Supporting Information

Cubane-type $\{M_4O_4\}$ ($M = Co^{II}$, Zn^{II}, Cu^{II}) clusters: synthesis, crystal structures, and luminescent and magnetic properties

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1. Selected bond lengths [Å] and angles [°] for complexes 1-3.

Table S1 Selected bond lengths [Å] and angles [°] for complex **1**.

Selected bond length			
Co(1)-O(1)	1.945(3)	Co(2)-O(2)	2.186(3)
Co(1)-O(2)#1	2.054(3)	Co(2)-O(4)	1.944(3)
Co(1)-O(2)	2.186(3)	Co(2)-O(5)	2.181(3)
Co(1)-N(1)	2.008(3)	Co(2)-O(5)#1	2.042(3)
Co(1)-O(5)#1	2.057(3)	Co(2)-N(2)	1.987(4)
Co(1)···Co(2)	3.0971(10)	Co(2)···Co(2)#1	3.1488(13)
Co(1)···Co(1)#1	3.177(10)	Co(1)···Co(2)#1	3.1802(10)
O(1)-Co(1)-N(1)	91.76(14)	O(2)-Co(2)-O(5)	78.97(10)
O(1)-Co(1)-O(2)#1	97.38(11)	O(2)-Co(2)-O(5)#1	84.95(10)
O(1)-Co(1)-O(5)#1	117.15(12)	O(4)-Co(2)-N(2)	92.97(14)
O(1)-Co(1)-O(2)	161.71(12)	O(4)-Co(2)-O(2)	114.80(12)
O(2)#1-Co(1)-O(5)#1	81.62(10)	O(4)-Co(2)-O(5)#1	96.29(12)
O(2)#1-Co(1)-O(2)	82.23(10)	O(4)-Co(2)-O(5)	166.15(13)
O(5)#1-Co(1)-O(2)	80.98(10)	O(5)#1-Co(2)-O(5)	83.05(10)
N(1)-Co(1)-O(2)#1	143.23(13)	N(2)-Co(2)-O(2)	124.84(14)
N(1)-Co(1)-O(2)	78.39(12)	N(2)-Co(2)-O(5)	79.27(13)
N(1)-Co(1)-O(5)#1	125.02(13)	N(2)-Co(2)-O(5)#1	140.77(14)
Co(1)#1-O(2)-Co(1)	96.96(10)	Co(2)#1-O(5)-Co(2)	96.33(10)
Co(2)-O(2)-Co(1)	94.16(10)	Co(2)-O(2)-Co(1)#1	101.91(10)
Co(2)#1-O(5)-Co(1)#1	98.14(11)	Co(1)#1-O(5)-Co(2)	97.20(10)
Symmetry transformations used to generate equivalent atoms: #1: -x,y,-z+1/2.			

Table S2 Hydrogen bond lengths [Å] and angles [°] for complex **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3A)...O(1)#1	0.82	2.21	2.780(6)	127.2
O(3)-H(3A)...O(7)#1	0.82	2.41	3.152(8)	150.7

O(3')-H(3')...O(1)#1	0.82	2.05	2.759(12)	144.1
O(3')-H(3')...O(7)#1	0.82	2.24	2.778(13)	123.4
O(6)-H(6)...N(1)#1	0.82	2.47	3.27(2)	164.8
O(6)-H(6)...O(4)#1	0.82	2.07	2.768(17)	142.8
O(6)-H(6)...O(5)	0.82	2.55	2.823(15)	101.2
C(16)-H(16)...O(3)#2	0.93	2.57	3.258(7)	131.2

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

Table S3 Selected bond lengths [Å] and angles [°] for complex **2**.

