Supplementary Material (ESI) for *CrystEngComm*

A series of tetranuclear-cluster-containing complexes based on pendent-arm macrocyclic ligand and different carboxylates: syntheses, structures, photoluminescence, and magnetic properties

Huan-Huan Chen,[a,b] Jin Yang,*[,a] Ying-Ying Liu,[a] and Jian-Fang Ma*[,a]

[a] *Key Lab for Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China*

[b] *School of Resources and Materials, Northeastern University at Qinhuangdao Branch, Qinhuangdao 066004, People's Republic of China*

* Correspondence authors

E-mail: yangjinnenu@yahoo.com.cn (J. Yang)

E-mail: jianfangma@yahoo.com.cn (J.-F. Ma)

Fax: +86-431-85098620 (J.-F. Ma)

Table S1a. Selected bond distances (Å) and angles (°) for **1**.

Co(1)-N(1)	2.179(2)	Co(1)-N(2)	2.166(2)
Co(1)-O(4)	2.086(2)	Co(1)-O(1)	2.113(3)
Co(1)-O(2)	2.046(2)	Co(1)-O(1)$^{\#1}$	2.191(3)
Co(2)-O(1)	2.321(3)	Co(2)-O(1W)	2.142(2)
Co(2)-O(6)	1.997(2)	Co(2)-O(2W)	2.050(2)
Co(2)-O(2)$^{\#1}$	2.0908(19)	Co(2)-O(4)	2.123(2)
O(1')$^{\#1}$-Co(1)-O(2)	72.8(7)	O(1')$^{\#1}$-Co(1)-O(4)	103.6(7)
O(2)-Co(1)-O(4)	174.28(7)	O(1')$^{\#1}$-Co(1)-O(1)	92.9(7)
O(2)-Co(1)-O(1)	96.17(11)	O(4)-Co(1)-O(1)	79.41(10)
O(1')$^{\#1}$-Co(1)-N(2)	92.6(8)	O(2)-Co(1)-N(2)	106.48(9)
O(4)-Co(1)-N(2)	77.91(8)	O(1)-Co(1)-N(2)	157.32(10)
O(1')$^{\#1}$-Co(1)-N(1)	150.6(7)	O(2)-Co(1)-N(1)	78.16(8)
O(4)-Co(1)-N(1)	105.68(8)	O(1)-Co(1)-N(1)	94.84(10)
N(2)-Co(1)-N(1)	91.02(9	O(4)-Co(1)-O(1)$^{\#1}$	97.03(9)
O(2)-Co(1)-O(1)$^{\#1}$	79.10(9)	O(1)-Co(1)-O(1)$^{\#1}$	88.00(13)
N(2)-Co(1)-O(1)$^{\#1}$	95.01(11)	N(1)-Co(1)-O(1)$^{\#1}$	157.26(10)
O(2)-Co(1)-O(1')	100.1(7)	O(4)-Co(1)-O(1')	75.1(7)
N(2)-Co(1)-O(1')	152.5(6)	O(4)-Co(2)-O(1)	74.10(10)
N(1)-Co(1)-O(1')	101.2(6)	O(1)$^{\#1}$-Co(1)-O(1')	83.2(6)
O(6)-Co(2)-O(2W)	94.63(9)	O(6)-Co(2)-O(2)$^{\#1}$	89.41(9)
O(2W)-Co(2)-O(2)$^{\#1}$	171.15(8)	O(6)-Co(2)-O(4)	172.74(8)
O(2W)-Co(2)-O(4)	88.45(8)	O(2)$^{\#1}$-Co(2)-O(4)	86.66(8)
O(6)-Co(2)-O(1')	94.7(7)	O(2W)-Co(2)-O(1')	102.2(6)
O(2)$^{\#1}$-Co(2)-O(1')	69.5(6)	O(4)-Co(2)-O(1')	78.2(7)
O(6)-Co(2)-O(1W)	97.90(10)	O(2W)-Co(2)-O(1W)	97.02(9)
O(2)$^{\#1}$-Co(2)-O(1W)	90.19(8)	O(4)-Co(2)-O(1W)	88.22(8)
O(1')-Co(2)-O(1W)	156.0(7)	O(6)-Co(2)-O(1)	99.00(11)
O(2W)-Co(2)-O(1)	96.30(10)	O(2)$^{\#1}$-Co(2)-O(1)	75.27(9)

O(1W)-Co(2)-O(1)	157.50(10)

Table S1b. Hydrogen bonds for **1** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1WA)···O(3)$^{\#1}$	0.855(17)	1.84(2)	2.681(3)	166(4)
O(2W)-H(2WA)···O(5)$^{\#2}$	0.864(18)	1.904(17)	2.757(3)	169(3)
O(2W)-H(2WB)···O(7)$^{\#3}$	0.872(17)	1.741(19)	2.606(3)	171(4)
O(1W)-H(1WB)···O(5)	0.841(17)	1.90(2)	2.704(3)	158(4)

Symmetry codes for **1**: $^{\#1}$ -x+2, -y+1, -z+2; $^{\#2}$ -x+1, -y+1, -z+2; $^{\#3}$ -x+2, -y+2, -z+3.

Table S2a. Selected bond distances (Å) and angles (°) for **2.**

Mn(1)-O(4)	2.047(2)	Mn(1)-O(1W)	2.123(3)
Mn(1)-O(6)	2.186(2)	Mn(1)-O(2)$^{\#1}$	2.235(2)
Mn(1)-O(2W)	2.237(3)	Mn(1)-O(1)	2.331(2)
Mn(2)-O(6)	2.135(2)	Mn(2)-O(2)	2.164(2)
Mn(2)-O(1)$^{\#1}$	2.197(2)	Mn(2)-O(1)	2.211(2)
Mn(2)-N(1)	2.235(3)	Mn(2)-N(2)	2.240(3)
Mn(2)-Mn(2)$^{\#1}$	3.1171(10)		
O(4)-Mn(1)-O(1W)	96.03(11)	O(4)-Mn(1)-O(6)	89.80(10)
O(1W)-Mn(1)-O(6)	170.02(10)	O(4)-Mn(1)-O(2)$^{\#1}$	174.31(10)
O(1W)-Mn(1)-O(2)$^{\#1}$	87.60(9)	O(6)-Mn(1)-O(2)$^{\#1}$	86.00(9)
O(4)-Mn(1)-O(2W)	98.80(11)	O(1W)-Mn(1)-O(2W)	100.18(10)
O(6)-Mn(1)-O(2W)	86.87(9)	O(2)$^{\#1}$-Mn(1)-O(2W)	84.81(9)
O(4)-Mn(1)-O(1)	100.71(10)	O(1W)-Mn(1)-O(1)	96.13(9)
O(6)-Mn(1)-O(1)	74.78(8)	O(2)$^{\#1}$-Mn(1)-O(1)	74.48(7)
O(2W)-Mn(1)-O(1)	153.01(8)	O(6)-Mn(2)-O(2)	176.92(9)
O(6)-Mn(2)-O(1)$^{\#1}$	98.39(8)	O(2)-Mn(2)-O(1)$^{\#1}$	78.66(8)
O(6)-Mn(2)-O(1)	78.33(8)	O(2)-Mn(2)-O(1)	100.66(9)
O(1)$^{\#1}$-Mn(2)-O(1)	89.98(7)	O(6)-Mn(2)-N(1)	106.98(9)

O(2)-Mn(2)-N(1)	75.95(9)	$O(1)^{\#1}$-Mn(2)-N(1)	154.61(9)
O(1)-Mn(2)-N(1)	94.22(9)	O(6)-Mn(2)-N(2)	75.56(9)
O(2)-Mn(2)-N(2)	105.47(10)	$O(1)^{\#1}$-Mn(2)-N(2)	95.01(9)
O(1)-Mn(2)-N(2)	153.87(9)	N(1)-Mn(2)-N(2)	92.16(10)
$O(6)$-Mn(2)-$Mn(2)^{\#1}$	87.67(7)	$O(2)$-Mn(2)-$Mn(2)^{\#1}$	89.58(7)
$O(1)^{\#1}$-Mn(2)-$Mn(2)^{\#1}$	45.18(6)	O(1)-Mn(2)-$Mn(2)^{\#1}$	44.81(5)
N(1)-Mn(2)-$Mn(2)^{\#1}$	133.54(8)	N(2)-Mn(2)-$Mn(2)^{\#1}$	134.29(8)

Table S2b. Hydrogen bonds for **2** (Å and °).

