 (**3**). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement of MOFs **1-3**

MOFs	**1**	**2**	**3**
Empirical formula	$C_{41.5}H_{37.5}Eu_2N_{0.5}O_{18.5}$	$C_{41.5}H_{37.5}Gd_2N_{0.5}O_{18.5}$	$C_{41.5}H_{37.5}Dy_2N_{0.5}O_{18.5}$
Formula weight	1143.14	1153.72	1164.22
T (K)	296(2)	150(2)	150(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_2/n$	$P4_2/n$	$P4_2/n$
a (Å)	21.2904(4)	21.2232(6)	21.1619(9)
b (Å)	21.2904(4)	21.2232(6)	21.1619(9)
c (Å)	19.3576(7)	19.3460(11)	19.2599(15)
V (Å^3)	8774.4(4)	8713.9(6)	8625.1(8)
Z	8	8	8
F (000)	4512	4528	4560
ρ (g cm^{-3})	1.731	1.759	1.793
μ (mm^{-1})	2.910	3.095	3.516
Crystal size (mm^3)	0.16×0.15×0.12	0.20×0.15×0.13	0.15×0.12×0.10
Reflections collected	61675	61506	60494
Independent reflections	7705 [R_{int} = 0.0669]	7699 [R_{int} = 0.0725]	7560 [R_{int} = 0.0970]
Data/restraints/parameters	7705/71/661	7699 /34/595	7560/58/580
GOF on F^2	1.048	1.071	1.033
R_1/wR_2 [$I > 2\sigma(I)$]	0.0306/0.0723	0.0329/0.0825	0.0366/0.0850
R_1/wR_2 (all data)	0.0478/0.0778	0.0438/0.0874	0.0568/0.0917
Largest diff. peak & hole (eÅ^{-3})	0.908, -0.689	1.383, -1.288	1.294, -1.065

Table S2 Selected bond lengths (Å) for MOFs **1**–**3**

1		**2**		**3**	
Eu1-O16[a]	2.335(3)	Gd1-O16	2.323(3)	Dy1-O16	2.295(4)
Eu1-O7	2.368(4)	Gd1-O7	2.361(4)	Dy1-O7	2.324(4)
Eu1-O1	2.366(3)	Gd1-O1	2.356(3)	Dy1-O1	2.322(4)
Eu1-O16	2.406(3)	Gd1-O16[e]	2.389(3)	Dy1-O16[j]	2.351(4)
Eu1-O2W	2.423(3)	Gd1-O1W	2.399(3)	Dy1-O2W	2.364(4)
Eu1-O16[c]	2.508(3)	Gd1-O4[f]	2.490(3)	Dy1-O4[n]	2.452(4)
Eu1-O3[b]	2.509(3)	Gd1-O16[g]	2.490(3)	Dy1-O16[m]	2.468(4)
Eu1-O8	2.840(3)	Gd1-O8	2.828(3)	Dy1-O8	2.860(4)
Eu2-O9[o]	2.280(4)	Gd2-O9[h]	2.271(4)	Dy2-O9[k]	2.252(5)
Eu2-O4[b]	2.310(3)	Gd2-O3[f]	2.297(3)	Dy2-O3[n]	2.262(4)
Eu2-O10[d]	2.317(4)	Gd2-O8	2.314(3)	Dy2-O8	2.280(4)
Eu2-O8	2.335(3)	Gd2-O10[i]	2.315(3)	Dy2-O10[o]	2.280(4)
Eu2-O2	2.403(4)	Gd2-O2	2.386(4)	Dy2-O2	2.367(4)
Eu2-O1W	2.432(4)	Gd2-O2W	2.423(4)	Dy2-O1W	2.397(4)
Eu2-O13	2.477(3)	Gd2-O13	2.465(3)	Dy2-O13	2.437(4)
Eu2-O14	2.576(4)	Gd2-O14	2.544(3)	Dy2-O14	2.529(4)
Eu1-Eu2	4.165(4)	Gd1-Gd2	4.161(4)	Dy1-Dy2	4.169(4)
Eu1-Eu1[a]	3.8975(4)	Gd1-Gd1[e]	3.8732(4)	Dy1-Dy1[l]	3.8171(5)
Eu1[a]-Eu1[c]	3.900(4)	Gd1-Gd1[g]	3.8669(5)	Dy1-Dy1[m]	3.8211(6)

Symmetry codes: a) *x*+1, 5/2-*y*, -*z*-1/2; b) *x*+1/2, 3–*y*, *z*+1/2; c) 5/2-*x*, *y*-1, -*z*-1/2; d) 2-*x*, *y*-1/2, *z*+1/2; e) 3/2-*x*, *y*+1, 1/2-*z*; f) *x*-3/2, 1-*y*, *z*+1/2; g) 5/2-*x*, 1/2-*y*, *z*; h) *x*-1, 3/2-*y*, -*z*-1/2; i) 1-*x*, *y*+1/2, *z*+1/2; j) *x*, -*y*-1/2, 3/2-*z*; k) -*x*-1/2, *y*, 1/2-*z*; l) -*x*-1/2, *y*, 3/2-*z*; m) –*x*-1/2, -*y*-1/2, *z*; n) -*x*, *y*+1/2, *z*+1/2; o) *x*+1/2, –*y*, *z*+1/2.

Table S3 Selected bond angles (°) for MOFs **1**–**3**

1					
O16[a]–Eu1–O1	77.37(12)	O7–Eu1–O8	48.02(11)	O9[d]–Eu2–O1W	84.75(16)
O16[a]–Eu1–O7	95.83(13)	O16–Eu1–O8	150.59(10)	O4[b]–Eu2–O1W	85.87(14)
O1–Eu1–O7	85.53(15)	O2W–Eu1–O8	69.24(12)	O10[e]–Eu2–O1W	71.34(15)
O16[a]–Eu1–O16	70.20(13)	O16[c]–Eu1–O8	106.42(10)	O8–Eu2–O1W	142.91(14)
O1–Eu1–O16	129.77(11)	O3[b]–Eu1–O8	107.90(10)	O2–Eu2–O1W	70.12(14)
O7–Eu1–O16	134.03(12)	O16[a]–Eu1–O4[b]	143.13(10)	O9[d]–Eu2–O13	75.17(14)
O16[a]–Eu1–O2W	143.39(12)	O1–Eu1–O4[b]	81.66(11)	O4[b]–Eu2–O13	125.83(13)
O1–Eu1–O2W	139.21(12)	O7–Eu1–O4[b]	112.47(11)	O10[e]–Eu2–O13	72.28(14)
O7–Eu1–O2W	87.51(15)	O16–Eu1–O4[b]	102.34(10)	O8–Eu2–O13	83.46(12)
O16–Eu1–O2W	81.36(11)	O2W–Eu1–O4[b]	64.21(11)	O2–Eu2–O13	144.75(14)
O16[a]–Eu1–O16[c]	69.10(12)	O16[c]–Eu1–O4[b]	143.15(10)	O1W–Eu2–O13	129.25(13)
O1–Eu1–O16[c]	132.97(11)	O3[b]–Eu1–O4[b]	43.96(10)	O9[d]–Eu2–O14	124.41(15)
O7–Eu1–O16[c]	66.75(12)	O8–Eu1–O4[b]	64.52(9)	O4[b]–Eu2–O14	74.62(13)
O16–Eu1–O16[c]	67.37(12)	O9[d]–Eu2–O4[b]	157.64(15)	O10[e]–Eu2–O14	72.27(14)

