Supplementary Information

Structural diversity and magnetic properties of Co(II)/Mn(II)/Ni(II) coordination polymers constructed from an unsymmetrical tetracarboxylic acid and varying N-donor ligands

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Table of Contents

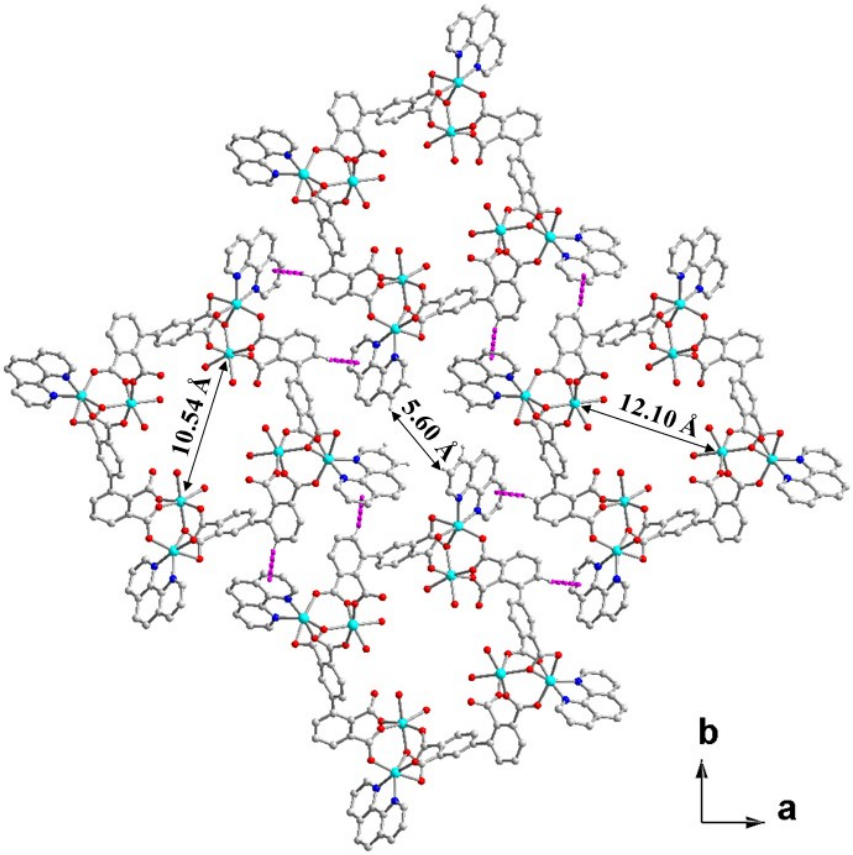

Fig. S1. The 3D supramolecular structure featuring 1D stacking channel of **1**.