Selected bond length			
Zn(1)-O(1)	1.939(2)	Zn(2)-O(2)	2.013(2)
Zn(1)-O(2)	2.221(2)	Zn(2)-O(4)	1.948(2)
Zn(1)-O(2)#1	2.051(2)	Zn(2)-O(5)	2.224(2)
Zn(1)-O(5)#1	2.016(2)	Zn(2)-O(5)#1	2.033(2)
Zn(1)-N(1)	2.026(3)	Zn(2)-N(2)	1.995(3)
Zn(1)···Zn(2)	3.0752(6)	Zn(2)···Zn(1)#1	3.1475(6)
Zn(1)···Zn(1)#1	3.2034(9)	Zn(2)···Zn(2)#1	3.1662(8)
O(1)-Zn(1)-O(2)#1	96.59(9)	O(2)-Zn(2)-O(5)	79.08(8)
O(1)-Zn(1)-O(2)	159.58(10)	O(2)-Zn(2)-O(5)#1	85.74(8)
O(1)-Zn(1)-O(5)#1	119.36(10)	O(4)-Zn(2)-O(5)	164.99(10)
O(5)#1-Zn(1)-O(2)#1	83.27(9)	O(4)-Zn(2)-O(2)	115.80(10)
O(5)#1-Zn(1)-O(2)	80.88(8)	O(4)-Zn(2)-O(5)#1	95.14(10)
O(2)#1-Zn(1)-O(2)	82.35(8)	O(5)#1-Zn(2)-O(5)	83.48(9)
O(1)-Zn(1)-N(1)	91.89(11)	O(4)-Zn(2)-N(2)	93.07(12)
O(5)#1-Zn(1)-N(1)	123.07(11)	N(2)-Zn(2)-O(2)	123.79(11)
N(1)-Zn(1)-O(2)#1	142.95(10)	N(2)-Zn(2)-O(5)	79.14(11)
N(1)-Zn(1)-O(2)	77.58(9)	N(2)-Zn(2)-O(5)#1	141.28(11)
Zn(1)#1-O(2)-Zn(1)	97.08(8)	Zn(2)-O(2)-Zn(1)#1	101.52(9)
Zn(1)#1-O(5)-Zn(2)	95.74(8)	Zn(2)-O(2)-Zn(1)	93.02(8)
Zn(1)#1-O(5)-Zn(2)#1	98.84(9)	Zn(2)#1-O(5)-Zn(2)	96.01(9)

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

Table S4 Hydrogen bond lengths [Å] and angles [°] for complex **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3A)...O(1)#1	0.82	2.19	2.759(5)	126.2
O(3)-H(3A)...O(7)#1	0.82	2.39	3.122(6)	148.7
O(3')-H(3')...O(1)#1	0.82	2.05	2.766(10)	145.2
O(3')-H(3')...O(7)#1	0.82	2.24	2.784(11)	124.7
O(6)-H(6)...O(8)#1	0.82	2.47	3.142(18)	140.3
O(6)-H(6)...O(4)#1	0.82	2.14	2.852(9)	145.6
O(6')-H(6')...O(4)#1	0.82	1.96	2.779(17)	173.4
O(6')-H(6')...O(8)#1	0.82	2.31	2.73(2)	112.2
C(16)-H(16)...O(3)#2	0.93	2.59	3.262(5)	129.6

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

Table S5 Selected bond lengths [Å] and angles [°] for complex **3**.

Selected bond length			
Cu(1)-O(1)	1.8925(18)	Cu(1)-N(1)	1.9287(2)
Cu(1)-O(2)	1.9709(17)	Cu(1)-O(2)#1	1.9486(16)
Cu(1)-O(2)#3	2.4660(16)		
Cu(1)···Cu(1)#1	3.1080(5)	Cu(1)···Cu(1)#3	3.4317(5)
Cu(1)···Cu(1)#2	3.1080(5)	Cu(1)#2···Cu(1)#3	3.1080(5)
Cu(1)#1···Cu(1)#2	3.4317(5)	Cu(1)#1···Cu(1)#3	3.1080(5)
O(1)-Cu(1)-O(2)#1	93.34(7)	O(1)-Cu(1)-N(1)	93.35(8)
O(1)-Cu(1)-O(2)	177.02(8)	N(1)-Cu(1)-O(2)#1	168.13(8)
O(2)#1-Cu(1)-O(2)	88.52(7)	N(1)-Cu(1)-O(2)	84.43(8)
Cu(1)#2-O(2)-Cu(1)	104.93(8)		

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

Table S6 Hydrogen bond lengths [Å] and angles [°] for complex **3**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(1)#3	0.82	2.11	2.924(3)	171.1
C(7)-H(7)...O(3)#4	0.93	2.55	3.442(4)	161.3

