Supplementary Information

Homochiral coordination polymers constructed from V-shaped oxybisbenzoyl-based amino acid derivatives: structures, magnetic and photoluminescence properties

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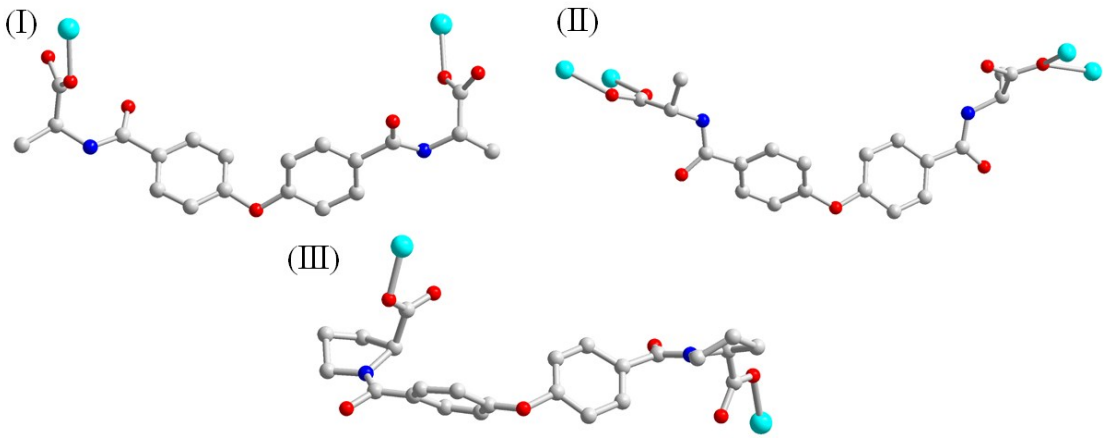
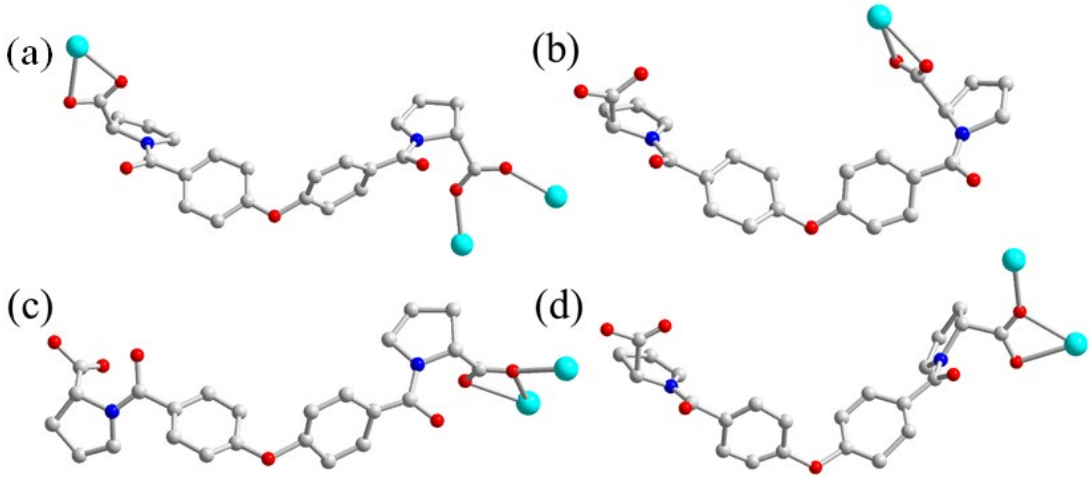


Scheme S1. Coordination modes of H_2ODBALa and H_2ODBPRo ligands for **1** (I), for **2** and **3** (II), for **4** (III).



Scheme S2. Four kinds of coordination modes of H_2ODBPRo ligands for **5**.

Synthesis methods of chiral ligands

The synthesis method of the chiral ligand H_2ODBALa is shown as follow: The 4,4'-oxybis(benzoyl chloride) (3 mmol, 0.8853g) was dissolved in 40 ml dehydrated methylene chloride, and then the suspension solution was added dropwise to 100 ml dehydrated methylene chloride solution containing *L*-alanine methyl ester hydrochloride (6.6 mmol, 0.9212 g, 1 equiv) and TEA (2.5 equiv) at 0 ^{o}C under nitrogen. After the resultant solution stirred at room temperature for 6h, the obtained ester was extracted with water and methylene chloride (1:1) and washed with saturated brine three times respectively, dried with $MgSO_4$ and evaporated in vacuo. The residue was then subjected to the steps of recrystallization, hydrolyzation, and acidification to obtain a target ligand. (0.8528 g, yield: 71 %) Molecular formula: $C_{20}H_{20}N_2O_7$ Molecular weight: 400.387.

The synthesis method of the chiral ligand H_2ODBPRo is similar to that of H_2ODBALa except that *L*-alanine methyl ester hydrochloride is replaced by *L*-proline methyl ester hydrochloride. Molecular formula: $C_{24}H_{24}O_7N_2$. Molecular weight: 452.457. Yield: 65%.