D-H···A <(DHA)	d(D-H)	d(H···A)	d(D···A)	
O(1W)-H(1WB)···$O(3)^{\#2}$	0.847(10)	1.921(19)	2.724(3)	158(4)
O(2W)-H(2WB)···$O(3)^{\#1}$	0.848(10)	1.893(13)	2.732(3)	170(4)
O(1W)-H(1WA)···$O(5)^{\#3}$	0.849(10)	1.737(14)	2.575(4)	169(4)
O(2W)-H(2WA)···O(7)	0.854(10)	1.887(16)	2.721(4)	165(4)

Symmetry codes for **2**: $^{\#1}$ -x+2, -y+1, -z+1; $^{\#2}$ x+1, y, z; $^{\#3}$ -x+2, -y, -z.

Table S3a. Selected bond distances (Å) and angles (°) for **3**.

Co(1)-O(5)	2.053(3)	Co(1)-O(9)	2.057(3)
Co(1)-O(1)	2.128(3)	Co(1)-N(2)	2.163(4)
Co(1)-N(4)	2.165(3)	Co(1)-O(2)	2.182(3)
$Co(2)$-$O(13)^{\#1}$	2.008(3)	Co(2)-O(3)	2.078(3)
Co(2)-O(2W)	2.093(3)	Co(2)-O(5)	2.095(3)
Co(2)-O(1W)	2.149(3)	Co(2)-O(2)	2.290(3)
Co(3)-O(7)	2.025(3)	Co(3)-O(9)	2.040(3)
Co(3)-O(11)	2.049(3)	Co(3)-O(3W)	2.123(3)
Co(3)-O(12)	2.196(3)	Co(3)-O(1)	2.250(3)
Co(3)-C(33)	2.453(4)	Co(4)-O(7)	2.071(3)
Co(4)-O(3)	2.072(3)	Co(4)-O(2)	2.127(3)
Co(4)-O(1)	2.148(3)	Co(4)-N(1)	2.159(3)

Co(4)-N(3)	2.168(4)		
O(5)-Co(1)-O(9)	173.19(12)	O(5)-Co(1)-O(1)	102.20(11)
O(9)-Co(1)-O(1)	78.48(11)	O(5)-Co(1)-N(2)	79.79(13)
O(9)-Co(1)-N(2)	106.95(13)	O(1)-Co(1)-N(2)	95.19(13)
O(5)-Co(1)-N(4)	101.47(13)	O(9)-Co(1)-N(4)	77.77(12)
O(1)-Co(1)-N(4)	156.24(12)	N(2)-Co(1)-N(4)	91.06(14)
O(5)-Co(1)-O(2	78.84(11)	O(9)-Co(1)-O(2)	94.49(11)
O(1)-Co(1)-O(2)	85.75(10)	N(2)-Co(1)-O(2)	158.32(12)
N(4)-Co(1)-O(2)	96.76(12)	O(13)$^{\#1}$-Co(2)-O(3)	167.05(13)
O(13)$^{\#1}$-Co(2)-O(2W)	90.43(12)	O(3)-Co(2)-O(2W)	84.99(12)
O(13)$^{\#1}$-Co(2)-O(5)	95.40(12)	O(3)-Co(2)-O(5)	88.60(12)
O(2W)-Co(2)-O(5)	173.27(12)	O(13)$^{\#1}$-Co(2)-O(1W)	100.77(13)
O(3)-Co(2)-O(1W)	91.51(12)	O(2W)-Co(2)-O(1W)	92.02(13)
O(5)-Co(2)-O(1W)	90.19(12)	O(13)$^{\#1}$-Co(2)-O(2)	93.68(12)
O(3)-Co(2)-O(2)	75.35(11)	O(2W)-Co(2)-O(2)	100.75(11)
O(5)-Co(2)-O(2)	75.57(11)	O(1W)-Co(2)-O(2)	160.64(12)
O(7)-Co(3)-O(9)	95.28(13)	O(7)-Co(3)-O(11)	163.45(13)
O(9)-Co(3)-O(11)	97.65(12)	O(7)-Co(3)-O(3W)	92.72(12)
O(9)-Co(3)-O(3W)	92.51(12)	O(11)-Co(3)-O(3W)	96.98(13)
O(7)-Co(3)-O(12)	103.52(12)	O(9)-Co(3)-O(12)	156.90(12)
O(11)-Co(3)-O(12)	61.66(11)	O(3W)-Co(3)-O(12)	99.80(12)
O(7)-Co(3)-O(1)	78.14(11)	O(9)-Co(3)-O(1)	76.04(11)
O(11)-Co(3)-O(1)	94.99(12)	O(3W)-Co(3)-O(1)	164.44(11)
O(12)-Co(3)-O(1)	94.62(11)	O(7)-Co(3)-C(33)	133.74(13)
O(9)-Co(3)-C(33)	127.48(13)	O(11)-Co(3)-C(33)	30.83(12)
O(3W)-Co(3)-C(33)	101.07(13)	O(12)-Co(3)-C(33)	30.88(12)
O(1)-Co(3)-C(33)	94.30(12)	O(7)-Co(4)-O(3)	170.89(12)
O(7)-Co(4)-O(2)	101.03(12)	O(3)-Co(4)-O(2)	79.12(11)
O(7)-Co(4)-O(1)	79.56(11)	O(3)-Co(4)-O(1)	91.37(12)
O(2)-Co(4)-O(1)	86.62(11)	O(7)-Co(4)-N(1)	102.25(13)

O(3)-Co(4)-N(1)	77.65(12)	O(2)-Co(4)-N(1)	156.67(13)
O(1)-Co(4)-N(1)	96.06(12)	O(7)-Co(4)-N(3)	77.84(13)
O(3)-Co(4)-N(3)	111.27(13)	O(2)-Co(4)-N(3)	94.22(12)
O(1)-Co(4)-N(3)	157.12(12)	N(1)-Co(4)-N(3)	92.15(14)

Table S3b. Hydrogen bonds for **3** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2W)-H(2WA)···O(14)$^{\#1}$	0.82	1.81	2.591(5)	159.7
O(2W)-H(2WB)···O(4)$^{\#3}$	0.81	2.00	2.762(4)	155.7
O(1W)-H(1WA)···O(6)	0.87	1.87	2.707(5)	161.1
O(1W)-H(1WB)···O(4)	0.86	1.94	2.747(5)	155.7
O(3W)-H(3WA)···O(10)	0.83	1.98	2.706(5)	145.7
O(3W)-H(3WB)···O(8)	0.84	1.93	2.734(5)	159.4

Symmetry codes for **3**: $^{\#1}$ x, y, z+1; $^{\#2}$ x, y, z-1; $^{\#3}$ -x,-y,-z+2.

Table S4a. Selected bond distances (Å) and angles (°) for **4.**

Zn(1)-O(3)	2.079(3)	Zn(1)-O(7	2.086(3)
Zn(1)-O(1)	2.137(3)	Zn(1)-N(1)	2.145(4)
Zn(1)-N(3)	2.156(4)	Zn(1)-O(2)	2.170(3)
Zn(2)-O(5)	2.092(3)	Zn(2)-O(9)	2.115(3)
Zn(2)-O(1)	2.133(3)	Zn(2)-O(2)	2.146(3)
Zn(2)-N(2)	2.146(4)	Zn(2)-N(4)	2.163(4)
Zn(4)-O(11)$^{\#1}$	1.995(4)	Zn(4)-O(9)	2.013(3)
Zn(4)-O(7)	2.035(3)	Zn(4)-O(3W)	2.084(4)
Zn(4)-O(1)	2.317(3)	Zn(4)-O(12)$^{\#1}$	2.350(4)
Zn(3)-O(13)	1.978(3)	Zn(3)-O(5)	2.085(3)
Zn(3)-O(1W)	2.091(4)	Zn(3)-O(3)	2.116(3)