O2W–Eu1–O16^{c}	79.07(11)	O9^{d}–Eu2–O10^{e}	109.17(14)	O8–Eu2–O14	72.12(13)
O16^{a}–Eu1–O3^{b}	103.68(11)	O4^{b}–Eu2–O10^{e}	86.83(14)	O2–Eu2–O14	136.93(12)
O1–Eu1–O3^{b}	84.75(13)	O9^{d}–Eu2–O8	88.71(14)	O1W–Eu2–O14	139.34(15)
O7–Eu1–O3^{b}	155.69(12)	O4^{b}–Eu2–O8	86.62(12)	O13–Eu2–O14	51.65(12)
O16–Eu1–O3^{b}	67.61(11)	O10^{e}–Eu2–O8	144.27(14)	Eu2^{f}–O4–Eu1^{f}	99.21(11)
O2W–Eu1–O3^{b}	85.41(12)	O9^{d}–Eu2–O2	78.56(15)	Eu2–O8–Eu1	106.78(12)
O16^{c}–Eu1–O3^{b}	133.99(11)	O4^{b}–Eu2–O2	79.17(13)	Eu1^{c}–O16–Eu1	110.57(12)
O16^{a}–Eu1–O8	136.41(11)	O10^{e}–Eu2–O2	139.71(15)	Eu1^{c}–O16–Eu1^{a}	107.23(12)
O1–Eu1–O8	76.44(12)	O8–Eu2–O2	72.79(13)	Eu1–O16–Eu1^{a}	104.95(12)

2

O16–Gd1–O1	77.68(12)	O4^{h}–Gd1–O16^{i}	134.39(11)	O8–Gd2–O2W	143.06(13)
O16–Gd1–O7	96.12(12)	O16–Gd1–O8	136.21(11)	O10^{k}–Gd2–O2W	70.87(14)
O1–Gd1–O7	85.54(14)	O1–Gd1–O8	74.81(11)	O2–Gd2–O2W	69.56(13)
O16–Gd1–O16^{g}	70.23(13)	O7–Gd1–O8	48.69(11)	O9^{j}–Gd2–O13	75.24(14)
O1–Gd1–O16^{g}	130.11(11)	O16^{g}–Gd1–O8	151.43(10)	O3^{h}–Gd2–O13	126.05(12)
O7–Gd1–O16^{g}	134.00(12)	O1W–Gd1–O8	69.88(11)	O8–Gd2–O13	83.73(12)
O16–Gd1–O1W	143.78(12)	O4^{h}–Gd1–O8	106.98(10)	O10^{k}–Gd2–O13	72.39(13)
O1–Gd1–O1W	138.50(12)	O16^{i}–Gd1–O8	107.59(10)	O2–Gd2–O13	145.27(13)
O7–Gd1–O1W	87.19(14)	O9^{j}–Gd2–O3^{h}	157.34(14)	O2W–Gd2–O13	128.54(13)
O16^{g}–Gd1–O1W	81.61(11)	O9^{j}–Gd2–O8	88.48(13)	O9^{j}–Gd2–O14	124.76(14)
O16–Gd1–O4^{h}	103.39(11)	O3^{h}–Gd2–O8	86.67(12)	O3^{h}–Gd2–O14	74.46(12)
O1–Gd1–O4^{h}	84.29(12)	O9^{j}–Gd2–O10^{k}	109.31(14)	O8–Gd2–O14	72.26(12)
O7–Gd1–O4^{h}	155.49(12)	O3^{h}–Gd2–O10^{k}	86.86(13)	O10^{k}–Gd2–O14	72.57(13)
O16^{g}–Gd1–O4^{h}	67.88(11)	O8–Gd2–O10^{k}	144.70(13)	O2–Gd2–O14	137.51(12)
O1W–Gd1–O4^{h}	85.77(12)	O9^{j}–Gd2–O2	78.21(14)	O2W–Gd2–O14	139.34(13)
O16–Gd1–O16^{i}	69.37(12)	O3^{h}–Gd2–O2	79.19(13)	O13–Gd2–O14	52.04(12)
O1–Gd1–O16^{i}	133.25(11)	O8–Gd2–O2	73.51(12)	Gd2–O8–Gd1	107.61(12)
O7–Gd1–O16^{i}	66.65(12)	O10^{k}–Gd2–O2	138.65(14)	Gd1–O16–Gd1^{l}	110.57(12)
O16^{g}–Gd1–O16^{i}	67.46(12)	O9^{j}–Gd2–O2W	84.32(14)	Gd1–O16–Gd1^{i}	106.85(12)
O1W–Gd1–O16^{i}	79.18(11)	O3^{h}–Gd2–O2W	86.33(13)	Gd1^{l}–O16–Gd1^{i}	105.06(12)