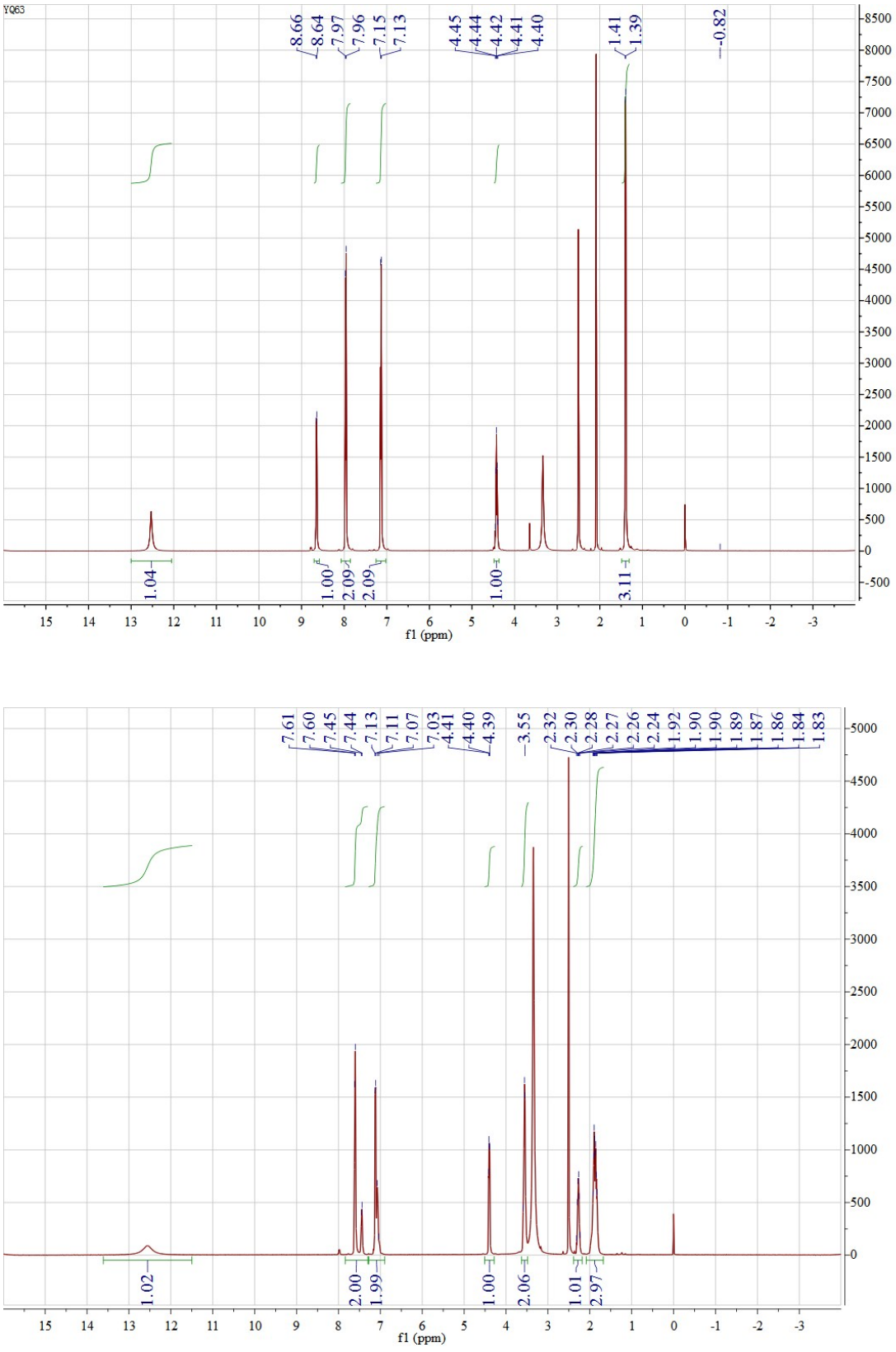


Fig. S1. The ^{1}H NMR spectra of $H_2ODBALa$ (top) and $H_2ODBPRo$ (bottom).

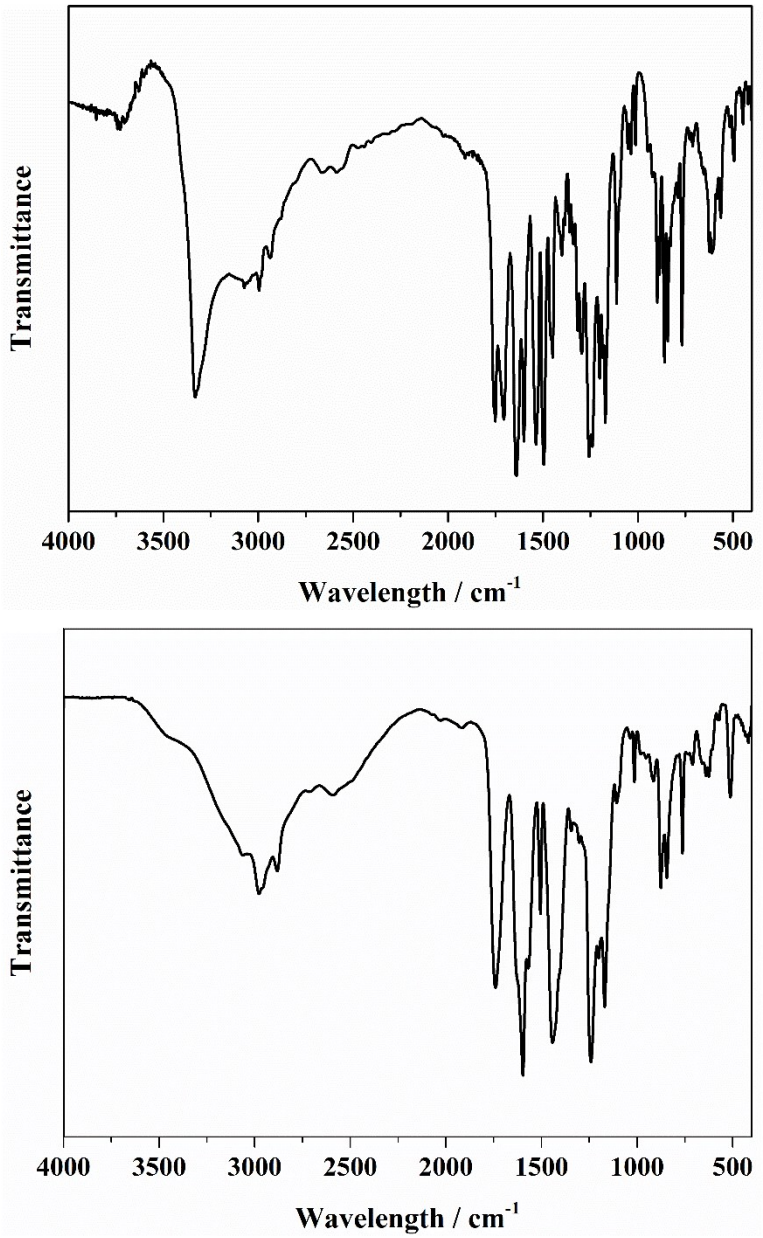


Fig. S2. IR spectra of H_2ODBALa (top) and H_2ODBPRo (bottom).