Zn(3)-O(2W)	2.126(4)	Zn(3)-O(2)	2.359(3)
O(3)-Zn(1)-O(7)	174.47(13)	O(3)-Zn(1)-O(1)	101.67(13)
O(7)-Zn(1)-O(1)	78.42(13)	O(3)-Zn(1)-N(1)	79.66(15)
O(7)-Zn(1)-N(1)	105.85(15)	O(1)-Zn(1)-N(1)	95.80(14)
O(3)-Zn(1)-N(3)	101.95(15)	O(7)-Zn(1)-N(3)	77.72(14)
O(1)-Zn(1)-N(3)	156.10(14)	N(1)-Zn(1)-N(3)	91.99(16)
O(3)-Zn(1)-O(2)	78.80(13)	O(7)-Zn(1)-O(2)	95.74(14)
O(1)-Zn(1)-O(2)	84.34(12)	N(1)-Zn(1)-O(2)	158.01(14)
N(3)-Zn(1)-O(2)	96.68(14)	O(5)-Zn(2)-O(9)	170.99(13)
O(5)-Zn(2)-O(1)	92.35(13)	O(9)-Zn(2)-O(1)	78.70(13)
O(5)-Zn(2)-O(2)	78.56(13)	O(9)-Zn(2)-O(2)	101.37(13)
O(1)-Zn(2)-O(2)	85.01(12)	O(5)-Zn(2)-N(2)	78.27(15)
O(9)-Zn(2)-N(2)	101.61(15)	O(1)-Zn(2)-N(2)	96.51(14)
O(2)-Zn(2)-N(2)	156.82(15)	O(5)-Zn(2)-N(4)	111.04(15)
O(9)-Zn(2)-N(4)	77.97(15)	O(1)-Zn(2)-N(4)	156.08(15)
O(2)-Zn(2)-N(4)	94.48(14)	N(2)-Zn(2)-N(4)	93.24(16)
$O(11)^{\#1}$-Zn(4)-O(9)	155.50(15)	$O(11)^{\#1}$-Zn(4)-O(7)	99.62(14)
O(9)-Zn(4)-O(7)	99.02(14)	$O(11)^{\#1}$-Zn(4)-O(3W)	101.43(16)
O(9)-Zn(4)-O(3W)	93.30(15)	O(7)-Zn(4)-O(3W)	93.09(15)
$O(11)^{\#1}$-Zn(4)-O(1)	92.96(14)	O(9)-Zn(4)-O(1)	76.56(13)
O(7)-Zn(4)-O(1)	75.36(12)	O(3W)-Zn(4)-O(1)	162.96(13)
$O(11)^{\#1}$-Zn(4)-$O(12)^{\#1}$	59.42(14)	O(9)-Zn(4)-$O(12)^{\#1}$	98.43(14)
O(7)-Zn(4)-$O(12)^{\#1}$	155.66(14)	O(3W)-Zn(4)-$O(12)^{\#1}$	102.71(15)
O(1)-Zn(4)-$O(12)^{\#1}$	92.42(12)	$O(11)^{\#1}$-Zn(4)-$C(88)^{\#1}$	30.04(15)
O(9)-Zn(4)-$C(88)^{\#1}$	126.79(16)	O(7)-Zn(4)-$C(88)^{\#1}$	128.18(16)
O(3W)-Zn(4)-$C(88)^{\#1}$	105.50(16)	O(1)-Zn(4)-$C(88)^{\#1}$	91.53(14)
$O(12)^{\#1}$-Zn(4)-$C(88)^{\#1}$	29.46(14)	O(13)-Zn(3)-O(5)	165.09(15)
O(13)-Zn(3)-O(1W)	92.11(15)	O(5)-Zn(3)-O(1W)	83.66(14)
O(13)-Zn(3)-O(3)	94.81(14)	O(5)-Zn(3)-O(3)	88.32(13)
O(1W)-Zn(3)-O(3)	171.30(14)	O(13)-Zn(3)-O(2W)	103.35(15)

O(5)-Zn(3)-O(2W)	91.24(14)	O(1W)-Zn(3)-O(2W)	94.16(16)
O(3)-Zn(3)-O(2W)	89.36(15)	O(13)-Zn(3)-O(2)	92.86(14)
O(5)-Zn(3)-O(2)	73.98(12)	O(1W)-Zn(3)-O(2)	100.52(14)
O(3)-Zn(3)-O(2)	73.90(12)	O(2W)-Zn(3)-O(2)	157.70(13)

Table S4b. Hydrogen bonds for **4** (Å and °).

D-H···A <(DHA)	d(D-H)	d(H···A)	d(D···A)	
O(1W)-H(1WA)···O(6)$^{\#1}$	0.819(18)	2.18(2)	2.738(5)	126(3)
O(1W)-H(1WA)···O(2W)	0.819(18)	2.57(2)	3.089(6)	122.6(12)
O(2W)-H(2WA)···O(4)	0.852(19)	1.91(4)	2.692(6)	152(7)
O(2W)-H(2WB)···O(6)	0.855(19)	1.89(2)	2.733(5)	167(6)
O(3W)-H(3WA)···O(8)	0.847(19)	1.89(3)	2.691(5)	157(7)
O(3W)-H(3WB)···O(10)	0.839(19)	1.89(3)	2.706(6)	163(7)

Symmetry codes for **4**: $^{\#1}$ x, y, z-1; $^{\#2}$ x, y, z+1; $^{\#3}$ -x+1, -y, -z+2.

Table S5. Selected bond distances (Å) and angles (°) for **5**.

Co(1)-O(2)	2.074(3)	Co(1)-O(2)$^{\#1}$	2.074(3)
Co(1)-O(4)	2.078(3)	Co(1)-O(4)$^{\#1}$	2.078(3)
Co(1)-O(1W)	2.079(6)	Co(1)-O(1)	2.309(4)
Co(2)-O(2)	2.083(3)	Co(2)-O(2)$^{\#2}$	2.083(3)
Co(2)-N(1)	2.153(3)	Co(2)-N(1)$^{\#2}$	2.153(3)
Co(2)-O(1)	2.155(2)	Co(2)-O(1)$^{\#3}$	2.155(2)
O(2)-Co(1)-O(2)$^{\#1}$	92.55(16)	O(2)-Co(1)-O(4)	168.25(13)
O(2)$^{\#1}$-Co(1)-O(4)	92.53(12)	O(2)-Co(1)-O(4)$^{\#1}$	92.53(12)
O(2)$^{\#1}$-Co(1)-O(4)$^{\#1}$	168.25(13)	O(4)-Co(1)-O(4)$^{\#1}$	80.61(17)
O(2)-Co(1)-O(1W)	92.11(13)	O(2)$^{\#1}$-Co(1)-O(1W)	92.11(13)
O(4)-Co(1)-O(1W)	98.28(16)	O(4)$^{\#1}$-Co(1)-O(1W)	98.28(16)
O(2)-Co(1)-O(1)	74.60(10)	O(2)$^{\#1}$-Co(1)-O(1)	74.60(10)

O(4)-Co(1)-O(1)	96.59(12)	O(4)$^{\#1}$-Co(1)-O(1)	96.59(12)
O(1W)-Co(1)-O(1)	160.46(18)	O(2)-Co(2)-O(2)$^{\#2}$	175.25(16)
O(2)-Co(2)-N(1)	78.63(12)	O(2)$^{\#2}$-Co(2)-N(1)	104.75(12)
O(2)-Co(2)-N(1)$^{\#2}$	104.75(12)	O(2)$^{\#2}$-Co(2)-N(1)$^{\#2}$	8.63(12)
N(1)-Co(2)-N(1)$^{\#2}$	92.35(19)	O(2)-Co(2)-O(1)	77.84(12)
O(2)$^{\#2}$-Co(2)-O(1)	98.61(13)	N(1)-Co(2)-O(1)	156.34(14)
N(1)$^{\#2}$-Co(2)-O(1)	95.90(12)	O(2)-Co(2)-O(1)$^{\#3}$	98.61(13)
O(2)$^{\#2}$-Co(2)-O(1)$^{\#3}$	77.84(12)	N(1)-Co(2)-O(1)$^{\#3}$	95.90(12)
N(1)$^{\#2}$-Co(2)-O(1)$^{\#3}$	156.34(14)	O(1)-Co(2)-O(1)$^{\#3}$	85.29(14)

Symmetry codes for **5**: $^{\#1}$ x,-y+1, z; $^{\#2}$ -x+2, y, -z; $^{\#3}$ -x+2, -y+1, -z; $^{\#4}$ -x+2, y, -z+1; $^{\#5}$ -x+2,-y+1,-z+1.