C(9)-H(9)...O(1)#2	0.98	2.52	3.011(4)	110.7

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

2. IR spectra of complexes 1-3

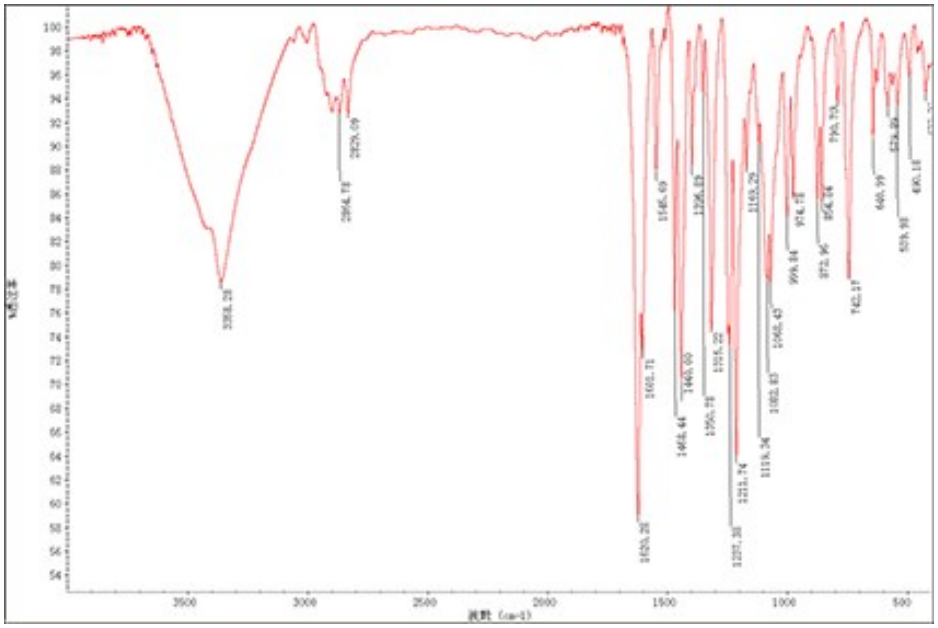

Fig. S1 IR spectrum of **1**.

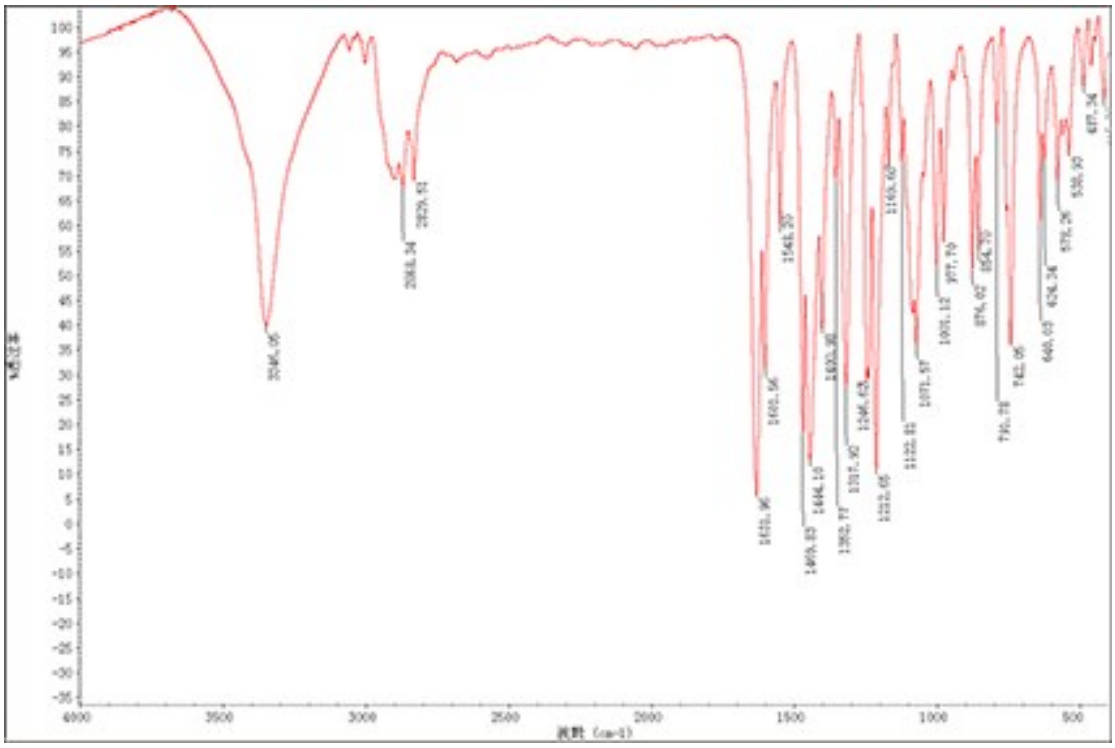

Fig. S2 IR spectrum of **2**.