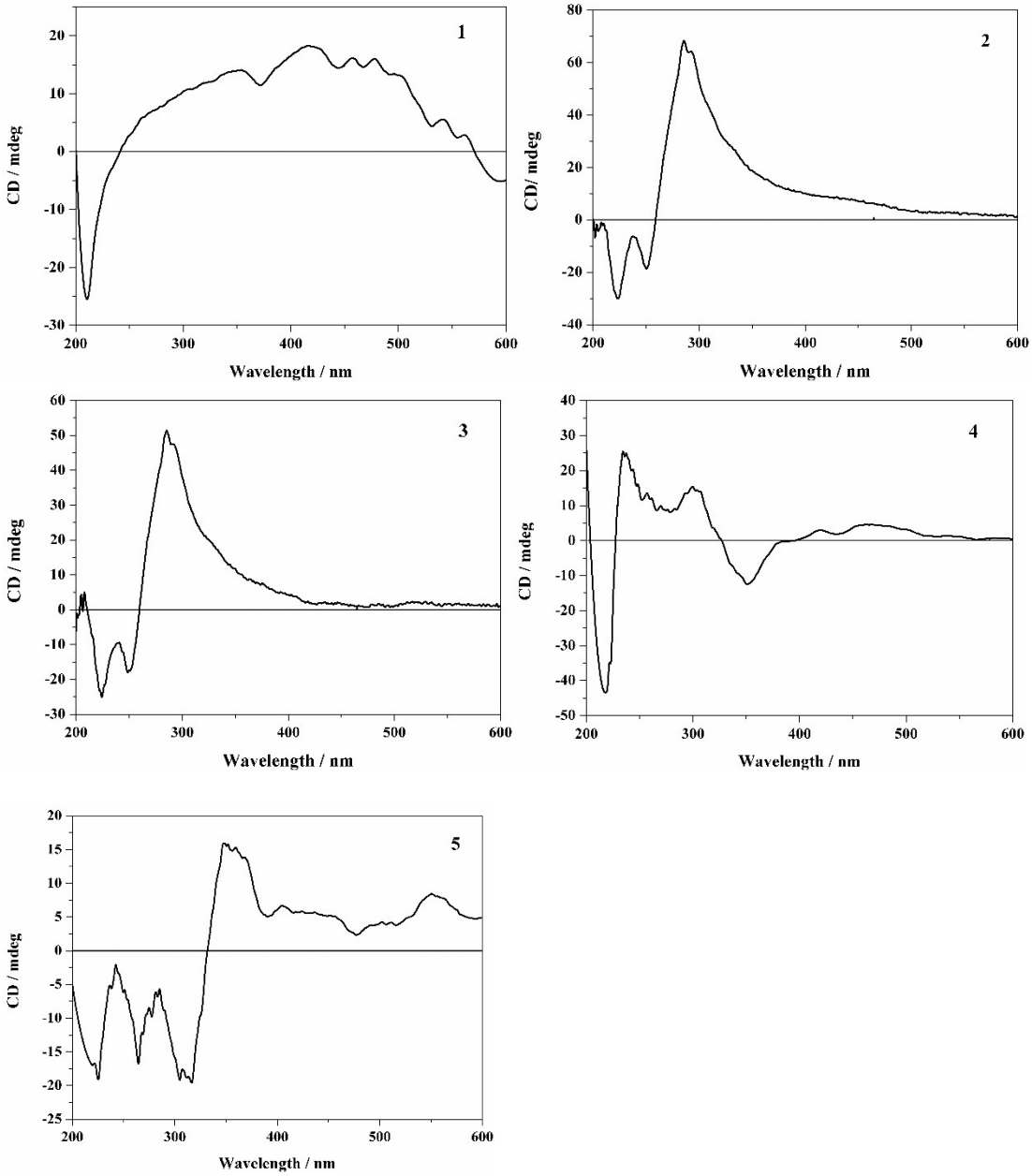


Fig. S3. Solid-state circular dichroism (CD) spectra of compounds **1-5**.

Considering that compounds **1-5** crystallize in the chiral space groups, their solid-state circular dichroism spectra (CD) were studied. All compounds display the strong cotton effect. As shown in Figure S1, the CD spectrum of **1** shows positive cotton effect in the range of about 260-540 nm and negative cotton effect at 215 nm. The CD spectra of compounds **2** and **3** exhibit positive cotton effect at 285 nm and negative cotton effect at 222 nm and 251 nm. The positive cotton effect of **4** occur at 235 nm and 301 nm, the negative cotton effect occur at 218 nm and 351 nm. The positive cotton effect of **5** appears at 350 nm, and the negative those appear at 225 nm, 264 nm and 317 nm. The results confirm their homochiral nature, which are in good accord with the structures obtained by single-crystal X-ray diffraction.

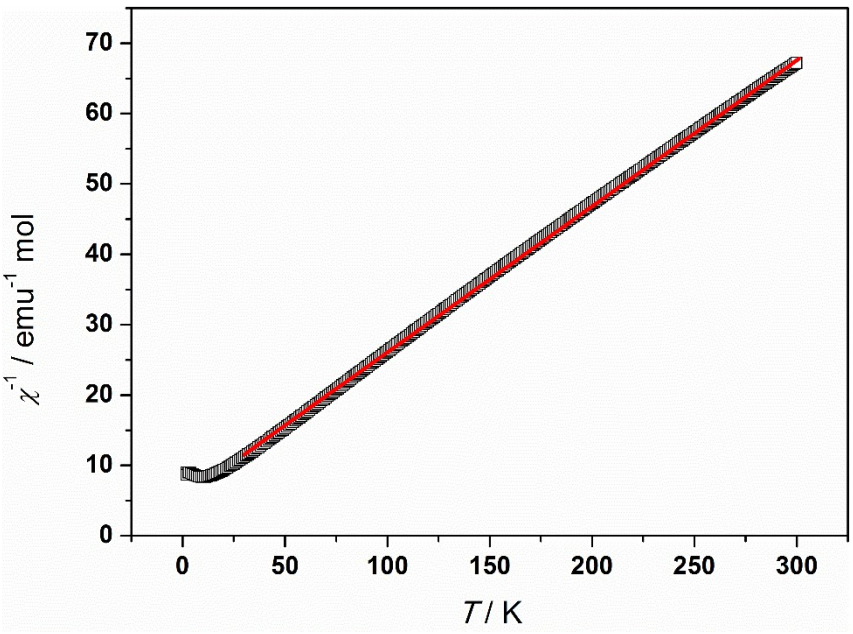


Fig. S4. Temperature dependence of χ^{-1} at 1 kOe for **2**. Open symbols are the experimental data, and red solid lines are the best fits to the Curie–Weiss law.