Table S6. Selected bond distances (Å) and angles (°) for **6.**

Zn(1)-O(2)$^{\#1}$	2.0810(17)	Zn(1)-O(2)	2.0810(17)
Zn(1)-N(1)$^{\#1}$	2.153(2)	Zn(1)-N(1)	2.153(2)
Zn(1)-O(1)	2.1539(15)	Zn(1)-O(1)$^{\#2}$	2.1539(15)
Zn(2)-O(2)$^{\#1}$	2.0720(17)	Zn(2)-O(2)$^{\#2}$	2.0720(17)
Zn(2)-O(4)	2.0750(19)	Zn(2)-O(4)$^{\#3}$	2.0750(19)
Zn(2)-O(1W)	2.089(3)	Zn(2)-O(1)	2.310(2)
O(2)$^{\#1}$-Zn(1)-O(2)	175.13(9)	O(2)$^{\#1}$-Zn(1)-N(1)$^{\#1}$	78.66(7)
O(2)-Zn(1)-N(1)$^{\#1}$	104.79(7)	O(2)$^{\#1}$-Zn(1)-N(1)	104.79(7)
O(2)-Zn(1)-N(1)	78.66(7)	N(1)$^{\#1}$-Zn(1)-N(1)	92.36(11)
O(2)$^{\#1}$-Zn(1)-O(1)	77.79(7)	O(2)-Zn(1)-O(1)	98.57(8)
N(1)$^{\#1}$-Zn(1)-O(1)	156.33(8)	N(1)-Zn(1)-O(1)	95.91(7)
O(2)$^{\#1}$-Zn(1)-O(1)$^{\#2}$	98.57(8)	O(2)-Zn(1)-O(1)$^{\#2}$	77.79(7)
N(1)$^{\#1}$-Zn(1)-O(1)$^{\#2}$	95.91(7)	N(1)-Zn(1)-O(1)$^{\#2}$	156.33(8)
O(1)-Zn(1)-O(1)$^{\#2}$	85.26(8)	O(2)$^{\#1}$-Zn(2)-O(2)$^{\#2}$	92.48(10)
O(2)$^{\#1}$-Zn(2)-O(4)	168.05(8)	O(2)$^{\#2}$-Zn(2)-O(4)	92.77(7)
O(2)$^{\#1}$-Zn(2)-O(4)$^{\#3}$	92.77(7)	O(2$^{\#2}$-Zn(2)-O(4$^{\#3}$	168.05(8)
O(4)-Zn(2)-O(4)$^{\#3}$	80.15(10)	O(2)$^{\#1}$-Zn(2)-O(1W)	92.22(8)

O(2)$^{\#2}$-Zn(2)-O(1W)	92.22(8)	O(4)-Zn(2)-O(1W)	98.29(9)
O(4)$^{\#3}$-Zn(2)-O(1W)	98.29(9)	O(2)$^{\#1}$-Zn(2)-O(1)	74.52(6)
O(2)$^{\#2}$-Zn(2)-O(1)	74.52(6)	O(4)-Zn(2)-O(1)	96.59(7)
O(4)$^{\#3}$-Zn(2)-O(1)	96.59(7)	O(1W)-Zn(2)-O(1)	160.51(11)

Symmetry codes for **6**: $^{\#1}$ -x, y, -z; $^{\#2}$ -x,-y+1,-z; $^{\#3}$ x, -y+1, z.

Table S7a. Selected bond distances (Å) and angles (°) for **7**.

Co(1)-O(2)	2.060(2)	Co(1)-O(4)	2.074(2)
Co(1)-O(1)	2.122(2)	Co(1)-N(2)	2.155(3)
Co(1)-N(1)	2.170(3)	Co(1)-O(1)$^{\#1}$	2.171(2)
Co(2)-O(8)	2.023(2)	Co(2)-O(2W)	2.082(3)
Co(2)-O(4)	2.085(2)	Co(2)-O(2)$^{\#1}$	2.098(3)
Co(2)-O(3W)	2.135(3)	Co(2)-O(1)	2.263(2)
O(2)-Co(1)-O(4)	170.62(10)		
O(2)-Co(1)-O(1)	102.73(10)	O(4)-Co(1)-O(1)	78.21(9)
O(2)-Co(1)-N(2)	101.98(11)	O(4)-Co(1)-N(2)	77.28(10)
O(1)-Co(1)-N(2)	155.27(10)	O(2)-Co(1)-N(1)	78.90(10)
O(4)-Co(1)-N(1)	110.41(11)	O(1)-Co(1)-N(1)	94.53(10)
N(2)-Co(1)-N(1)	90.96(12)	O(2)-Co(1)-O(1)$^{\#1}$	78.57(9)
O(4)-Co(1)-O(1)$^{\#1}$	92.20(10)	O(1)-Co(1)-O(1)$^{\#1}$	87.25(9)
N(2)-Co(1)-O(1)$^{\#1}$	96.88(10)	N(1)-Co(1)-O(1)$^{\#1}$	157.23(10)
O(8)-Co(2)-O(2W)	90.21(10)	O(8)-Co(2)-O(4)	166.21(10)
O(2W)-Co(2)-O(4)	85.93(10)	O(8)-Co(2)-O(2)$^{\#1}$	95.41(10)
O(2W)-Co(2)-O(2)$^{\#1}$	174.10(9)	O(4)-Co(2)-O(2)$^{\#1}$	88.20(10)
O(8)-Co(2)-O(3W)	101.71(11)	O(2W)-Co(2)-O(3W)	89.94(11)
O(4)-Co(2)-O(3W)	91.53(10)	O(2)$^{\#1}$-Co(2)-O(3W)	90.67(10)
O(8)-Co(2)-O(1)	93.07(10)	O(2W)-Co(2)-O(1)	102.23(10)
O(4)-Co(2)-O(1)	74.89(9)	O(2)$^{\#1}$-Co(2)-O(1)	75.73(9)
O(3W)-Co(2)-O(1)	160.85(10)		

Table S7b. Hydrogen bonds for **7** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2W)-H(2WA)···O(5)$^{\#3}$	0.842(18)	1.881(18)	2.722(4)	176(4)
O(3W)-H(3WB)···O(3)$^{\#1}$	0.834(18)	1.90(2)	2.712(4)	166(4)
O(2W)-H(2WB)···O(9)	0.831(18)	1.766(19)	2.582(4)	166(4)
O(3W)-H(3WA)···O(5)	0.848(18)	1.93(2)	2.744(4)	161(5)

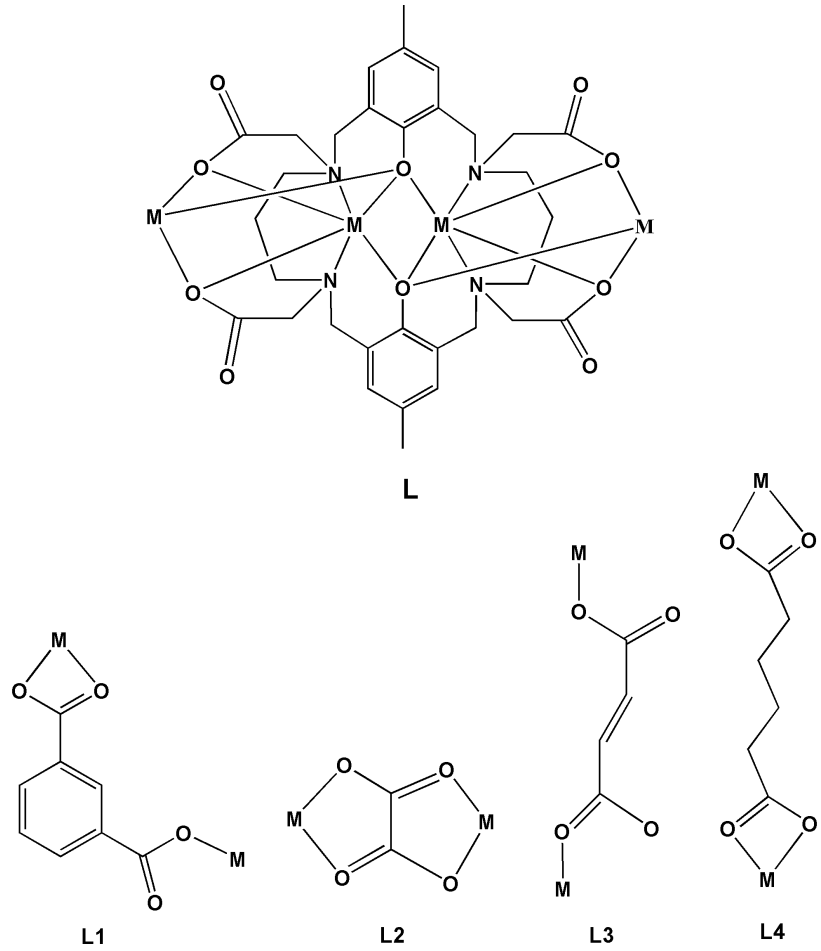
Symmetry codes for **7**: $^{\#1}$ -x+2, -y+1, -z; $^{\#2}$ -x+2, -y+2, z+1; $^{\#3}$ -x+1, -y+1, -z.