3

O16–Dy1–O7	96.70(15)	O1–Dy1–O16^{p}	133.47(14)	O9^{n}–Dy2–O1W	83.39(16)
O16–Dy1–O1	77.97(15)	O16^{m}–Dy1–O16^{p}	67.74(18)	O3^{q}–Dy2–O1W	86.46(15)
O7–Dy1–O1	84.34(16)	O2W–Dy1–O16^{p}	79.19(14)	O10^{r}–Dy2–O1W	70.86(16)
O16–Dy1–O16^{m}	70.61(18)	O4^{q}–Dy1–O16^{p}	135.11(14)	O8–Dy2–O13	83.29(15)
O7–Dy1–O16^{m}	135.26(15)	O16–Dy1–O8	136.57(14)	O10^{r}–Dy2–O13	72.58(16)
O1–Dy1–O16^{m}	130.74(14)	O7–Dy1–O8	48.14(13)	O2–Dy2–O13	145.24(16)
O16–Dy1–O2W	144.51(15)	O1–Dy1–O8	74.09(13)	O1W–Dy2–O13	128.34(15)
O7–Dy1–O2W	86.67(16)	O16^{m}–Dy1–O8	151.04(13)	O9^{n}–Dy2–O14	125.56(17)
O1–Dy1–O2W	137.42(15)	O2W–Dy1–O8	68.98(14)	O3^{q}–Dy2–O14	73.87(15)
O16^{m}–Dy1–O2W	82.20(14)	O4^{q}–Dy1–O8	105.20(13)	O10^{r}–Dy2–O14	73.11(16)
O16–Dy1–O4^{q}	104.32(14)	O16^{p}–Dy1–O8	108.05(13)	O8–Dy2–O14	72.34(15)
O7–Dy1–O4^{q}	153.39(14)	O9^{n}–Dy2–O3^{q}	157.62(17)	O2–Dy2–O14	137.08(14)
O1–Dy1–O4^{q}	84.27(15)	O9^{n}–Dy2–O10^{r}	108.56(17)	O1W–Dy2–O14	139.67(15)

O16^{m}–Dy1–O4^{q}	68.55(14)	O3^{q}–Dy2–O10^{r}	86.66(16)	O13–Dy2–O14	52.92(15)
O2W–Dy1–O4^{q}	85.59(14)	O9^{n}–Dy2–O2	78.41(17)	Dy1^{o}–O16–Dy1^{p}	104.74(16)
O16–Dy1–O16^{p}	69.74(17)	O3^{q}–Dy2–O2	79.35(16)	Dy1–O16–Dy1^{o}	110.48(18)
O7–Dy1–O16^{p}	67.69(15)	O10^{r}–Dy2–O2	138.28(17)	Dy1–O16–Dy1^{p}	106.61(16)

Symmetry codes: a) 5/2-*y*, *x*+1, -*z*-1/2; b) 3–*y*, *x*+1/2, *z*+1/2; c) *y*-1, 5/2-*x*, -*z*-1/2; d) 5/2-*y*, *x*+1, -*z*-3/2; e) *y*-1/2, 2-*x*, *z*+1/2; f) *y*-1/2, 3-*x*, *z*-1/2; g) *y*+1, 3/2-*x*, 1/2-*z*; h) 1-*y*, *x*-3/2, *z*+1/2; i) 5/2-*x*, 1/2-*y*, *z*; j) 3/2-*y*, *x*-1, -*z*-1/2; k) *y*+1/2, 1-*x*, *z*+1/2; l) 3/2-*y*, *x*-1,1/2-*z*; m) -*y*-1/2, *x*, 3/2-*z*; n) *y*, -*x*-1/2, 1/2-*z*; o) *y*, -*x*-1/2, 3/2-*z*; p) –*x*-1/2, -*y*-1/2, *z*; q) *y*+1/2, -*x*, *z*+1/2; r) –*y*, *x*+1/2,*z*+1/2.

Table S4 Hydrogen-bonding geometry (Å, °) for MOF **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
O1W–H1WA···O13^{i}	0.84(4)	1.95(5)	2.782(6)	168(5)
O1W–H1WB···O17^{ii}	0.85(4)	1.94(4)	2.789(11)	171(4)
O2W–H2WA···O3^{ii}	0.85	1.92	2.654(5)	144
C16–H16A···O11^{iii}	0.96	2.52	3.340(10)	144
C23–H23A···O13	0.93	2.54	3.415(7)	157
C35A–H35A···O1W^{i}	0.93	2.53	3.43(2)	164
C40A–H40B···O6^{ii}	0.96	2.43	3.19(2)	136

Symmetry codes: i) 2–*x*, 3-*y*, -*z*-1; ii) *y*-1, -*x*-3/2, -*z*-3/2, iii) *y*, -*x*-1/2, -*z*-3/2.

4. Molecular Structures.

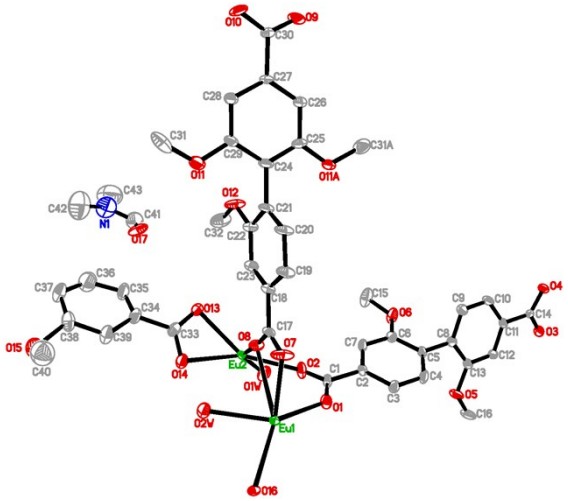


Fig. S1 ORTEP drawing (at 50% probability) of the asymmetric unit for MOF **1** (Hydrogen atoms and disordered atoms (C35B, C36B, C37B, C40B and O15B) are omitted for clarity).

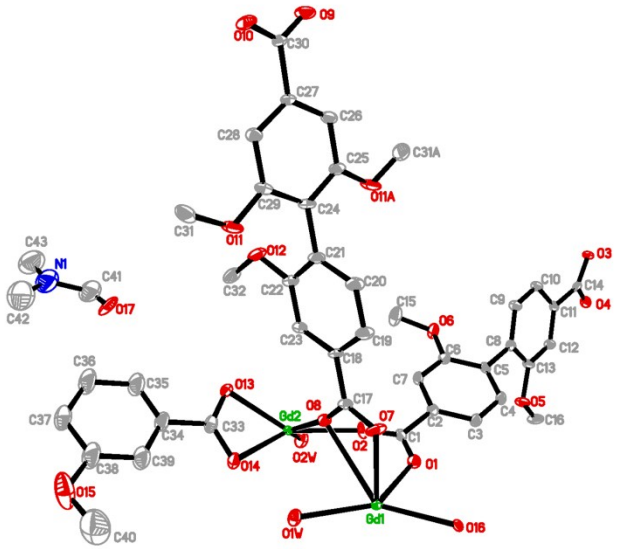


Fig. S2 ORTEP drawing (at 50% probability) of the asymmetric unit for MOF **2** (Hydrogen atoms are omitted for clarity).