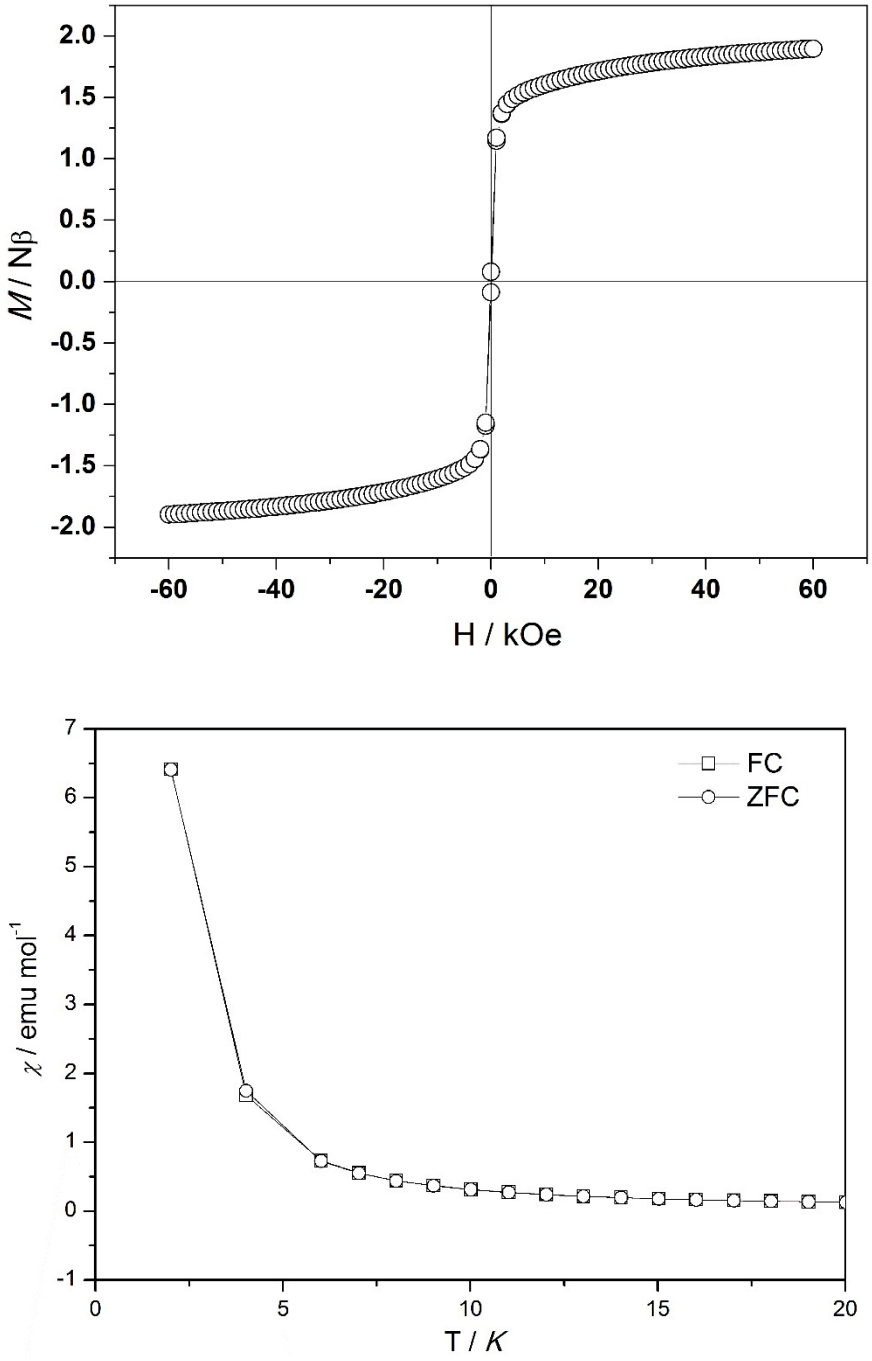


Fig. S5. Filed dependence of magnetization of **3** at 2 K (top). The curves of the FC and ZFC magnetic susceptibilities for **3** (bottom). Square symbols are the FC data, and circular ones are the ZFC data.

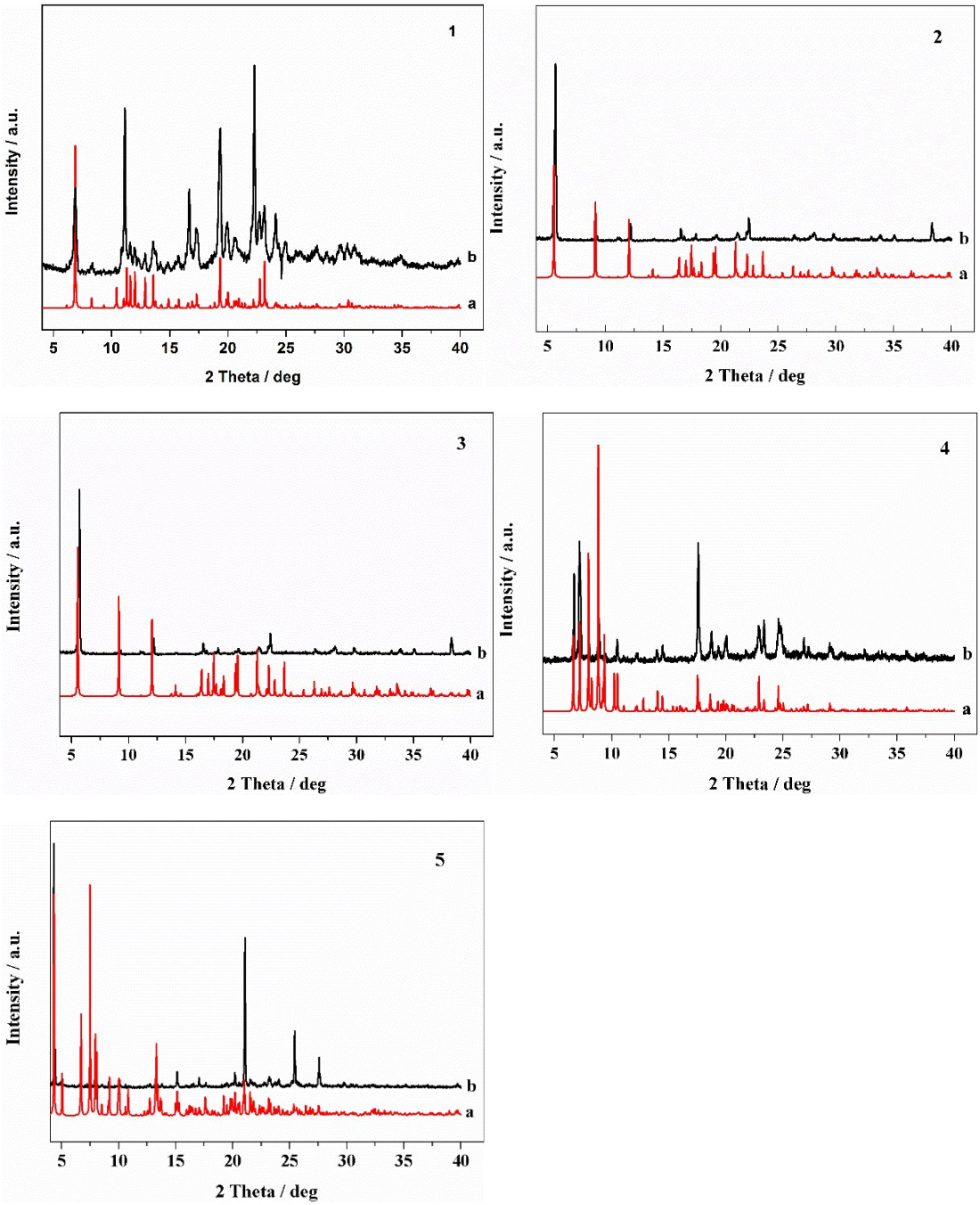


Fig. S6. PXRD patterns of compounds **1-5.** a) Simulated from single crystal structure data. b) Experimental data. The differences between the calculated and observed patterns in intensity may be due to the orientation of the crystals.

