Electronic Supplementary Information (ESI)

A Series of 3D Metal Organic Frameworks Based on [24-MC-6] Metallacrown Clusters: Structure, Magnetic and Luminescent Properties

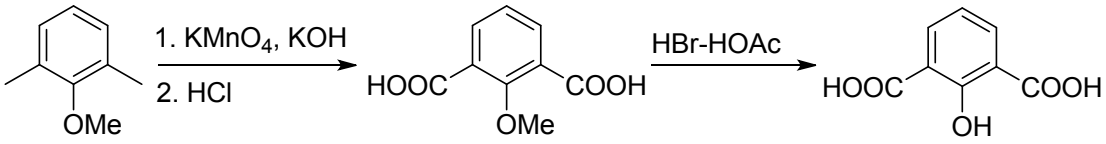
Kai Wang,[a,b] Hua-Hong Zou,[b] Zi-Lu Chen,[b] Zhong Zhang,[b] Wei-Yin Sun,[a] Fu-Pei Liang,*[b,c]

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing, 210093, China*

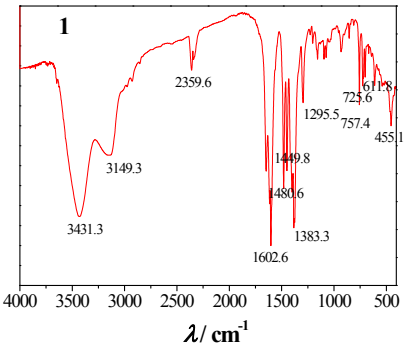
[b]*State Key Laboratory Cultivation Base for the Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmacy, Guangxi Normal University, Guilin, 541004, China*

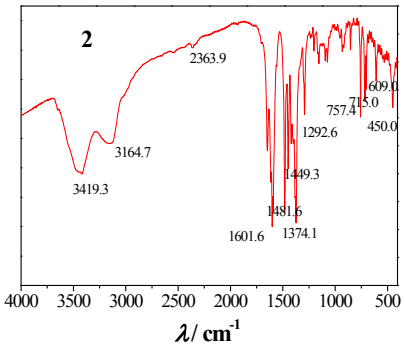
[c]*College of Chemistry and Bioengineering, Guilin University of Technology, Guilin, 541004, China*

E-mail address: fliangoffice@yahoo. com (F. Liang)



Scheme S1. The synthetic routes for H_3ipO





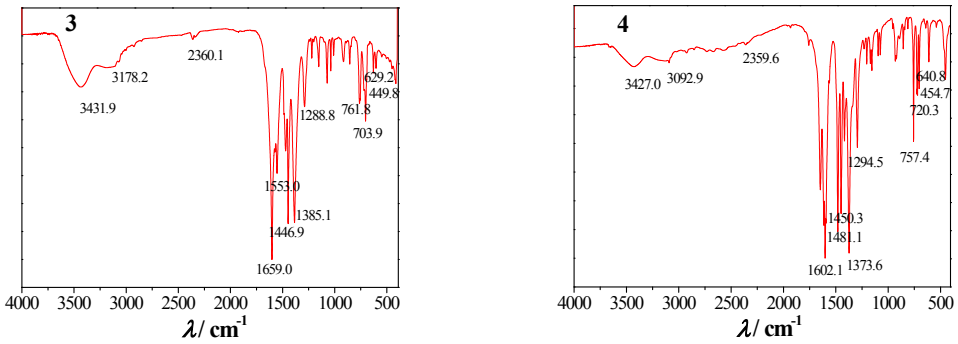


Figure S1. the IR spectras of **1-4**.

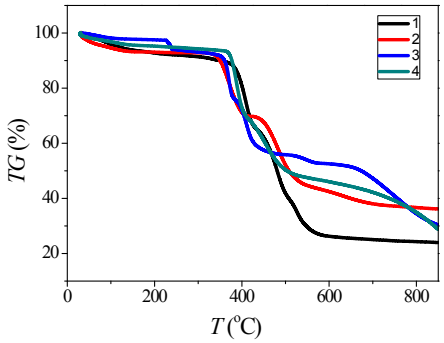


Figure S2. TG curves for **1-4** under nitrogen atmosphere.