Table S8. Selected bond distances (Å) and angles (°) for **8**.

Co(1)-O(4)	2.327(5)	Co(1)-O(2)	2.290(5)
Co(1)-O(1)$^{\#1}$	2.131(4)	Co(1)-O(1)	2.147(5)
Co(1)-N(2)	2.253(6)	Co(1)-N(1)	1.946(5)
Co(2)-O(1W)	2.271(6)	Co(2)-O(4)$^{\#1}$	2.090(5)
Co(2)-O(6)	1.954(5)	Co(2)-O(7)	1.976(5)
Co(2)-O(2)	2.033(5)		
O(6)-Co(2)-O(7)	74.6(2)	O(6)-Co(2)-O(2)	160.05(19)
O(7)-Co(2)-O(2)	89.9(2)	O(6)-Co(2)-O(4)$^{\#1}$	89.9(2)
O(7)-Co(2)-O(4)$^{\#1}$	163.4(2)	O(2)-Co(2)-O(4)$^{\#1}$	103.70(19)
O(6)-Co(2)-C(19)	37.1(3)	O(7)-Co(2)-C(19)	37.6(3)
O(2)-Co(2)-C(19)	125.8(3)	O(4)$^{\#1}$-Co(2)-C(19)	126.4(3)
O(6)-Co(2)-O(1W)	98.8(2)	O(7)-Co(2)-O(1W)	79.5(2)
O(2)-Co(2)-O(1W)	90.4(2)	O(4)$^{\#1}$-Co(2)-O(1W)	109.39(18)
N(1)-Co(1)-O(1)$^{\#1}$	153.1(2)	N(1)-Co(1)-O(1)	107.60(19)
O(1)$^{\#1}$-Co(1)-O(1)	73.37(17)	N(1)-Co(1)-N(2)	77.5(2)
O(1)$^{\#1}$-Co(1)-N(2)	113.36(17)	O(1)-Co(1)-N(2)	155.0(2)
N(1)-Co(1)-O(2)	97.1(2)	O(1)$^{\#1}$-Co(1)-O(2)	109.62(17)
O(1)-Co(1)-O(2)	84.17(17)	N(2)-Co(1)-O(2)	70.86(19)
N(1)-Co(1)-O(4)	87.0(2)	O(1)$^{\#1}$-Co(1)-O(4)	66.20(16)
O(1)-Co(1)-O(4)	92.49(18)	N(2)-Co(1)-O(4)	112.4(2)

O(2)-Co(1)-O(4)	175.34(18)

Symmetry codes for **8**: [#1] -x+2, -y, -z+1; [#2] -x+2, y, -z+1/2.



Scheme S1 Coordination modes of L in **1-8** (M = Mn, Co, Zn), L^1 in **3** and **4**, L^2 in **5** and **6**, L^3 in **7**, and L^4 in **8**.

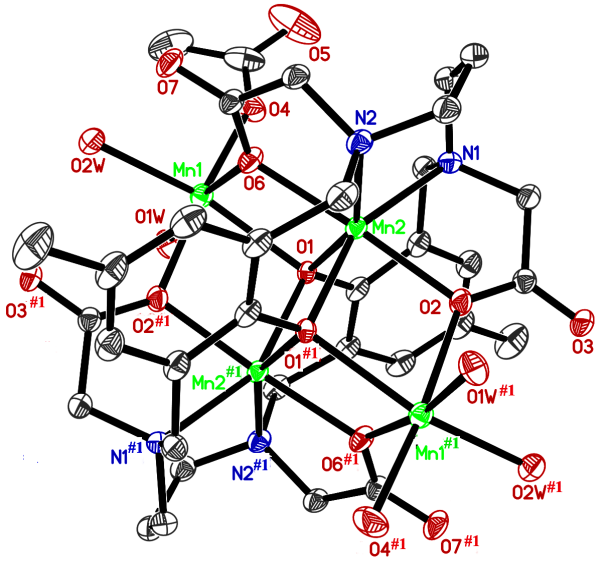


Fig. S1 Coordination environments of the Mn(II) ions in **2** with hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry code: #1 -x+2, -y+1, -z+1.

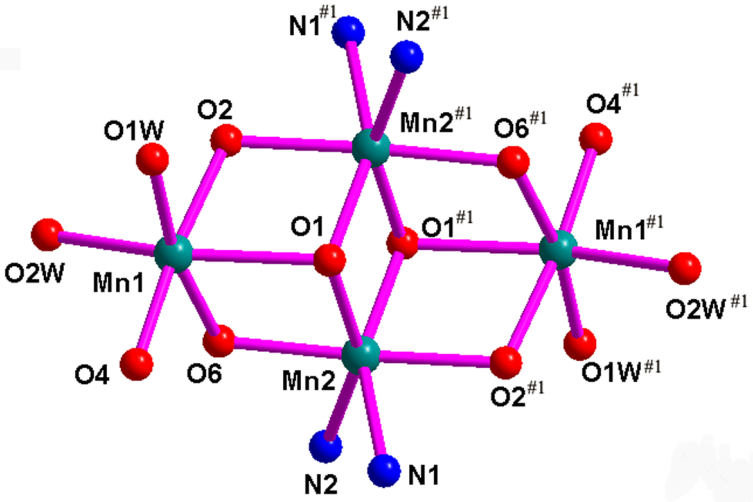


Fig. S2 Schematic drawing of the centrosymmetric tetranuclear manganese-oxygen cluster of **2**.

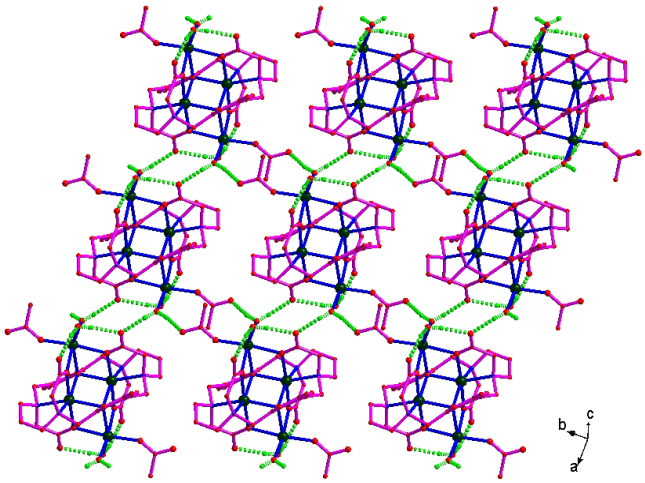


Fig. S3 The hydrogen-bonded 2D layer structure of **2**. The hydrogen bonds are represented by dashed lines.