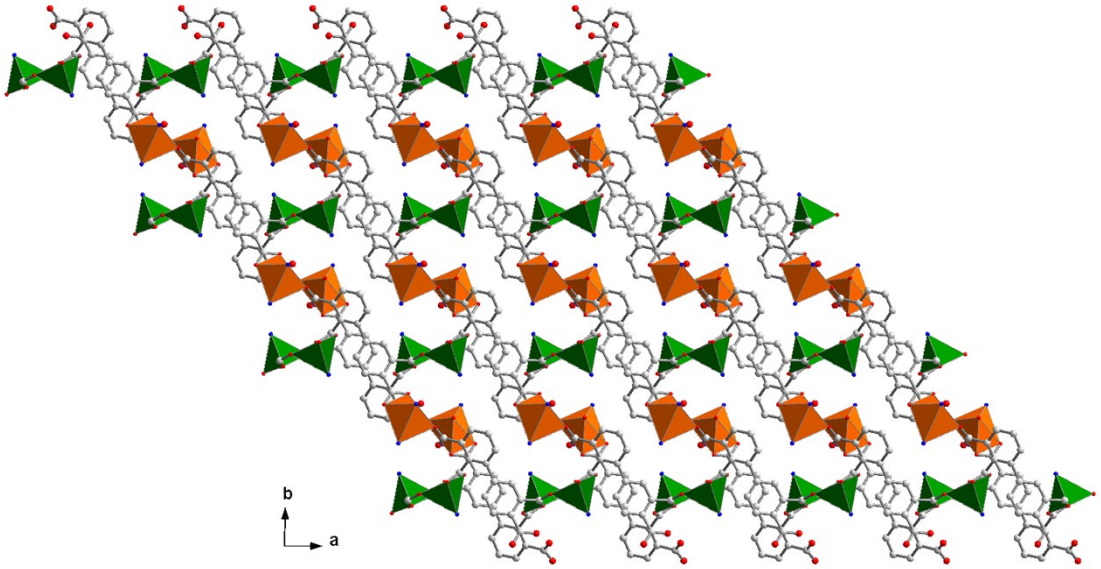

Fig. S2. The 2D double-layered network of **6** viewed along the *c* axis.

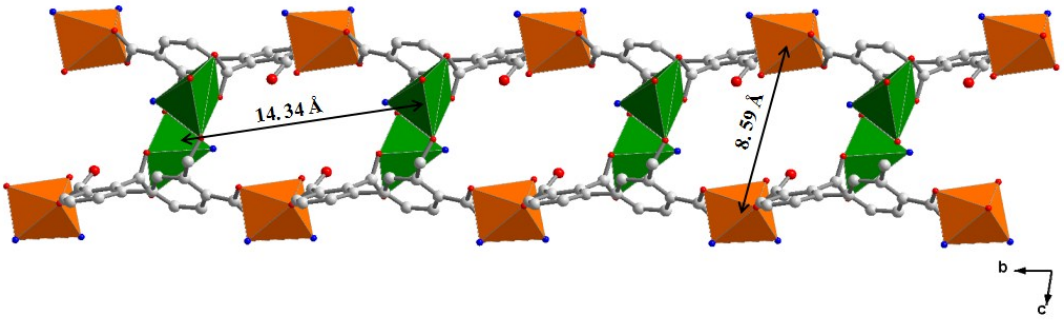

Fig. S3. The hexagonal channels in the 2D double-layered network of **6**.