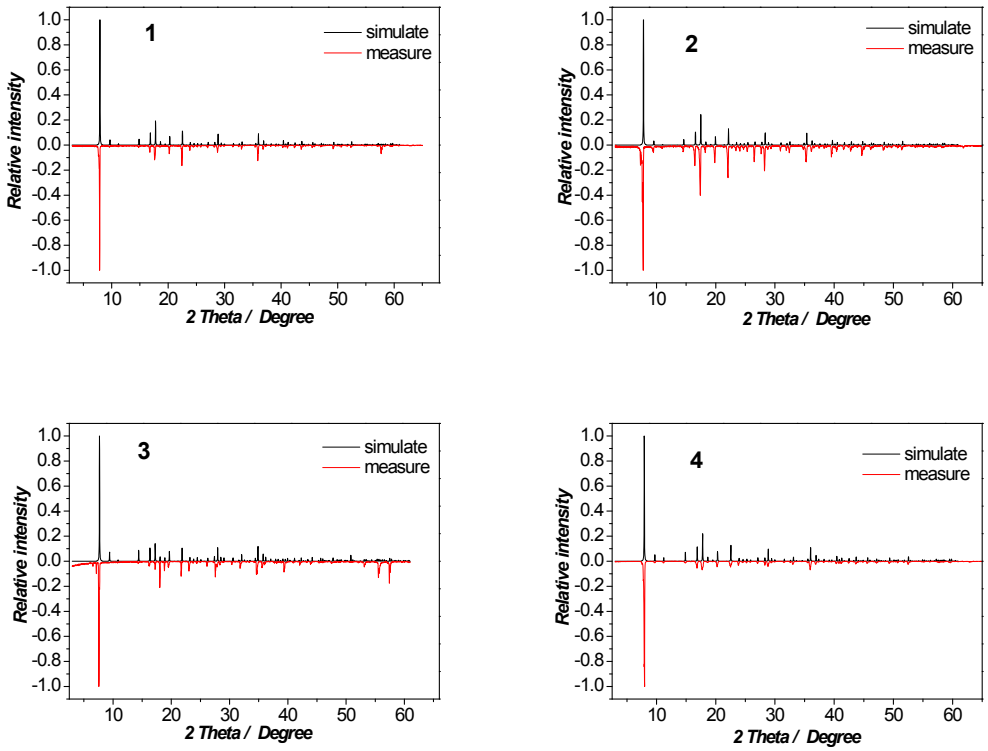


Figure S3. The PXRD patterns of complexes **1-4**.

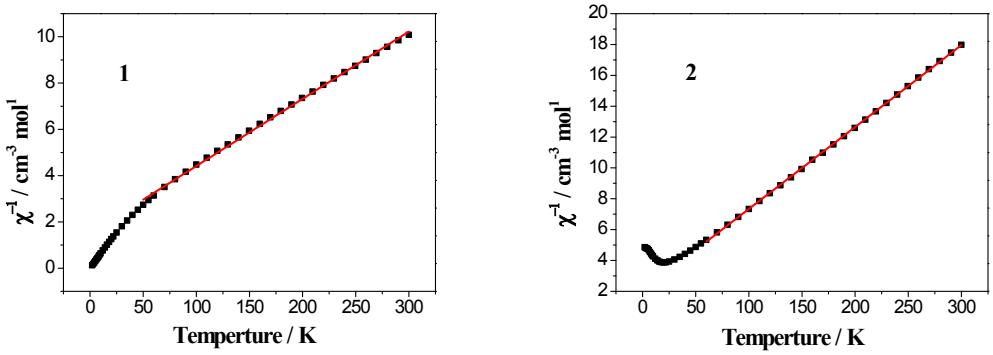


Figure S4. χm^{-1} vs T for **1** and **2**, the red line represents the best fit of the data with Curie-Weiss law.

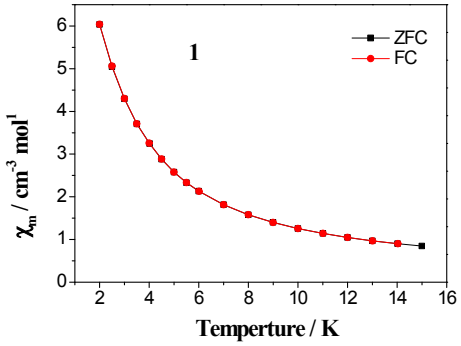


Figure S5. The FC/ZFC curves for compound **1** at 20 Oe (left).

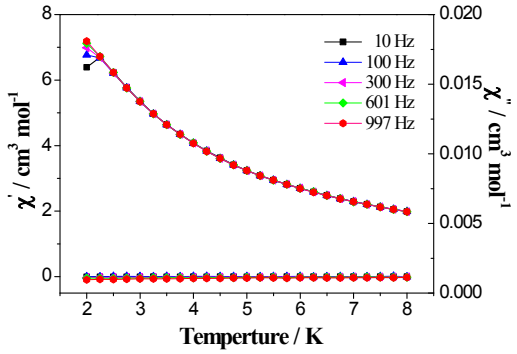


Figure S6. Temperature dependence of AC susceptibility at various frequencies of compound **1** (right).