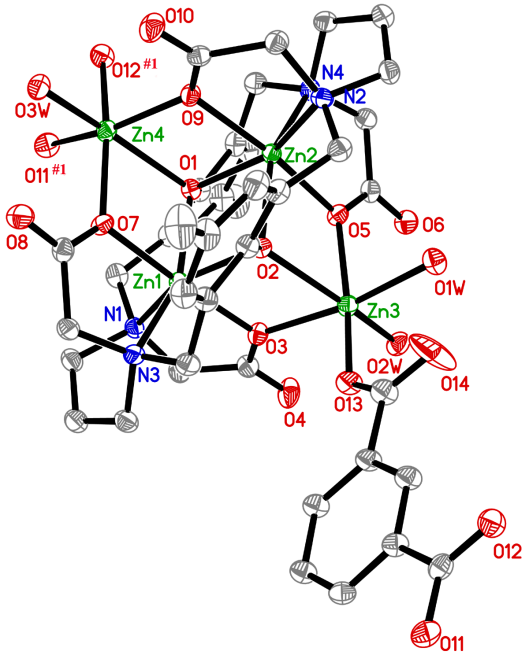


Fig. S4 Coordination environments of the Zn(II) ions in **4** with the hydrogen atoms and solvent water molecule omitted for clarity (30% probability displacement ellipsoids). Symmetry code: $^{\#1}$ x, y, z-1.

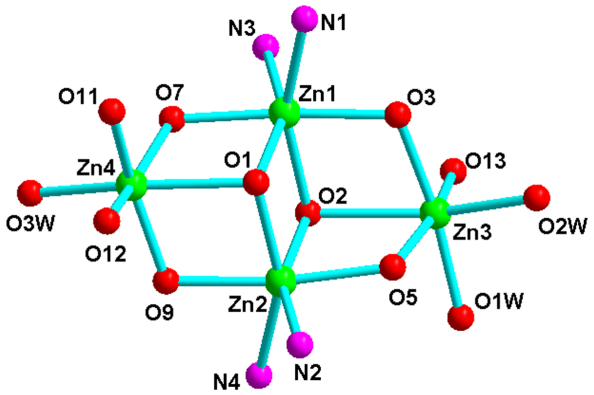


Fig. S5 Schematic drawing of the tetranuclear zinc-oxygen cluster of **4.**

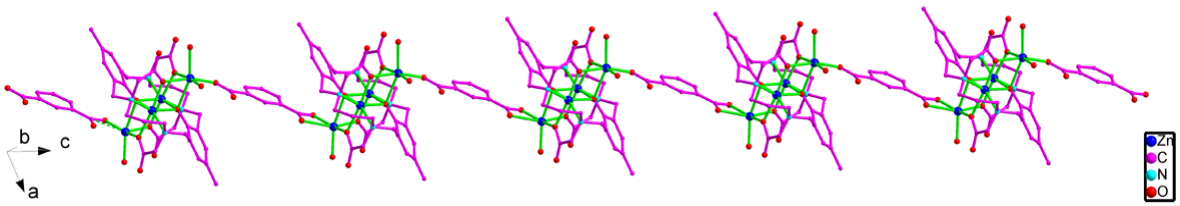


Fig. S6 The infinite 1D chain structure constructed by L anions and L^1 anions in **4**.

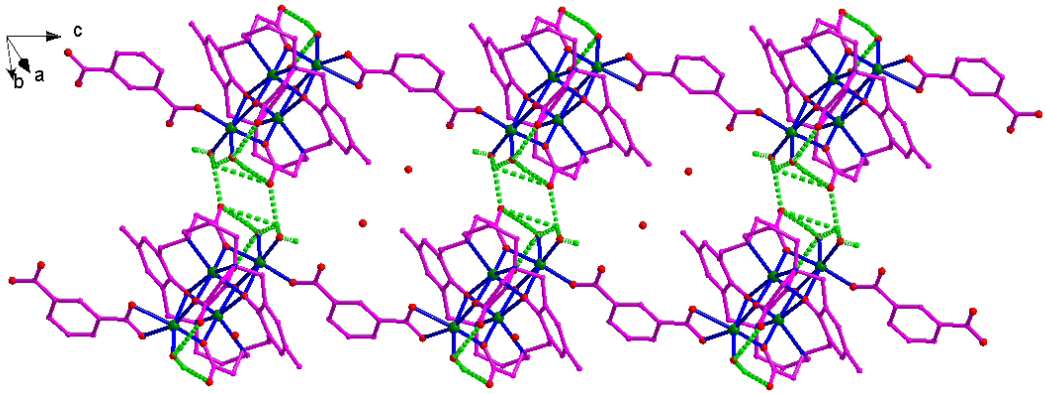


Fig. S7 The supramolecular double-chain structure constructed by O–H···O interactions in **4**. The hydrogen bonds are represented by dashed lines.

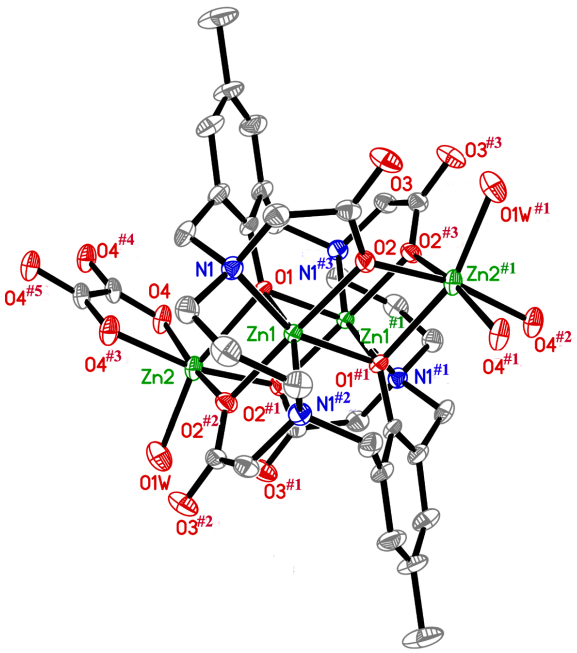


Fig. S8 Coordination environments of the Zn(II) ions in **6** with the hydrogen atoms and solvent water molecule omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: #1 -x, y, -z; #2 -x, -y+1, -z; #3 x, -y+1, z; #4 -x, y, -z+1; #5 -x, -y+1, -z+1.

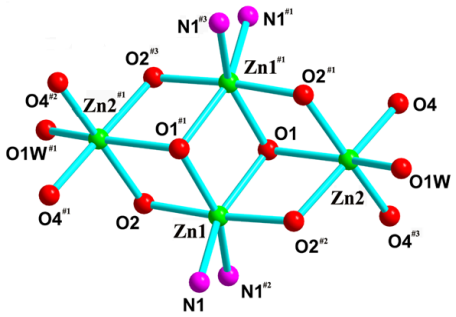


Fig. S9 Schematic drawing of the tetranuclear zinc-oxygen cluster of **6.**

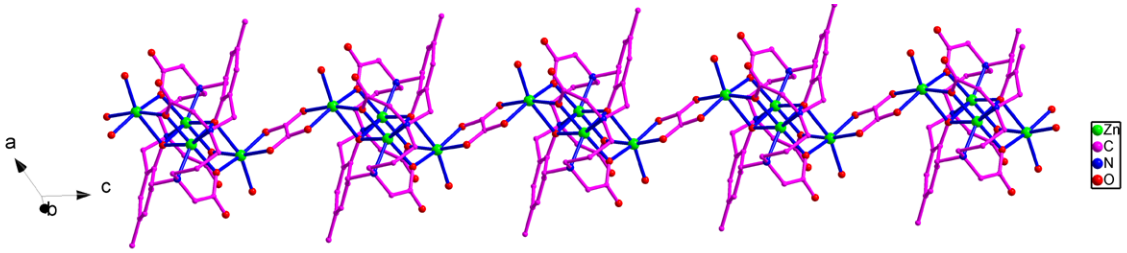


Fig. S10 The infinite 1D chain structure constructed by L anions and L^2 anions in **6**.

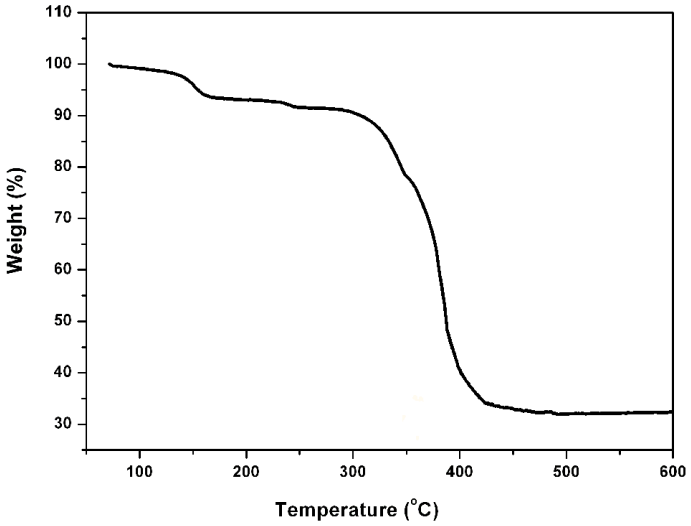


Fig. S11 TGA curve of **1**.