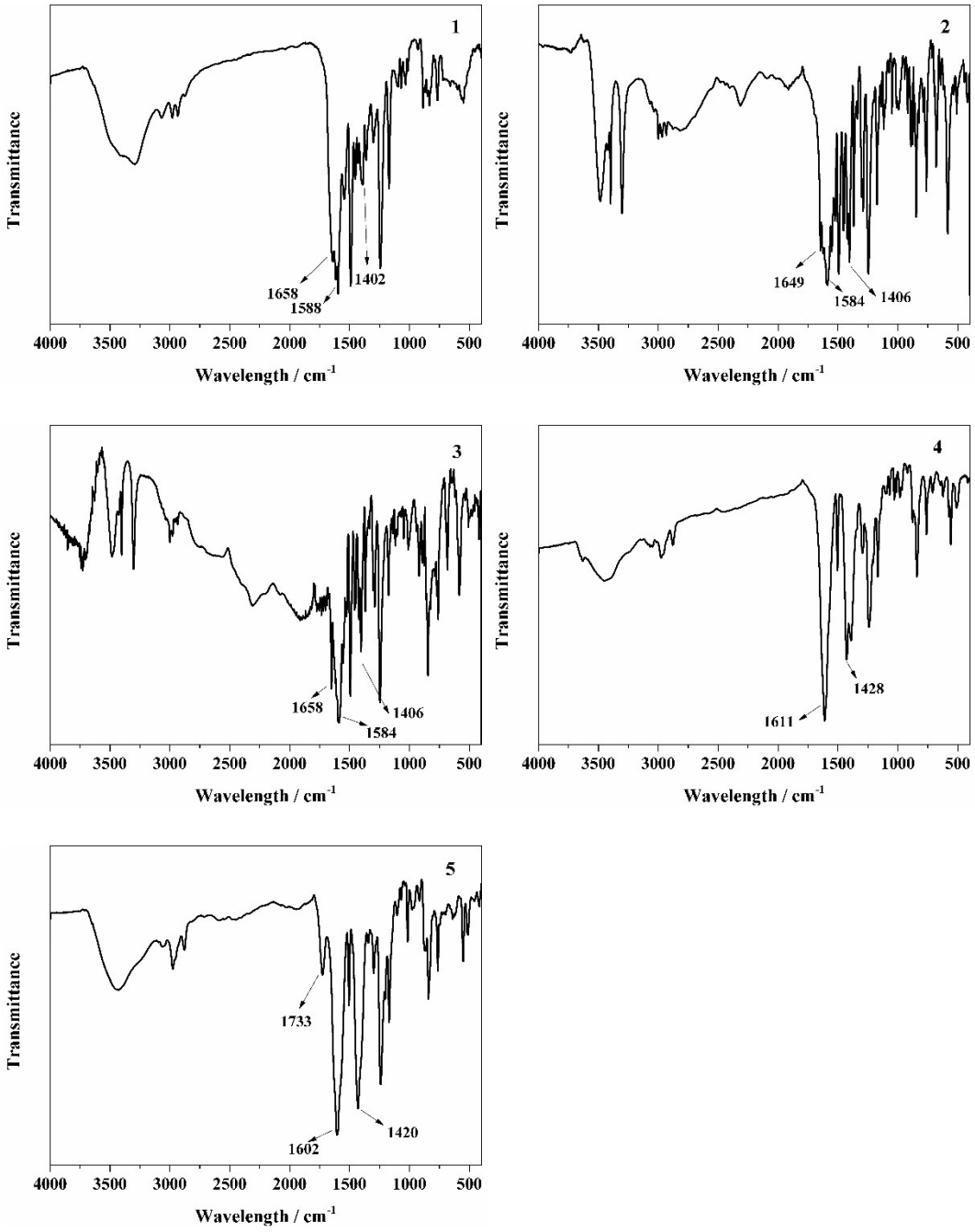


Fig. S7. Infrared spectra of compounds **1-5**.

The absence of the ν(C=O) absorption band of compounds **1-4** in the area of 1700 cm^{-1} indicates full deprotonation of carboxylate groups in all compounds, whereas the ν(C=O) absorption band of compound **5** at 1733 cm^{-1} prove the carboxylate groups are partially deprotonation in the structure, which are consistent with the results of sing-crystal X-ray analysis. Asymmetric and symmetric ν(C=O) absorptions of carboxylate groups are evidenced by strong bands at around 1600 cm^{-1} and 1400 cm^{-1}. The stretching ν(C=O) of amide groups are evidenced by strong spectral bands at around 1650 cm^{-1}, which confirms the existence of amide groups.