Table S1 Crystal Data and Structure Refinement Parameters for Compounds **1-4**

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_8H_6O_6Co$	$C_8H_6O_6Mn$	$C_8H_6O_6Cd$	$C_{48}H_{38}O_{37}Zn_6$
Formula weight	257.06	253.07	310.54	1599.07
Temp/K	160.15	160.15	160.15	160.15
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	$Ia\bar{3}$	$Ia\bar{3}$	$Ia\bar{3}$	$Ia\bar{3}$
a/Å	22.308(2)	22.680(2)	22.990(18)	22.283(5)
α/deg	90	90	90	90
V/Å^3	11101(2)	11666(2)	12150.7(16)	11064(4)
Z	48	48	48	8
D_c/g cm^{-3}	1.831	1.715	2.024	1.903
$m\mu$/mm^{-1}	1.859	1.362	2.161	2.671
F(000)	6117	6000	7070	6323
Reflections collected	9624	8042	10260	6269
Independent reflections	1898	1714	2321	1622
Data/restrains/parameters	1898/0/139	1714/0/143	2221/0/139	1622/34/135
R_{int}	0.057	0.040	0.019	0.094
GOF	1.052	1.187	1.053	1.010
R_1[a] (I> 2σ(I))	R_1 = 0.0367,	R_1= 0.0424,	R_1= 0.0241,	R_1= 0.0436,
wR_2[b](all data)	R_1 = 0.0549,	R_1 = 0.0583,	R_1= 0.0254,	R_1= 0.0814,

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b]$wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

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

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Co1	O3	2.166(3)	Co1	O1^4	2.021(3)
Co1	O5^1	2.098(3)	O3	C7	1.369(4)
Co1	O5	2.067(3)	C8	O4	1.244(5)
Co1	O4^2	2.039(3)	C1	O2	1.297(5)
Co1	O2^3	2.103(3)	C1	O1	1.241(5)

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O5	Co1	O3	79.31(10)	O1^4	Co1	O5	94.65(10)
O5^1	Co1	O3	174.74(10)	O1^4	Co1	O5^1	90.42(10)
O4^2	Co1	O3	85.34(10)	O1^4	Co1	O4^2	170.62(11)
O4^2	Co1	O5	90.03(10)	O1^4	Co1	O2^3	89.42(10)
O4^2	Co1	O5^1	97.18(10)	C7	O3	Co1	121.0(2)

O2[3]	Co1	O3	92.73(10)	C8	O5	Co1	125.2(2)
O2[3]	Co1	O5	170.87(10)	C8	O5	Co1[5]	122.5(2)
O2[3]	Co1	O5[1]	92.10(10)	C8	O4	Co1[6]	139.6(2)
O2[3]	Co1	O4[2]	84.83(11)	C1	O2	Co1[3]	124.2(2)
O1[4]	Co1	O3	87.54(10)	C1	O1	Co1[7]	139.5(3)

Symmetry codes: [1]+y, 1/2-z, 1/2+x; [2]1/2-z, -x, 1/2+y; [3]-x, 1/2-y, +z; [4]-1/2+z, -x, +y; [5]-1/2+z, +x, 1/2-y; [6]-y, -1/2+z, 1/2-x; [7]-y, +z, 1/2+x

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

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O5	2.163(3)	O1	Mn1[7]	2.104(3)
Mn1	O5[1]	2.164(3)	O2	Mn1[4]	2.176(3)
Mn1	O4[2]	2.130(3)	C1	O1	1.247(5)
Mn1	O1[3]	2.104(3)	C1	O2	1.292(5)
Mn1	O3	2.247(3)	C8	O5	1.283(5)
Mn1	O2[4]	2.176(3)	C8	O4	1.240(5)
O5	Mn1[5]	2.164(3)	C7	O3	1.373(5)
O4	Mn1[6]	2.130(3)			

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	Mn1	O5[1]	97.11(13)	O1[4]	Mn1	O4[3]	170.87(11)
O5	Mn1	O3	75.16(10)	O1[4]	Mn1	O3	87.50(10)
O5[1]	Mn1	O3	172.00(11)	O1[4]	Mn1	O2[2]	91.87(11)
O5[1]	Mn1	O2[2]	93.41(11)	O2[2]	Mn1	O3	94.50(10)
O5	Mn1	O2[2]	167.83(11)	Mn1	O5	Mn1[5]	109.70(12)
O4[3]	Mn1	O5[1]	97.45(11)	C8	O5	Mn1	127.5(2)
O4[3]	Mn1	O5	88.32(11)	C8	O5	Mn1[5]	122.7(2)
O4[3]	Mn1	O3	84.58(10)	C8	O4	Mn1[6]	140.9(3)
O4[3]	Mn1	O2[2]	84.24(11)	C1	O1	Mn1[7]	141.3(3)
O1[4]	Mn1	O5[1]	91.01(11)	C7	O3	Mn1	122.6(2)
O1[4]	Mn1	O5	94.05(10)	C1	O2	Mn1[2]	125.1(2)