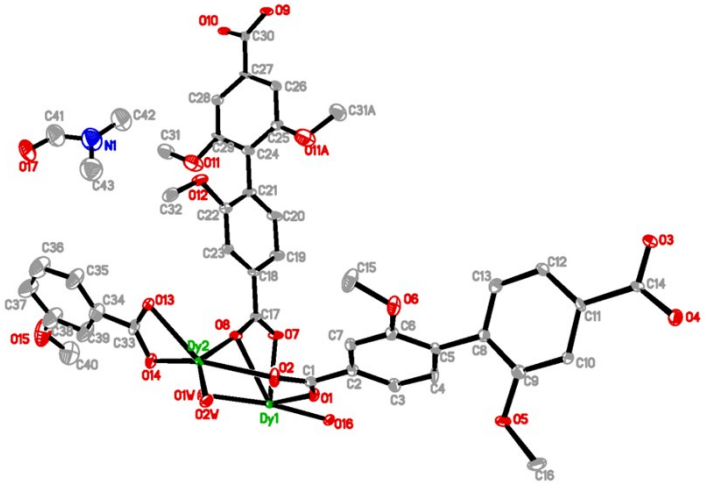
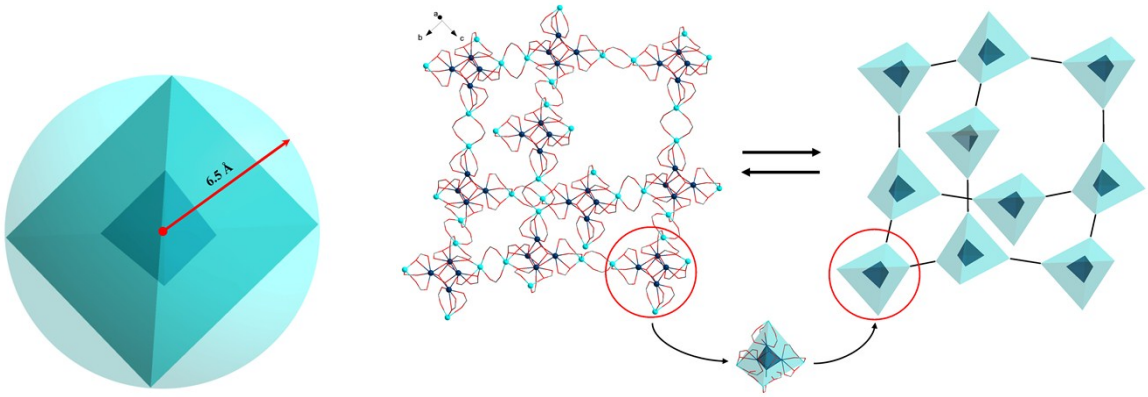


Fig. S3 ORTEP drawing (at 50% probability) of the asymmetric unit for MOF **3** (Hydrogen atoms are omitted for clarity).



(a) (b)

Fig. S4 (a) An outscribed sphere of 1.3 nm diameter surrounds the [Eu_4@Eu_4] SBU. (b) The diamond net of **1** built from the 4-connected SBU by missing all the biphenyl groups of L^{2-} ligands.

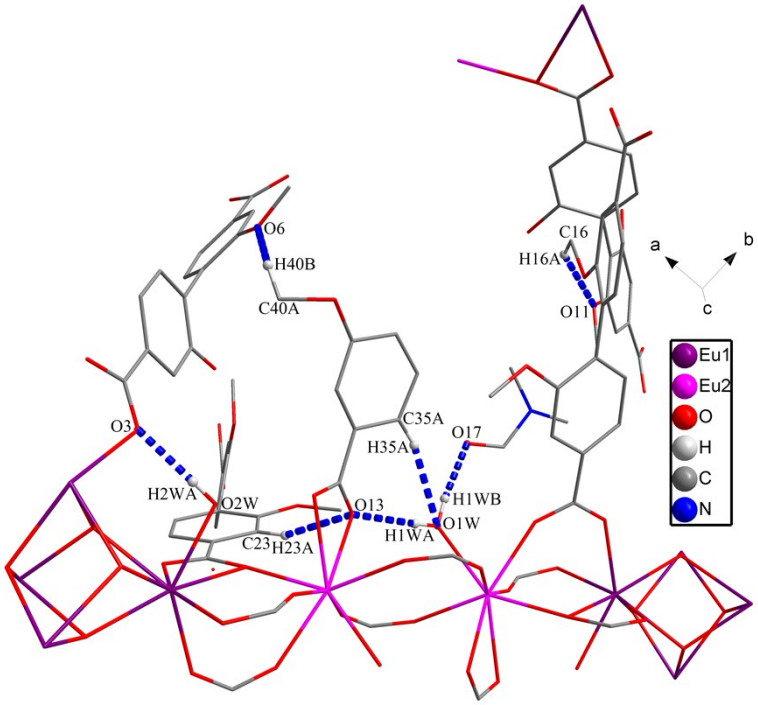
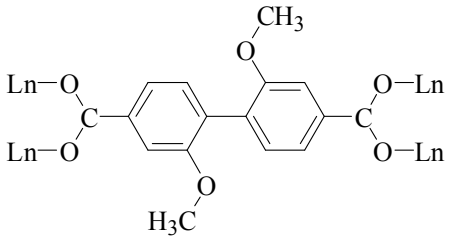
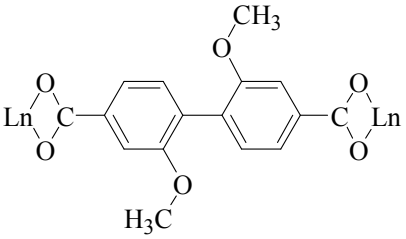


Fig. S5 The network of **1** stabilized by weak hydrogen bonds (blue dotted lines).

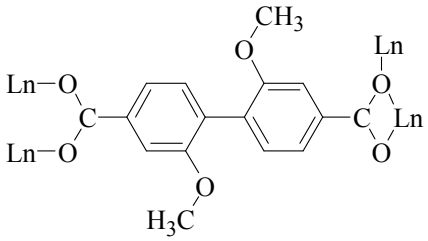
5. Coordination Modes of L^{2-} Ligands in 1-3.



Type I



Type II



Type III

Scheme S1 Three kinds of coordination modes of ligand L^{2-} in MOFs **1-3**.