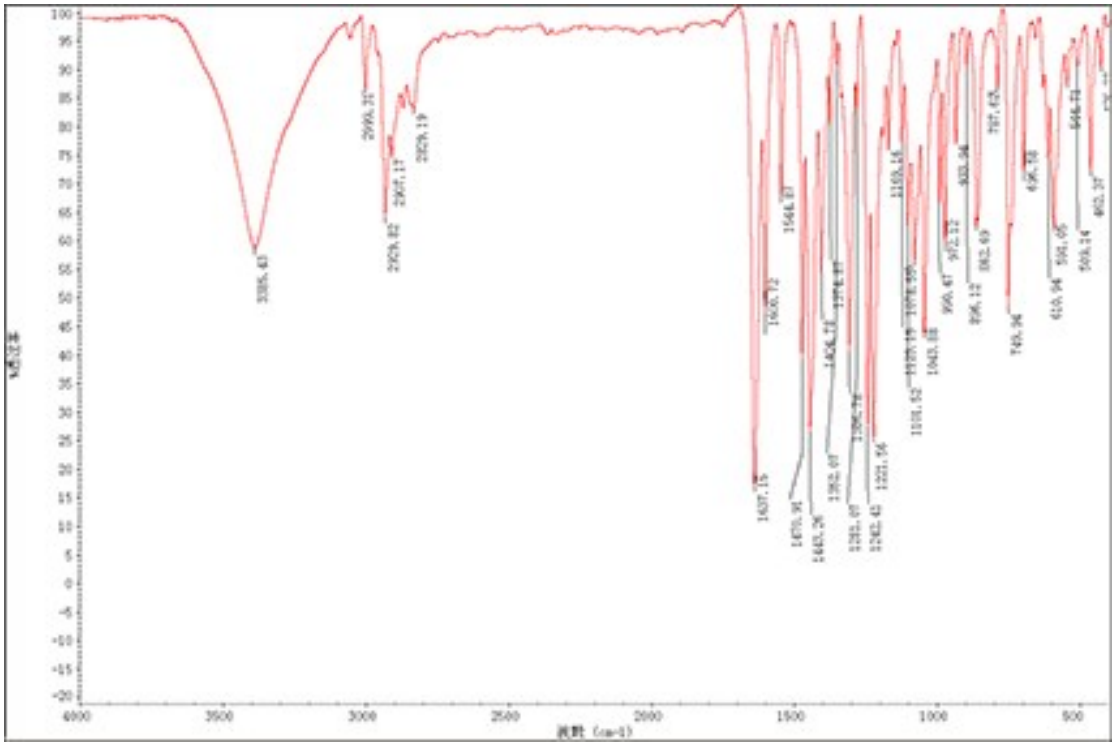

Fig. S3 IR spectrum of **3**.

3. XRD patterns of complexes 1-3

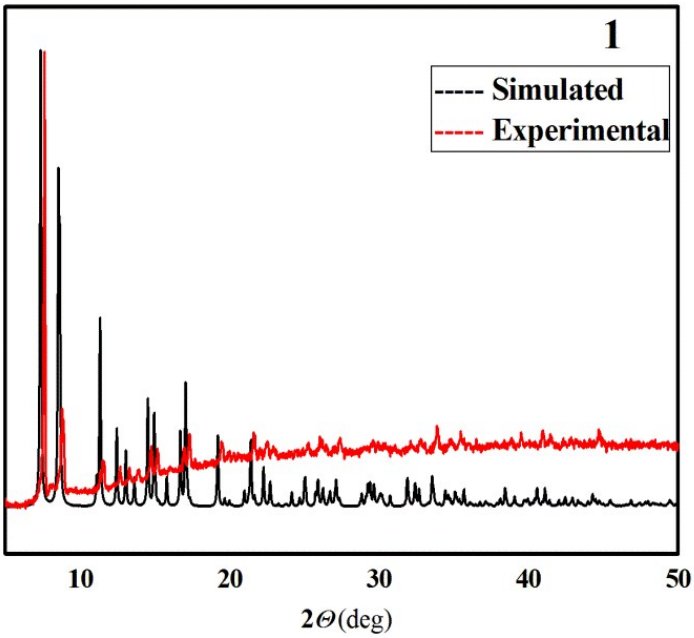

Fig.S4 XRD pattern of **1**.