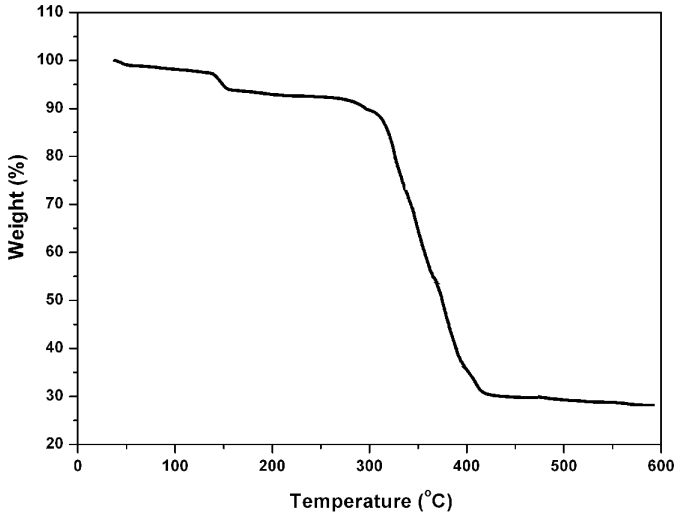


Fig. S12 TGA curve of **2**.

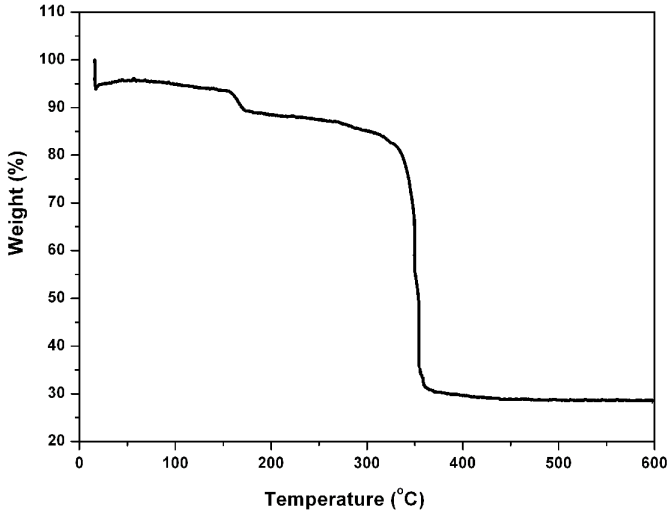


Fig. S13 TGA curve of **3**

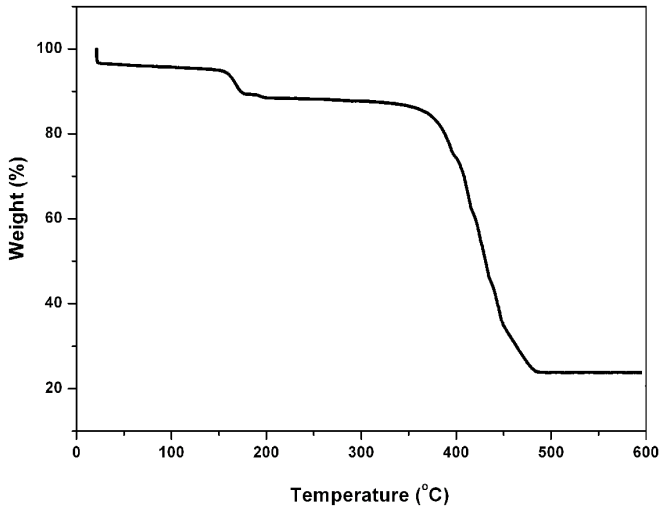


Fig. S14 TGA curve of **4.**

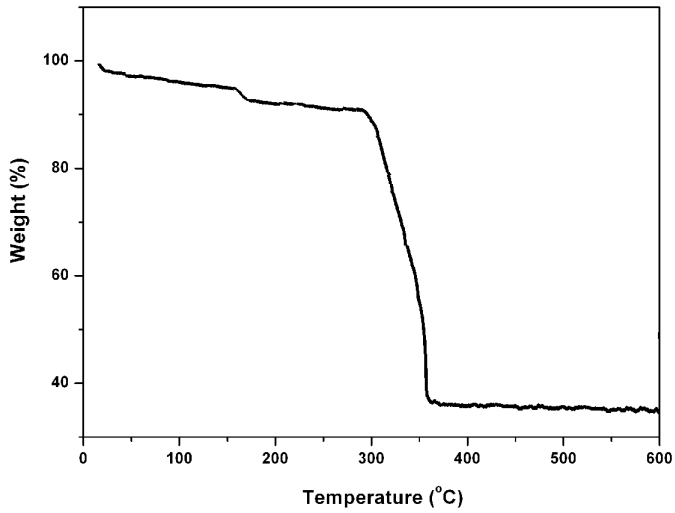


Fig. S15 TGA curve of **5.**

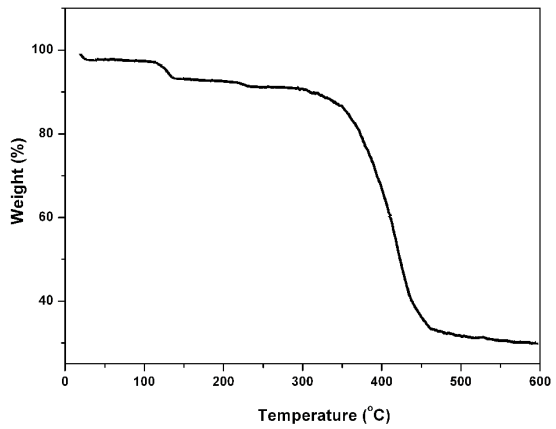


Fig. S16 TGA curve of **6.**

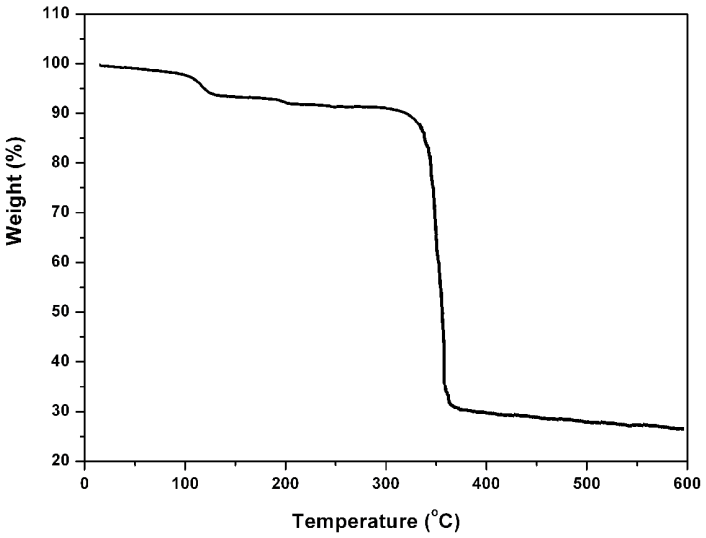


Fig. S17 TGA curve of **7.**

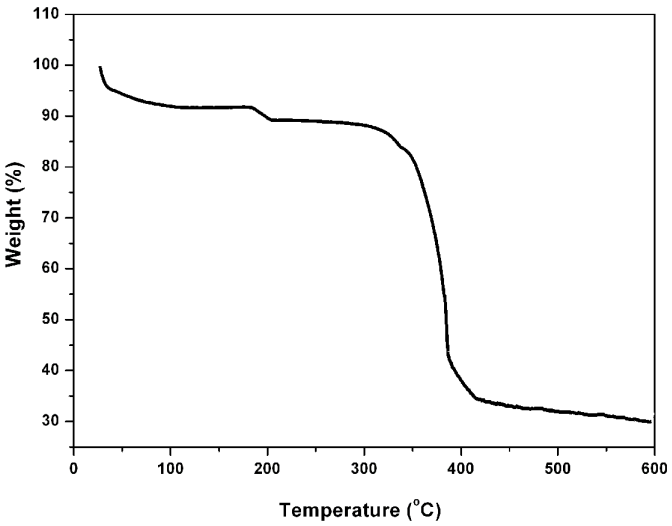


Fig. S18 TGA curve of **8.**

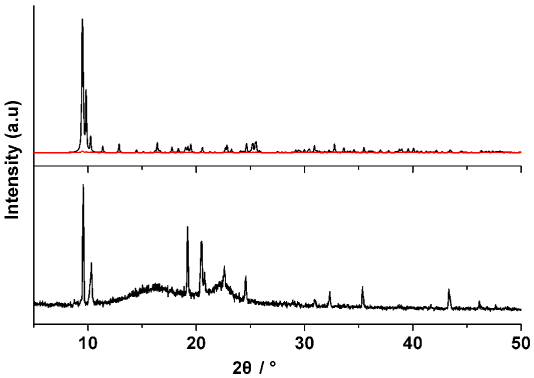


Fig. S19 The simulated (top) and experimental (bottom) XRPD patterns for compound **1.**

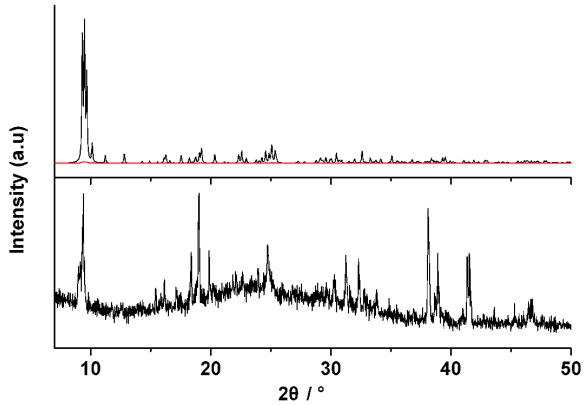


Fig. S20 The simulated (top) and experimental (bottom) XRPD patterns for compound **2.**