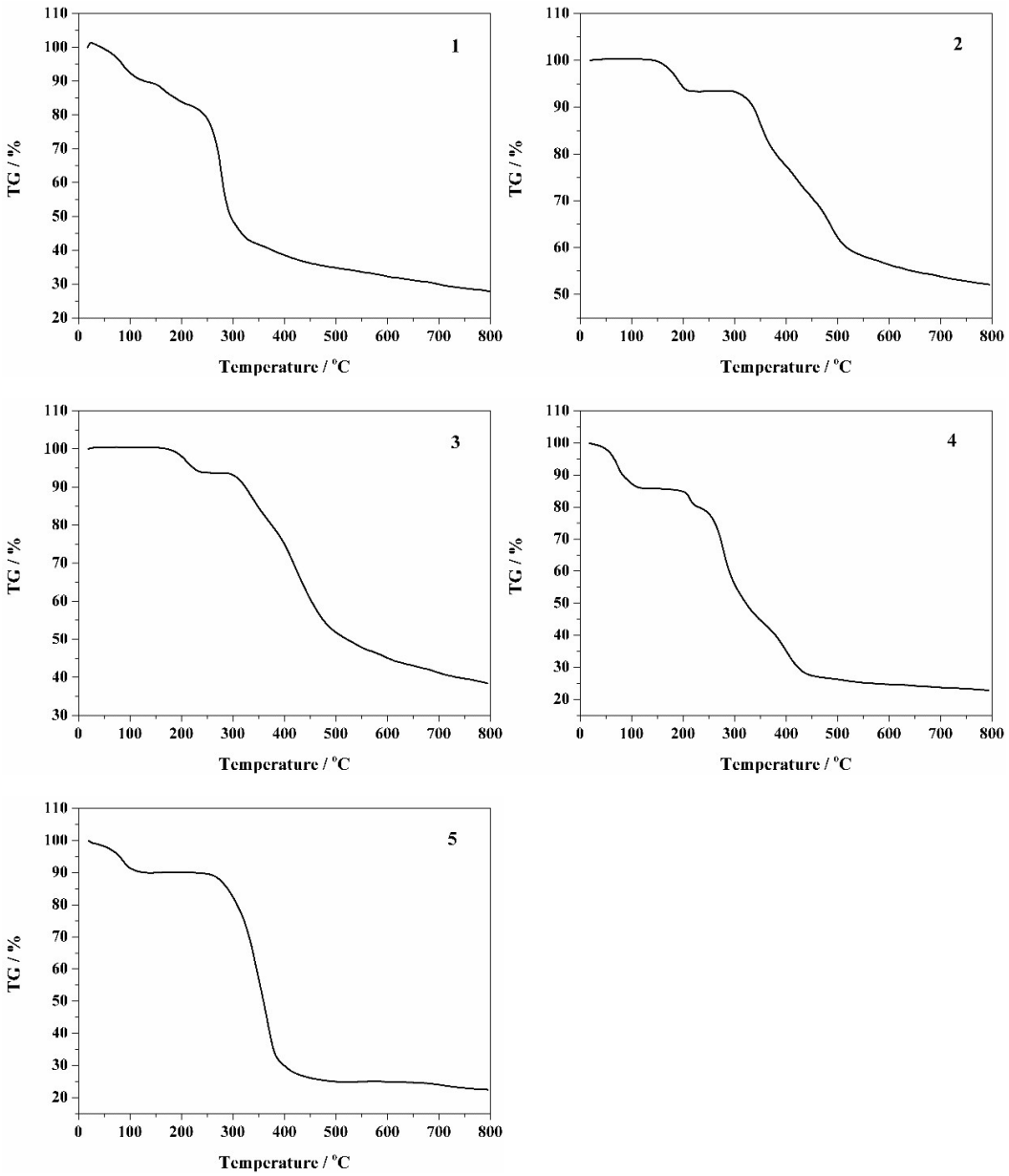


Fig. S8. TGA curves of compounds **1-5**.

For **1**, the weight loss of about 8.55 % from the room temperature to 110 °C corresponds to the departure of seven lattice water molecules (calcd 8.80 %). And then one coordinated water is released when the temperature rises to 150 °C, and the remaining framework is thermally stable up to 240 °C, at which the framework begins to collapse. For **2** and **3** are isostructural 3D frameworks and the weight loss of about 6.81 % and 6.49 % corresponding to the liberation of one coordination and one lattice water molecules are observed from room temperature to 150 °C and 170 °C, respectively. (calcd 7.35 % and 7.29 %). Upon further heating, the frameworks of anhydrous compounds begin to decompose from 310 °C. For **4**, the weight loss of about 14.55 % from the room temperature to 110 °C corresponds to the loss of fourteen lattice water molecules (calcd 15.32 %). Upon heating, the framework begins to collapse at 210 °C. For **5**, the weight loss of about 8.83 % from the room temperature to 110 °C indicate that the loss of thirteen lattice water molecules (calcd 8.28 %). Upon heating, the framework begins to collapse at 270 °C.

Table S1. Crystallographic data and structure refinement details of **1**-**5**.

Compound	**1**	**2**	**3**
Formula	$C_{64}H_{62}N_8O_{15}Cu_2$	$C_{20}H_{22}N_2O_9Mn$	$C_{20}H_{22}N_2O_9Co$
Molecular weight	1310.32	483.27	487.26
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	16.1213(6)	6.5725(5)	6.3508(9)
b (Å)	8.9632(3)	10.1493(7)	10.4298(14)
c (Å)	25.9147(7)	31.853(2)	31.772(4)
□ (°)	90	90	90
□ (°)	96.817(3)	90	90
□ (°)	90	90	90
Z	2	4	4
V(Å^3)	3718.2(2)	2124.8(3)	2104.5(5)
ρ_{calcd} (g cm^{-3})	1.170	1.530	1.557
□ (Mo K□) (mm^{-1})	1.220	0.677	0.872
F(000)	1360	1012	1020
Reflections collected/unique	42347 / 11320	29549 / 5342	29106 / 5060
R_{int}	0.0798	0.0366	0.0620
Data / restraints / parameters	11320 / 49 / 808	5342 / 6 / 305	5061 / 6 / 305
Goodness-of-fit on F^2	1.020	1.036	1.016
*R*1/*wR*2[*I*>2□(*I*)]	0.0589 , 0.1623	0.0303 , 0.0718	0.0379 , 0.0698
*R*1/wR2[all data]	0.0725 , 0.1718	0.0364 , 0.0747	0.0583 , 0.0766
Largest residues (e A^{-3})	0.581 and -0.477	0.301 and -0.252	0.455 and -0.448
Flack parameter	-0.04(3)	0.016(6)	0.021(11)
Compound	**4**	**5**	
Formula	$C_{63}H_{72}N_8O_{14}Cu_2$	$C_{122}H_{112}Cd_{2.5}N_{12}O_{28}$	
Molecular weight	1392.41	2476.94	
Crystal system	monoclinic	monoclinic	
Space group	$P2_1$	*C*2	
a (Å)	13.3695(15)	42.4758(9)	
b (Å)	19.989(2)	13.9687(3)	
c (Å)	15.6098(17)	23.1291(6)	
□ (°)	90	90	
□ (°)	96.395(4)	105.610(3)	
□ (°)	90	90	
Z	2	4	
V(Å^3)	4145.6(8)	13217.1(6)	
ρ_{calcd} (g cm^{-3})	1.115	1.277	

(Mo K□) (mm^{-1})	0.571	3.811
F(000)	1444	5228
Reflections collected/unique	49024 / 14529	63646 / 20801
R_{int}	0.1172	0.1300
Data / restraints / parameters	14529 / 49 / 866	20801 / 884 / 1563
Goodness-of-fit on F^2	0.980	1.047
$R1/wR2[I>2\square(I)]$	0.0654/ 0.1616	0.0922/ 0.2483
R1/wR2[all data]	0.1375/ 0.2068	0.1066/ 0.2636
Largest residues (e A^{-3})	0.420 and -0.455	1.097 and -1.779
Flack parameter	0.051(11)	0.006(9)

Table S2. Bond lengths [Å] and angles [°] for **1**.