6. The PXRD Patterns.

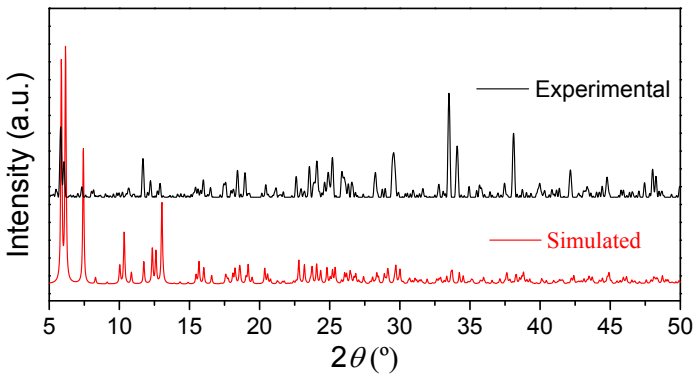


Fig. S6 Experimental and simulated powder X-ray diffraction patterns of MOF **1**.

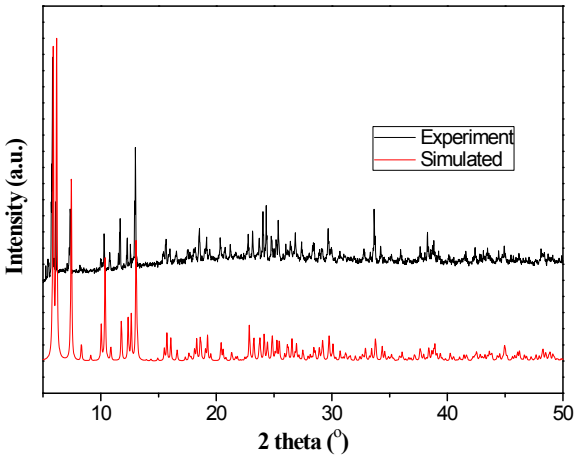


Fig. S7 Experimental and simulated powder X-ray diffraction patterns of MOF **2**.

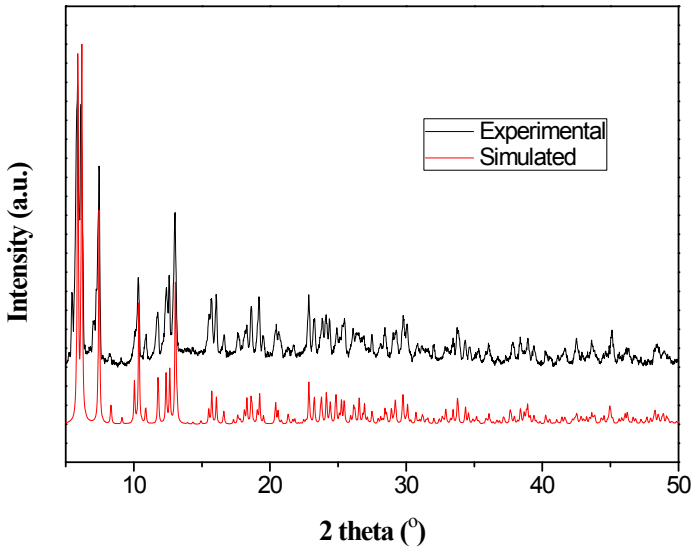


Fig. S8 Experimental and simulated powder X-ray diffraction patterns of MOF **3**.

7. The Thermogravimetric Analysis.

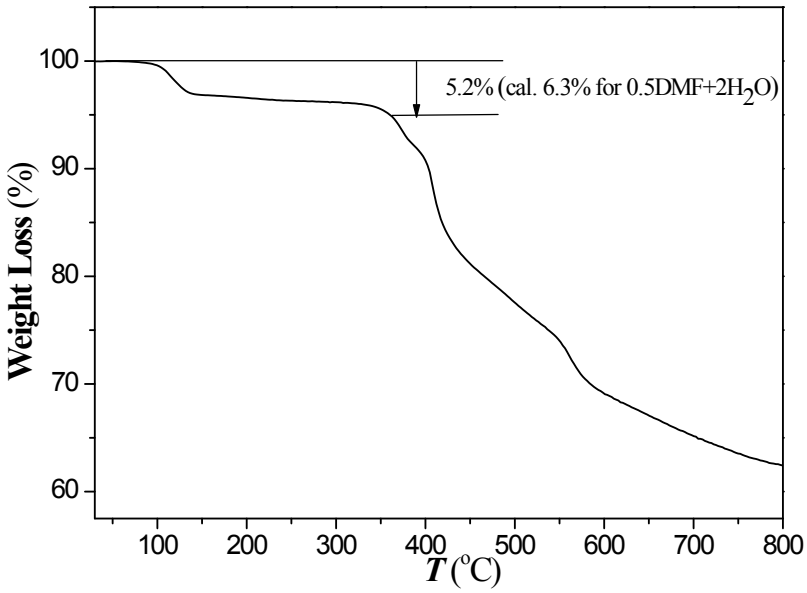


Fig. S9 TGA curve for MOF **1**.

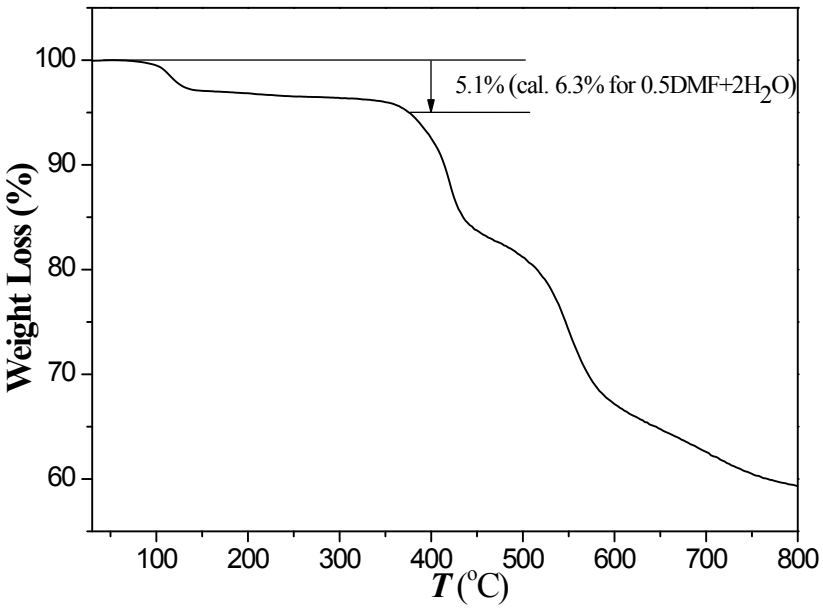


Fig. S10 TGA curve for MOF **2**.