Symmetry codes: [1]-1/2+z, 1-x, +y; [2]1/2-x, +y, 1-z; [3]-1/2+y, 3/2-z, 1-x; [4]1-y, 1-z, 1-x; [5]1-y, +z, 1/2+x; [6]1-z, 1/2+x, 3/2-y; [7]1-z, 1-x, 1-y

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

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cd2	O4[1]	2.218(2)	O1	C1	1.245(4)
Cd2	O5	2.273(2)	O4	C8	1.248(4)
Cd2	O5[2]	2.265(2)	O5	C8	1.277(4)

Cd2	O3	2.371(2)	O3	C7	1.362(4)
Cd2	$O2^3$	2.278(2)	O2	C1	1.283(4)
Cd2	$O1^4$	2.205(2)			

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	Cd2	$O4^1$	88.65(8)	C1	O1	$Cd2^7$	140.1(2)
$O5^2$	Cd2	$O4^1$	101.61(8)	$O1^4$	Cd2	$O5^2$	90.64(8)
O3	Cd2	$O4^1$	83.49(8)	$O1^4$	Cd2	O5	96.15(8)
O3	Cd2	O5	72.00(8)	$O1^4$	Cd2	O3	85.89(8)
O3	Cd2	$O5^2$	166.41(8)	$O1^4$	Cd2	$O2^3$	90.63(8)
$O2^3$	Cd2	$O4^1$	82.59(9)	C8	O4	$Cd2^5$	135.8(2)
$O2^3$	Cd2	O5	167.93(8)	C8	O5	Cd2	130.23(19)
$O2^3$	Cd2	$O5^2$	94.52(8)	C8	O5	$Cd2^6$	124.56(19)
$O2^3$	Cd2	O3	98.64(8)	C7	O3	Cd2	122.28(18)
$O1^4$	Cd2	$O4^1$	166.38(9)	C1	O2	$Cd2^3$	124.03(19)

Symmetry codes: [1]3/2-y, 1-z, -1/2+x; [2]1-z, +x, -1/2+y; [3]3/2-x, +y, -z; [4]+y, 1/2-z, -1/2+x; [5]1/2+z, 3/2-x, 1-y; [6]+y, 1/2+z, 1-x; [7]1/2+z, +x, 1/2-y

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

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	$O1^1$	2.074(3)	O4	C7	1.294(6)
Zn1	O1	2.078(3)	O1	C1	1.288(6)
Zn1	O3	2.206(4)	O3	C8	1.368(6)
Zn1	$O5^2$	2.012(3)	O5	C7	1.241(6)
Zn1	$O2^3$	2.046(3)	O2	C1	1.240(6)
Zn1	$O4^4$	2.092(3)			

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	Zn1	O1	77.67(14)	C7	O4	$Zn1^4$	123.5(3)
O3	Zn1	$O1^1$	172.95(14)	$O4^4$	Zn1	$O1^1$	93.75(13)
$O5^2$	Zn1	O1	95.18(14)	$O4^4$	Zn1	O3	92.98(14)
$O5^2$	Zn1	$O1^1$	91.79(14)	$O4^4$	Zn1	$O5^2$	89.26(14)
$O5^2$	Zn1	O3	86.21(15)	$O4^4$	Zn1	$O2^3$	84.66(13)
$O2^3$	Zn1	O1	89.26(13)	C1	O1	Zn1	126.5(3)
$O2^3$	Zn1	$O1^1$	98.26(14)	C1	O1	$Zn1^5$	122.4(3)
$O2^3$	Zn1	O3	84.44(14)	C8	O3	Zn1	121.7(3)
$O2^3$	Zn1	$O5^2$	168.56(14)	C7	O5	$Zn1^6$	139.0(4)
$O4^4$	Zn1	O1	169.32(13)	C1	O2	$Zn1^7$	138.2(3)

Symmetry codes: [1]1-z, +x, 1/2+y; [2]1-y, 1-z, 1-x; [3]1/2-y, 1-z, 1/2+x; [4]+x, 1-y, 3/2-z; [5]+y, -1/2+z, 1-x; [6]1-z, 1-x, 1-y; [7]-1/2+z, 1/2-x, 1-y