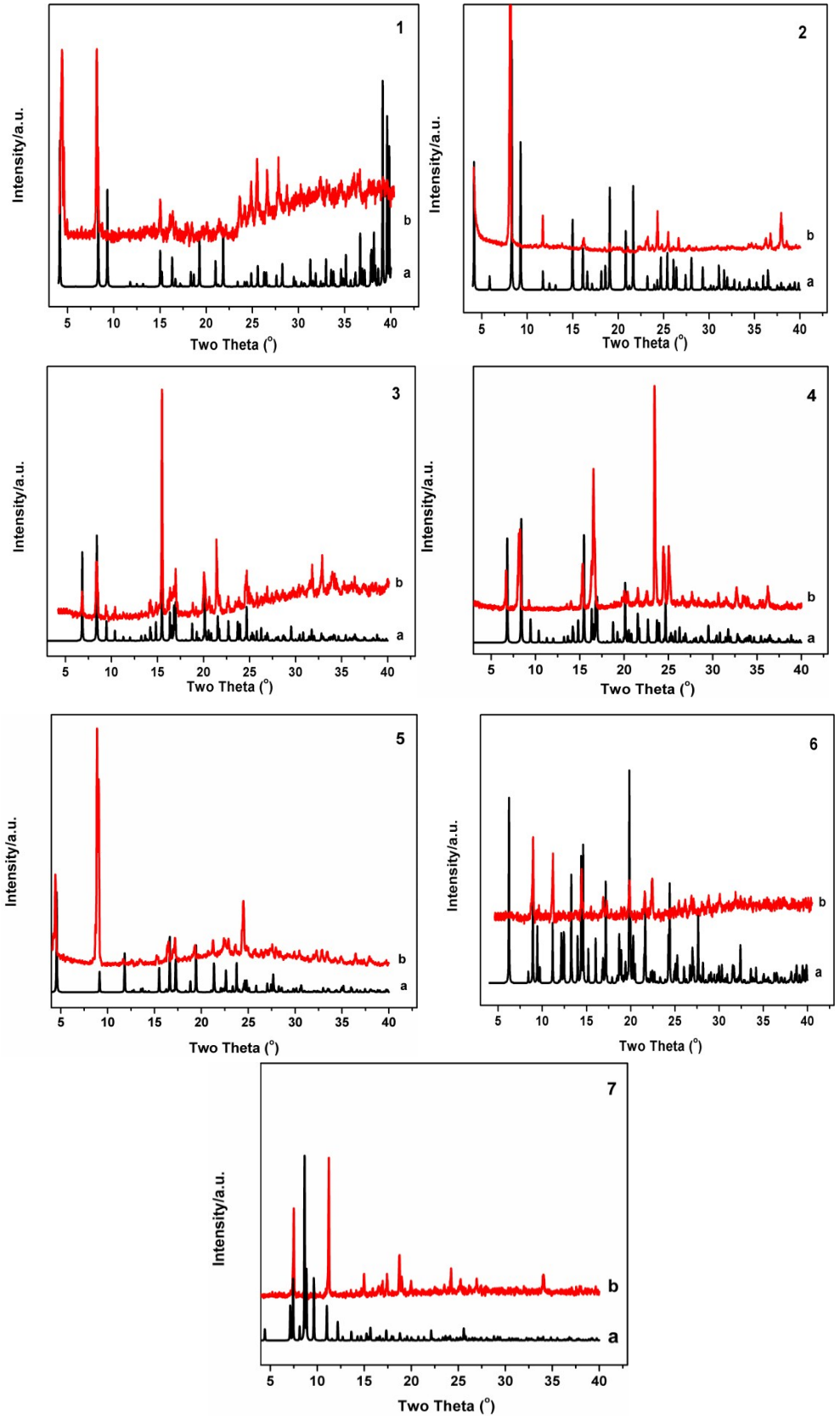

Fig. S4. PXRD patterns of **1-7.** a) Simulated from single crystal structure data. b) Experimental data. The differences between the calculated and observed patterns in intensity may be due to the orientation of the crystals.