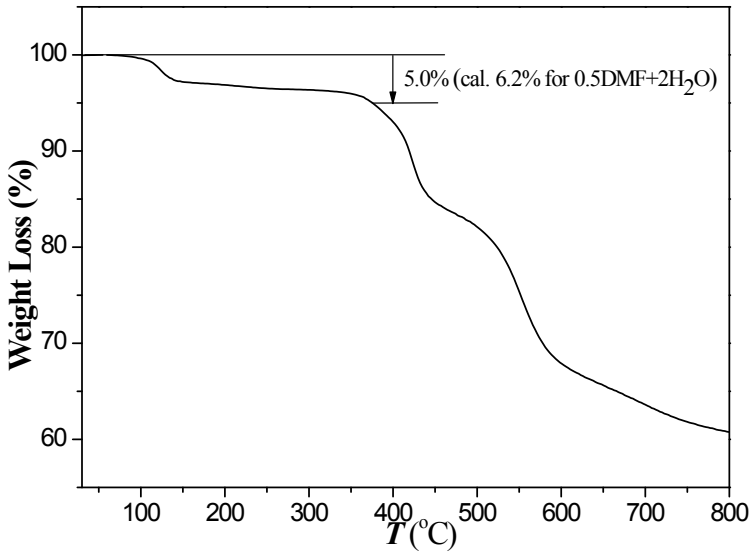


Fig. S11 TGA curve for MOF **3**.

8. The Photoluminescence of MOF 1.

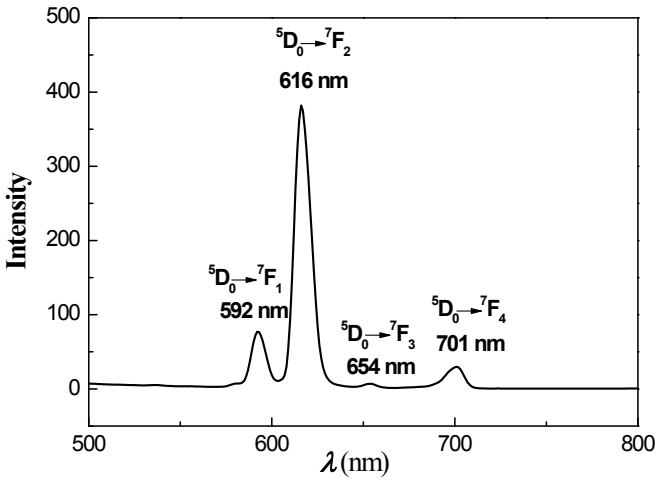


Fig. S12 The photoluminescence emission spectra of the MOF **1** (λ_{ex} = 394 nm) at room temperature.

9. The Magnetic Properties of MOFs 2 and 3.

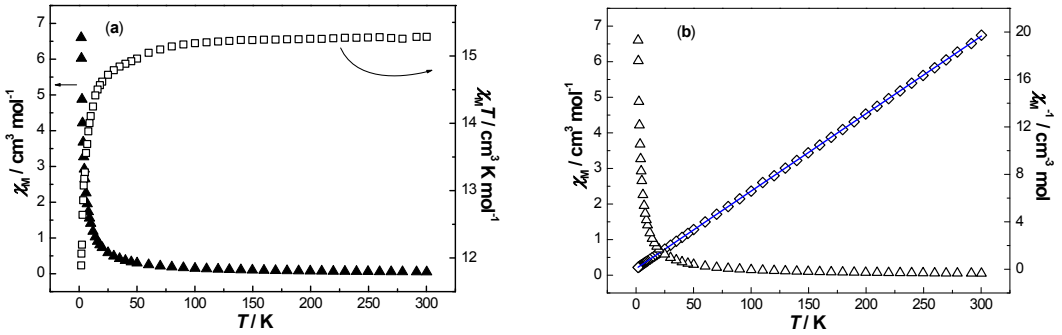


Fig. S13 Variable-temperature susceptibilities of **2** under a field of 100 Oe. (a) The plot of χ_M and $\chi_M T$ *vs. T*. (b) The plot of χ_M and χ_M^{-1} *vs. T*. The solid blue lines were derived from the fitting by the Curie-Weiss law.

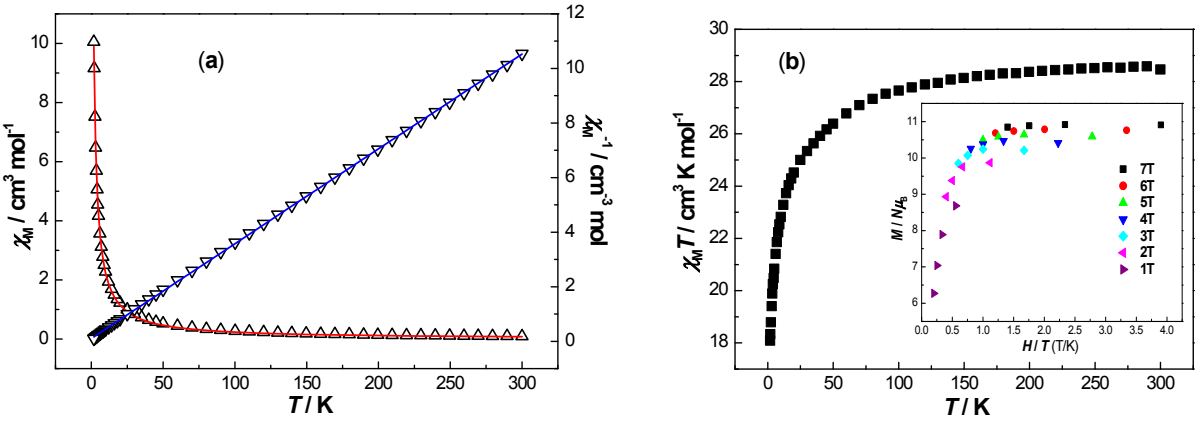


Fig. S14 Temperature dependence of the molar magnetic susceptibilities of **3**. (a) The plots of χ_M and χ_M^{-1} *vs. T*. Solid blue lines were derived from the fitting by the Curie-Weiss law. (b) The plot of $\chi_M T$ *vs. T*. Inset: Reduced magnetization data for **3** at low temperatures.