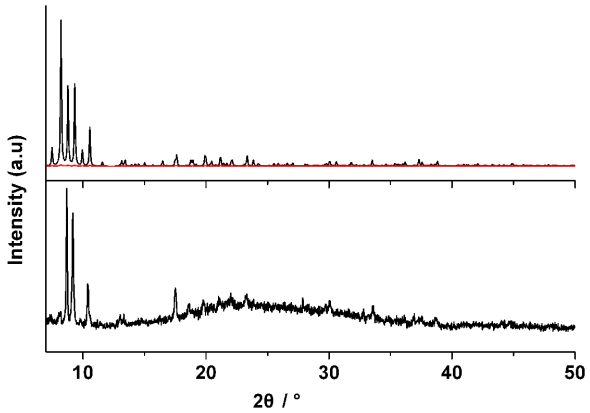


Fig. S21 The simulated (top) and experimental (bottom) XRPD patterns for compound **3.**

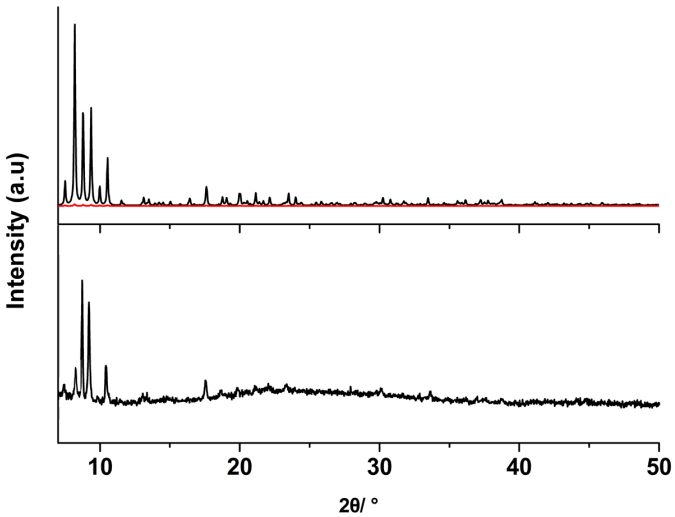


Fig. S22. The simulated (top) and experimental (bottom) XRPD patterns for compound

4.

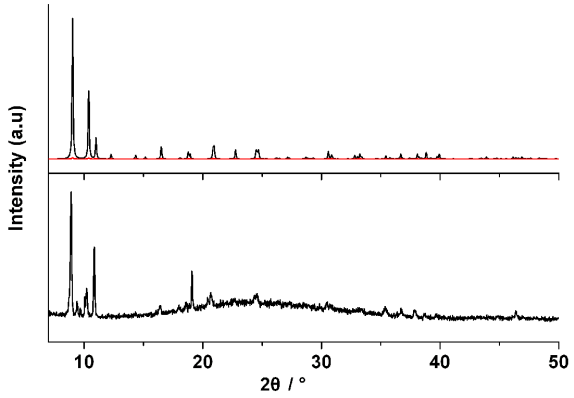


Fig. S23 The simulated (top) and experimental (bottom) XRPD patterns for compound **5.**

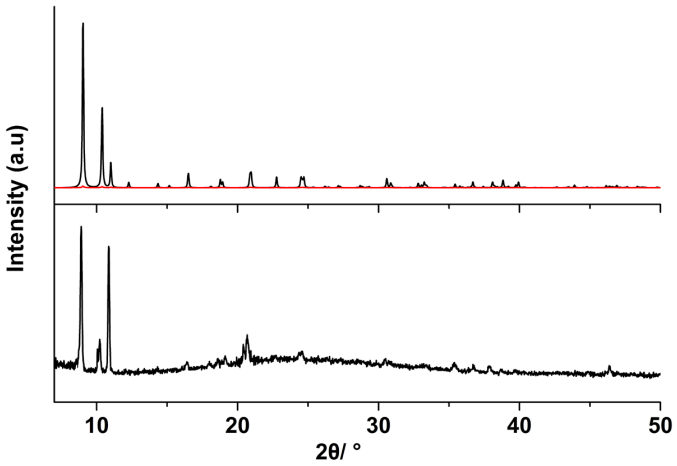


Fig. S24. The simulated (top) and experimental (bottom) XRPD patterns for compound **6.**

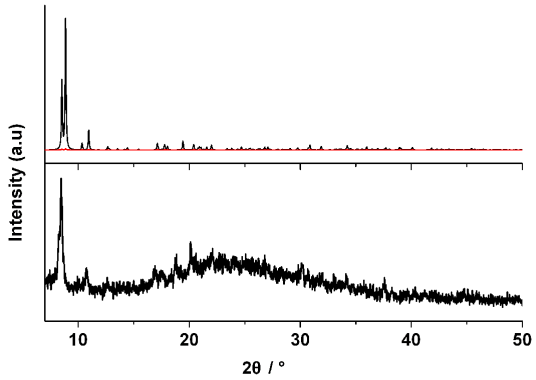


Fig. S25 The simulated (top) and experimental (bottom) XRPD patterns for compound

7.

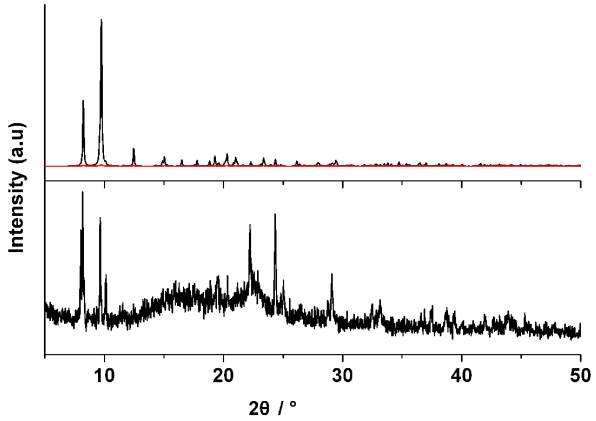


Fig. S26 The simulated (top) and experimental (bottom) XRPD patterns for compound **8.**