Bond	Distance	Bond	Distance
Cu(1)-O(14)	1.937(5)	Cu(2)-O(7)	1.969(4)
Cu(1)-O(2)	1.935(5)	Cu(2)-N(6)#1	2.033(4)
Cu(1)-N(7)	1.986(5)	Cu(2)-N(8)	2.010(5)
Cu(1)-N(5)	2.020(5)	Cu(2)-O(15)	2.365(5)
Cu(2)-O(9)	1.958(4)		
Moiety	Angle	Moiety	Angle
O(2)-Cu(1)-O(14)	175.9(2)	O(7)-Cu(2)-N(8)	86.82(18)
O(2)-Cu(1)-N(7)	88.7(2)	O(9)-Cu(2)-N(6)#1	90.88(18)
O(14)-Cu(1)-N(7)	88.8(2)	O(7)-Cu(2)-N(6)#1	91.62(17)
O(2)-Cu(1)-N(5)	91.4(2)	N(8)-Cu(2)-N(6)#1	167.5(2)
O(14)-Cu(1)-N(5)	91.0(2)	O(9)-Cu(2)-O(15)	94.73(19)
N(7)-Cu(1)-N(5)	178.3(3)	O(7)-Cu(2)-O(15)	93.06(18)
O(9)-Cu(2)-O(7)	171.8(2)	N(8)-Cu(2)-O(15)	102.3(2)
O(9)-Cu(2)-N(8)	89.06(18)	N(6)#1-Cu(2)-O(15)	90.1(2)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z+1

Table S3. Bond lengths [Å] and angles [°] for **2.**

Bond	Distance	Bond	Distance
Mn(1)-O(2)#1	2.1003(13)	Mn(1)-O(8)	2.2097(14)
Mn(1)-O(1)	2.1077(14)	Mn(1)-O(8)#3	2.2738(14)
Mn(1)-O(7)#2	2.1917(12)	Mn(1)-O(7)#4	2.2809(12)
Moiety	Angle	Moiety	Angle
O(2)#1-Mn(1)-O(1)	177.53(6)	O(7)#2-Mn(1)-O(8)#3	79.77(5)
O(2)#1-Mn(1)-O(7)#2	92.01(5)	O(8)-Mn(1)-O(8)#3	165.06(4)
O(1)-Mn(1)-O(7)#2	87.79(5)	O(2)#1-Mn(1)-O(7)#4	94.23(5)
O(2)#1-Mn(1)-O(8)	88.43(6)	O(1)-Mn(1)-O(7)#4	86.57(5)
O(1)-Mn(1)-O(8)	89.42(5)	O(7)#2-Mn(1)-O(7)#4	164.61(4)
O(7)#2-Mn(1)-O(8)	115.02(5)	O(8)-Mn(1)-O(7)#4	79.24(5)
O(2)#1-Mn(1)-O(8)#3	93.29(6)	O(8)#3-Mn(1)-O(7)#4	85.84(5)
O(1)-Mn(1)-O(8)#3	89.10(5)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2, -y+1/2, -z+2 #2 -x-3/2, -y+1, z-1/2

#3 x-1/2, -y+1/2, -z+2 #4 -x-1, y-1/2, -z+5/2

Table S4. Bond lengths [Å] and angles [°] for **3**.

Bond	Distance	Bond	Distance
Co(1)-O(2)#1	2.0241(19)	Co(1)-O(8)	2.128(2)
Co(1)-O(1)	2.025(2)	Co(1)-O(8)#3	2.156(2)
Co(1)-O(7)#2	2.1262(18)	Co(1)-O(7)#4	2.1720(19)
Moiety	Angle	Moiety	Angle
O(2)#1-Co(1)-O(1)	176.17(9)	O(7)#2-Co(1)-O(8)#3	79.79(8)
O(2)#1-Co(1)-O(7)#2	91.85(8)	O(8)-Co(1)-O(8)#3	169.78(6)
O(1)-Co(1)-O(7)#2	87.64(8)	O(2)#1-Co(1)-O(7)#4	94.65(8)
O(2)#1-Co(1)-O(8)	89.93(8)	O(1)-Co(1)-O(7)#4	86.45(8)
O(1)-Co(1)-O(8)	86.67(8)	O(7)#2-Co(1)-O(7)#4	168.93(7)
O(7)#2-Co(1)-O(8)	109.62(8)	O(8)-Co(1)-O(7)#4	79.38(8)
O(2)#1-Co(1)-O(8)#3	93.82(9)	O(8)#3-Co(1)-O(7)#4	90.83(8)
O(1)-Co(1)-O(8)#3	89.83(8)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2, -y+1/2, -z+2 #2 -x-3/2, -y+1, z-1/2

#3 x-1/2, -y+1/2, -z+2 #4 -x-1, y-1/2, -z+5/2

Table S5. Bond lengths [Å] and angles [°] for **4.**

Bond	Distance	Bond	Distance
Cu(1)-O(14)#1	1.969(8)	Cu(2)-O(7)	1.944(9)
Cu(1)-O(1)	1.989(8)	Cu(2)-O(8)	1.992(8)
Cu(1)-N(6)#2	1.995(8)	Cu(2)-N(8)#3	2.017(8)
Cu(1)-N(5)	2.017(8)	Cu(2)-N(7)	2.042(10)
Moiety	Angle	Moiety	Angle
O(14)#1-Cu(1)-O(1)	170.1(3)	O(7)-Cu(2)-O(8)	169.9(3)
O(14)#1-Cu(1)-N(6)#2	93.4(4)	O(7)-Cu(2)-N(8)#3	91.9(3)
O(1)-Cu(1)-N(6)#2	90.3(3)	O(8)-Cu(2)-N(8)#3	90.4(3)
O(14)#1-Cu(1)-N(5)	86.0(3)	O(7)-Cu(2)-N(7)	87.6(3)
O(1)-Cu(1)-N(5)	91.5(3)	O(8)-Cu(2)-N(7)	91.2(3)
N(6)#2-Cu(1)-N(5)	172.8(5)	N(8)#3-Cu(2)-N(7)	173.4(5)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z-1 #2 x+1, y, z #3 x-1, y, z