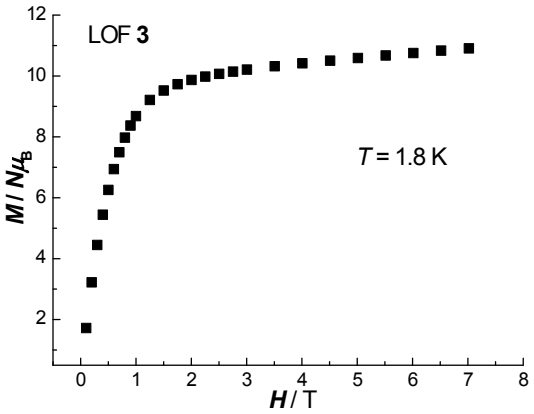


Fig. S15 M-H plot for **3** at 1.8 K.

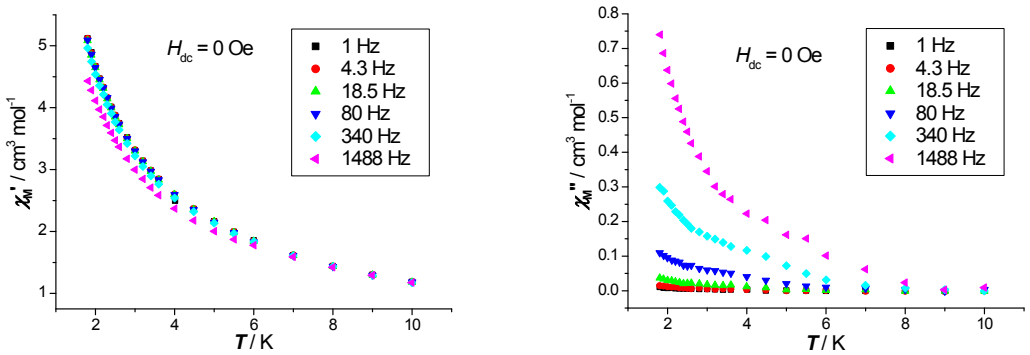


Fig. S16 Temperature dependence of the real χ' and imaginary χ'' components of the AC susceptibility measured in H_{dc} = 0 Oe applied field at different ac frequency for **3**.

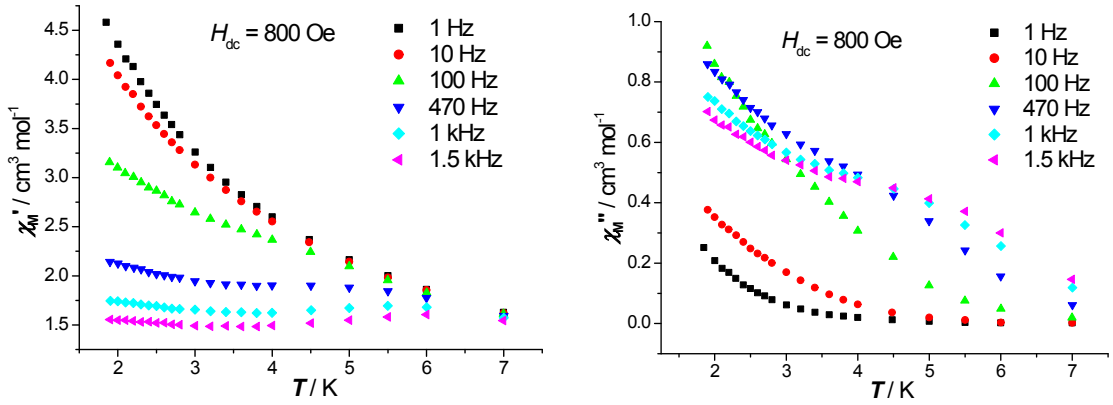


Fig. S17 Temperature dependence of the real χ' and imaginary χ'' components of the AC susceptibility measured in H_{dc} = 800 Oe applied field at different ac frequency for **3**.

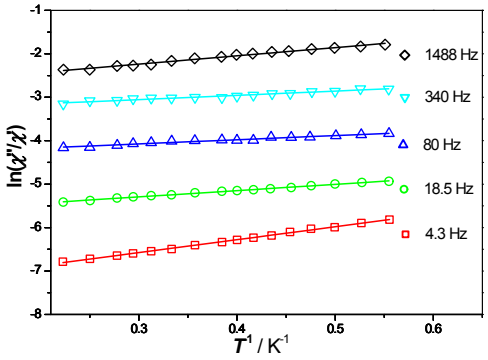


Fig. S18 ln(χ''/χ') *vs.* 1/*T* plots for **3** at different frequencies of the 5.0 Oe ac field. The solid lines are the best-fit curves (see text).

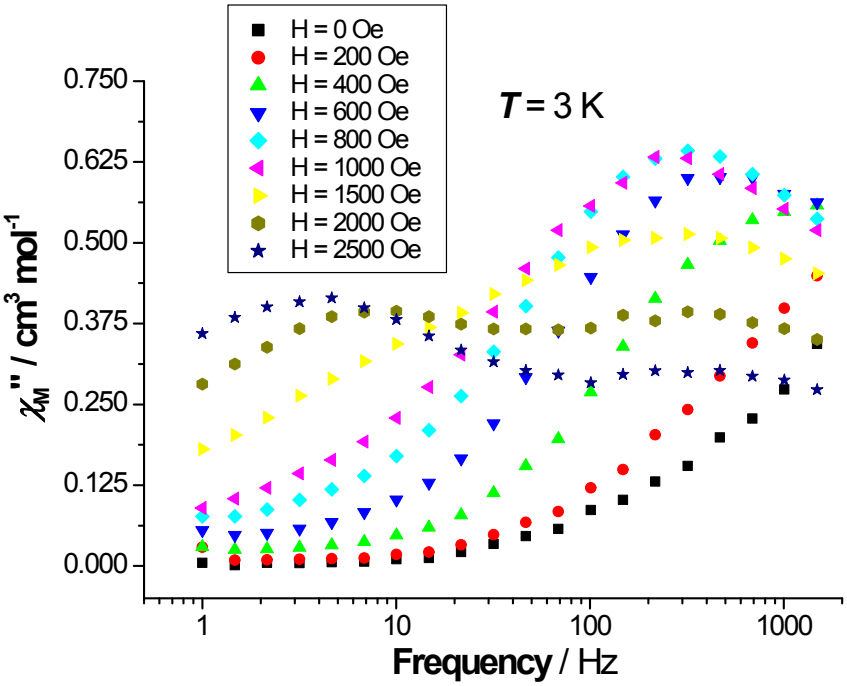


Fig. S19 Frequency dependence at 3 K of the imaginary χ'' components of the AC susceptibilities measured in different DC applied field for **3**.