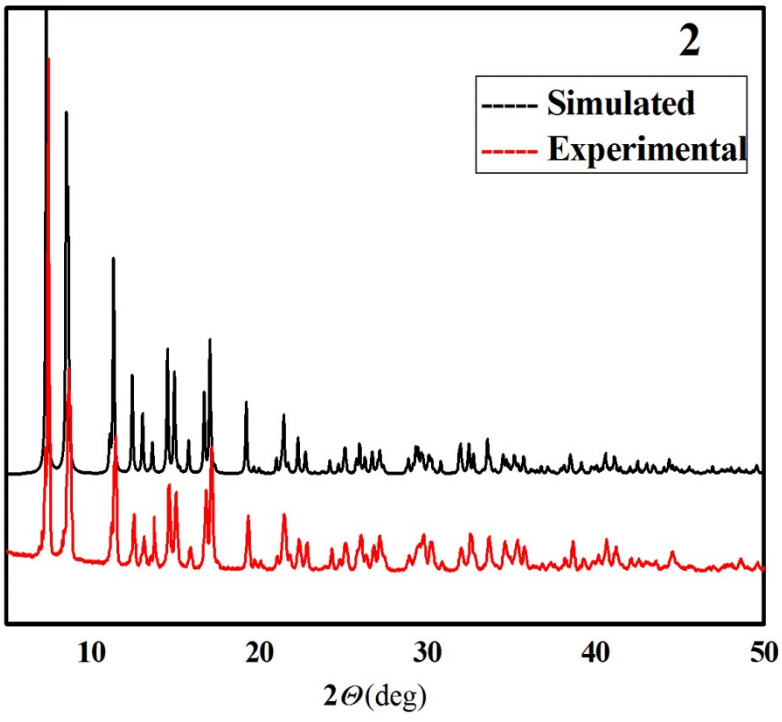

Fig.S5 XRD pattern of **2**.

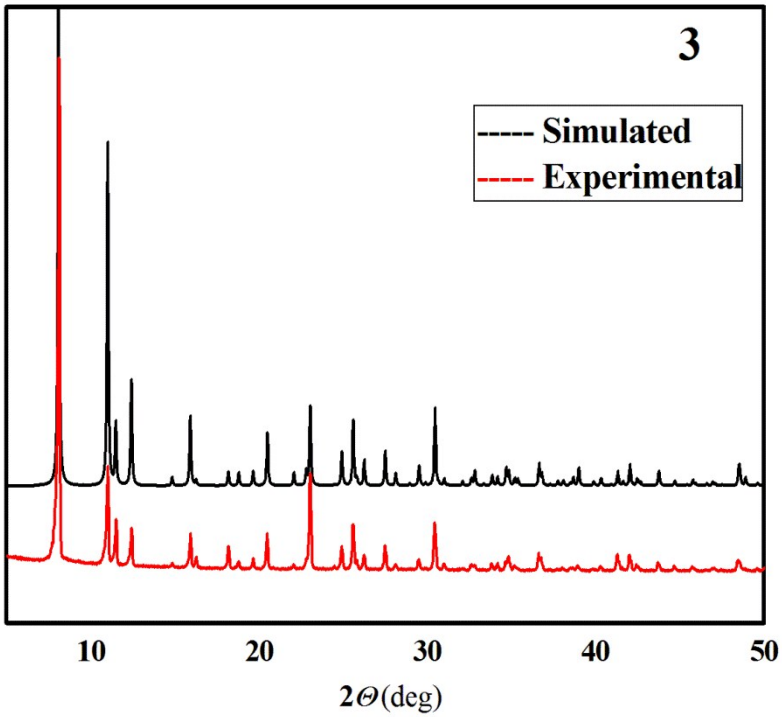

Fig.S6 XRD pattern of **3**.