Table S6. Bond lengths [Å] and angles [°] for **5.**

Bond	Distance	Bond	Distance
Cd(1)-N(9)	2.260(13)	Cd(2)-O(15)	2.353(9)
Cd(1)-O(1)	2.310(8)	Cd(2)-O(15)#3	2.353(9)
Cd(1)-O(8)	2.344(10)	Cd(3)-O(13)	2.281(10)
Cd(1)-O(1)#1	2.362(9)	Cd(3)-N(11)	2.334(17)
Cd(1)-N(10)#2	2.408(15)	Cd(3)-O(23)	2.352(16)
Cd(1)-O(9)	2.477(10)	Cd(3)-N(12)#2	2.355(13)
Cd(1)-O(2)#1	2.567(9)	Cd(3)-O(15)#3	2.443(10)
Cd(2)-N(13)	2.295(13)	Cd(3)-O(16)#3	2.474(10)
Cd(2)-O(14)	2.352(10)	Cd(3)-O(22)	2.506(16)
Cd(2)-O(14)#3	2.352(10)		
Moiety	Angle	Moiety	Angle
N(9)-Cd(1)-O(1)	87.2(4)	O(14)#3-Cd(2)-O(15)	90.3(3)
N(9)-Cd(1)-O(8)	95.2(4)	N(13)-Cd(2)-O(15)#3	91.9(11)
O(1)-Cd(1)-O(8)	139.2(3)	O(14)-Cd(2)-O(15)#3	90.3(3)
N(9)-Cd(1)-O(1)#1	88.5(4)	O(14)#3-Cd(2)-O(15)#3	89.8(3)
O(1)-Cd(1)-O(1)#1	74.1(3)	O(15)-Cd(2)-O(15)#3	176.7(6)
O(8)-Cd(1)-O(1)#1	146.6(3)	O(13)-Cd(3)-N(11)	85.6(5)
N(9)-Cd(1)-N(10)#2	179.8(4)	O(13)-Cd(3)-O(23)	129.5(5)
O(1)-Cd(1)-N(10)#2	93.0(4)	N(11)-Cd(3)-O(23)	93.1(5)
O(8)-Cd(1)-N(10)#2	84.7(4)	O(13)-Cd(3)-N(12)#2	87.1(5)
O(1)#1-Cd(1)-N(10)#2	91.4(4)	N(11)-Cd(3)-N(12)#2	172.1(5)
N(9)-Cd(1)-O(9)	95.0(4)	O(23)-Cd(3)-N(12)#2	93.8(6)
O(1)-Cd(1)-O(9)	85.4(3)	O(13)-Cd(3)-O(15)#3	94.7(4)
O(8)-Cd(1)-O(9)	53.8(3)	N(11)-Cd(3)-O(15)#3	85.7(5)
O(1)#1-Cd(1)-O(9)	159.0(3)	O(23)-Cd(3)-O(15)#3	135.6(4)
N(10)#2-Cd(1)-O(9)	85.2(4)	N(12)#2-Cd(3)-O(15)#3	91.9(5)
N(9)-Cd(1)-O(2)#1	90.5(4)	O(13)-Cd(3)-O(16)#3	147.4(4)
O(1)-Cd(1)-O(2)#1	127.6(3)	N(11)-Cd(3)-O(16)#3	92.3(5)
O(8)-Cd(1)-O(2)#1	93.2(3)	O(23)-Cd(3)-O(16)#3	83.1(4)
O(1)#1-Cd(1)-O(2)#1	53.5(3)	N(12)#2-Cd(3)-O(16)#3	92.3(5)
N(10)#2-Cd(1)-O(2)#1	89.3(4)	O(15)#3-Cd(3)-O(16)#3	52.7(3)
O(9)-Cd(1)-O(2)#1	146.9(3)	O(13)-Cd(3)-O(22)	79.0(4)
N(13)-Cd(2)-O(14)	93.5(7)	N(11)-Cd(3)-O(22)	98.6(6)
N(13)-Cd(2)-O(14)#3	84.2(7)	O(23)-Cd(3)-O(22)	51.2(5)
O(14)-Cd(2)-O(14)#3	177.8(7)	N(12)#2-Cd(3)-O(22)	82.9(5)
N(13)-Cd(2)-O(15)	91.4(11)	O(15)#3-Cd(3)-O(22)	172.0(5)
O(14)-Cd(2)-O(15)	89.8(3)	O(16)#3-Cd(3)-O(22)	133.4(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+2 #2 x, y+1, z #3 -x, y, -z+1

Table S7. Hydrogen bond parameters [Å,°] for **1**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C9-H9A	0.930	2.524	152.43	3.375	O11 [x+1, y, z]
C62-H62A	0.930	2.594	128.07	3.251	O10
N2-H2B	0.860	2.182	163.41	3.016	O6 [-x+1, y+1/2, -z+2]
N4-H4A	0.860	2.207	148.81	2.976	O12 [-x, y+1/2, -z+1]
O15-H15C	0.850	1.930	146.81	2.681	O6

Table S8. Hydrogen bond parameters [Å,°] for **4**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C4-H4B	0.970	2.636	150.10	3.511	O5 [-x+1, y-1/2, -z+1]
C28-H28B	0.970	2.619	152.90	3.510	O12[-x+1,y+1/2, -z+2]
C49-H49A	0.930	2.542	129.90	3.218	O2
C58-H58A	0.930	2.617	133.20	3.323	O10 [-x, y-1/2, -z+1]
C59-H59A	0.930	2.516	134.35	3.235	O2 [x-1, y, z]
C61-H61A	0.930	2.593	128.49	3.254	O9
C70-H70A	0.930	2.603	145.91	3.413	O3 [-x+2, y+1/2, -z+1]
C71-H71A	0.930	2.486	129.46	3.160	O9 [x+1, y, z]

Table S9. Hydrogen bond parameters [Å,°] for **5**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C2-H2A	0.980	2.617	145.33	3.468	O9
C38-H38A	0.930	2.496	152.64	3.350	O5 [x-1/2, y-1/2, z]
C50-H50A	0.980	2.203	155.02	3.119	O14
C62-H62A	0.930	2.501	156.40	3.374	O6 [-x+1, y, -z+2]
C69-H69B	0.970	2.442	148.00	3.305	O19 [-x+1/2, y-1/2, -z+2]
C106-H10F	0.930	2.609	132.33	3.308	O2 [-x+1, y-1, -z+2]
C107-H10G	0.930	2.512	142.11	3.296	O3 [x, y-1, z]
C113-H11D	0.930	2.588	133.14	3.295	O12
C123-H12C	0.930	2.654	128.15	3.311	O14
C121-H12F	0.930	2.353	127.03	3.006	O14 [-x, y, -z+1]
C130-H13A	0.930	2.465	126.13	3.106	O17 [x, y-1, z]

Table S10. Some characteristics of H_2ODBALa, H_2ODBPRo and metal ions for **1-5**.

No.	metal(II) ion and coordination geometry	dimension	configuration	coordination mode of carboxylate groups	dihedral angel	structure
1	Cu1, square-planar; Cu2, tetragonal-pyramid.	1D	*cis*-configuration	bis-monodentate (μ-η^1:η^1)	70.210° 70.132°	ring-like unit
2,3	Mn1 and Co1, octahedral.	3D	*trans*-configuration	*syn-syn* bidentate bridging and monodentate bridging (μ-η^2:η^2)	57.382°	1D helical chain
4	Cu1 and Cu2, square-planar.	2D	*trans*-configuration	bis-monodentate (μ-η^1:η^1)	61.896° 72.075°	1D helical chain
5	Cd1 and Cd3, pentagonal-bipyramid; Cd2, octahedral.	2D	*trans*-configuration (a) *cis*-configuration (b) *trans*-configuration (c) *trans*-configuration (d)	*syn-syn* bidentate bridging and bidentate chelating (μ-η^2:η^1) (a) bidentate chelating (μ-η^1:η^0) (b) chelating monodentate bridging (μ-η^2:η^0) (c) chelating monodentate bridging (μ-η^2:η^0) (d)	79.308° (a) 46.787° (b) 69.925° (c) 72.295° (d)	1D helical chain (a) decorated part (b) decorated part (c) decorated part (d)