10. The FT-IR Spectra.

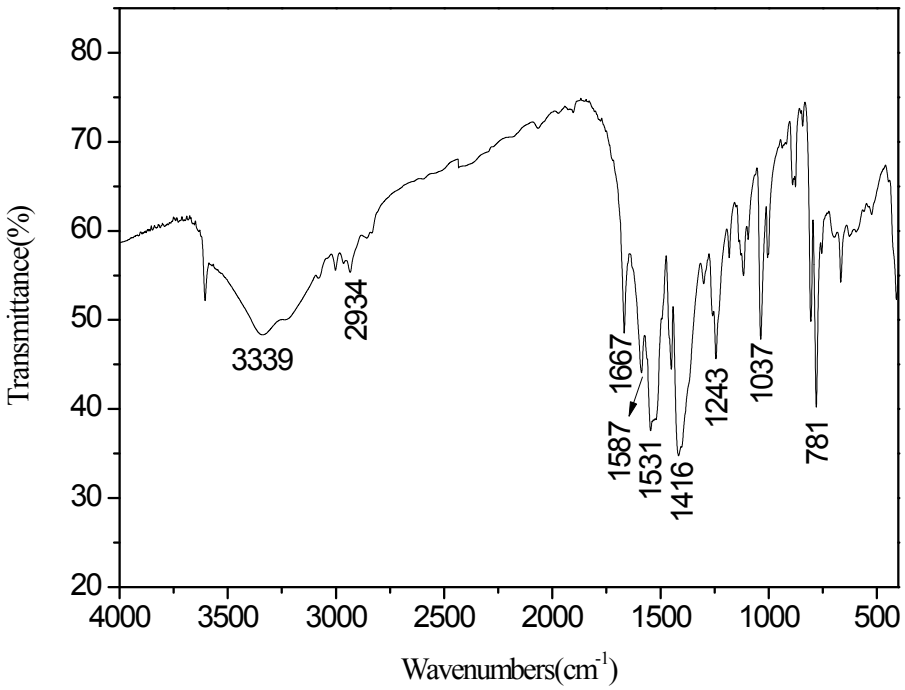


Fig. S20 The IR spectra of MOF **1**.

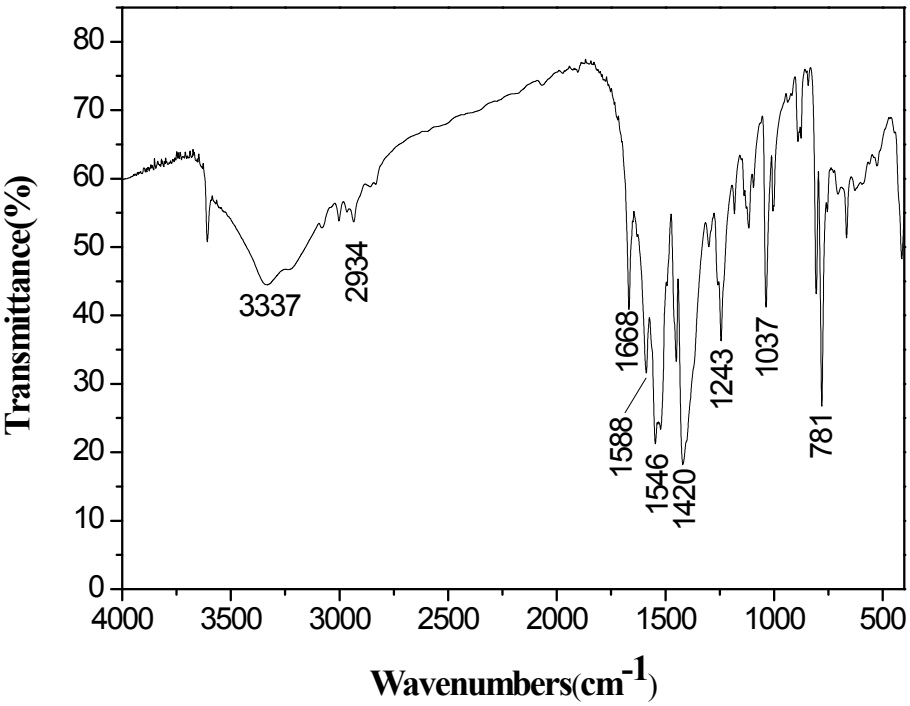


Fig. S21 The IR spectra of MOF **2**.

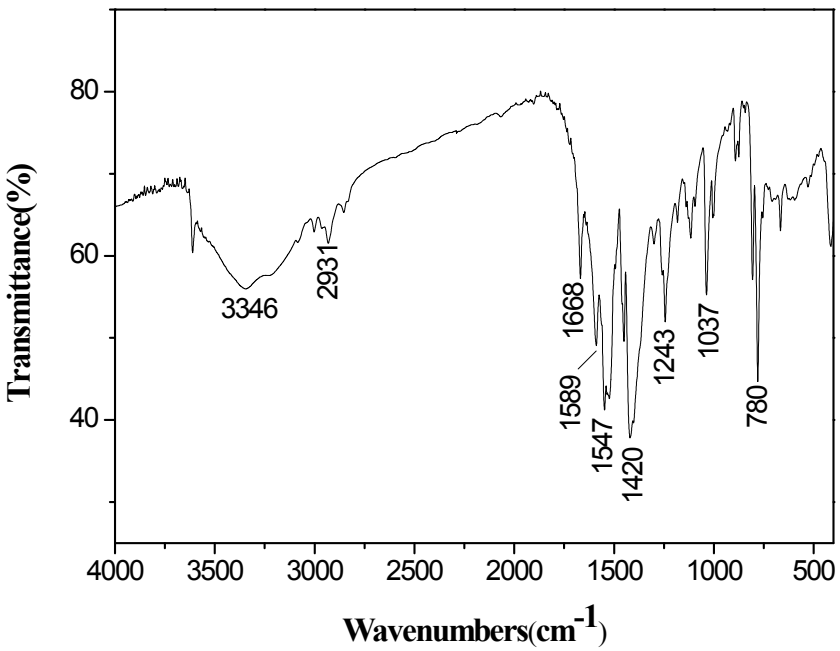


Fig. S22 The IR spectra of MOF **3**.

11. References.

1. X. Wang, J. Zhao, Y. Zhao, H. Xu, X. Shen, D. R. Zhu and S. Jing, *Dalton Trans.*, 2015, **44**, 9281-9288.

2. O. Kahn, *Molecular Magnetism*; VCH, Weinheim, Germany, 1993.

3. G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2007, **64**, 112.