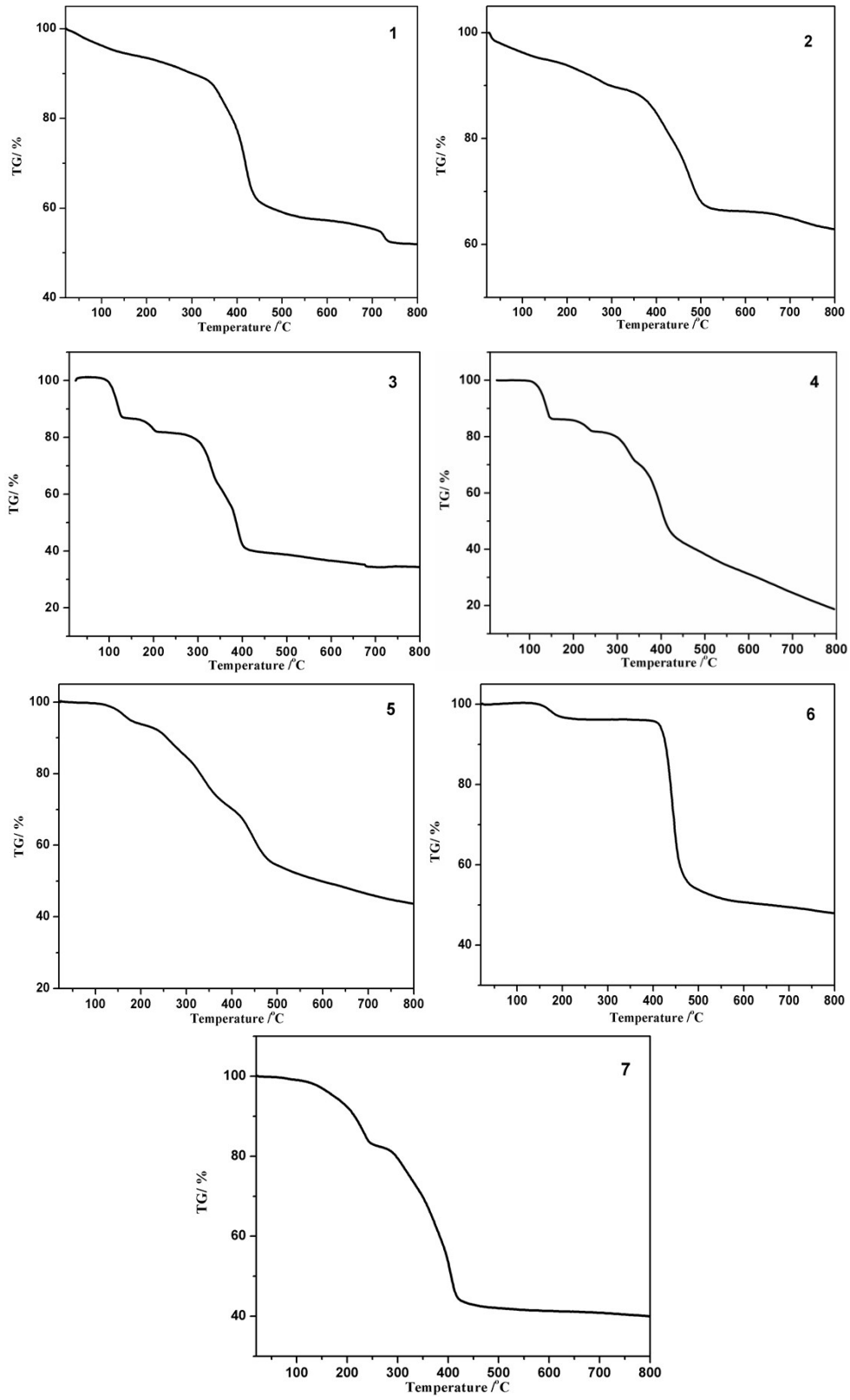

Fig. S5. TGA curves of **1-7**.

For **1**, the weight loss of about 12.6 % from the room temperature to 340 °C corresponds to the departure of three lattice and two coordinated water molecules (calcd 12.38 %), and the remaining framework is thermally stable up to 350 °C, at which the framework begins to collapse. For **2**, the weight loss of about 12.44 % from the room temperature to 350 °C corresponds to the loss of three

lattice and two coordinated water molecules (calcd 12.64 %), and the remaining framework is thermally stable up to 368 °C, at which the framework begins to collapse. For **3**, the weight loss of about 15.4 % from the room temperature to 175 °C corresponds to the release of one lattice and seven coordinated water molecules (calcd 15.7 %), and the remaining framework is thermally stable up to 282 °C. The framework begins to collapse upon further heating. For **4**, the weight loss of about 15.63 % from the room temperature to 149 °C corresponds to the departure of one lattice and seven coordinated water molecules (calcd 15.72 %), and the remaining framework is thermally stable up to 239 °C. The framework begins to collapse upon further heating. For **5**, the weight loss of about 8.24 % from the room temperature to 241 °C is the equal of the departure of two lattice and four coordinated water molecules (calcd 8.39 %), and the remaining framework is thermally stable up to 242 °C, at which the framework begins to collapse. For **6**, the weight loss of about 4.16 % from the room temperature to 397 °C is the equal of the departure of two lattice and two coordinated water molecules (calcd 4.80 %), and the remaining framework is thermally stable up to 403 °C, at which the framework begins to collapse. For **7**, the weight loss of about 23.90 % from the room temperature to 282 °C is the equivalent of the departure of thirteen lattice and four coordinated water molecules (calcd 24.52 %), and the remaining framework is thermally stable up to 284 °C, at which the framework begins to collapse. For complexes **1**-**7**, the theoretical calculated percent of metal oxide are 20.74 %, 20.08 %, 16.30 %, 16.36 %, 17.74 %, 19.89 % and 23.90 %, respectively, but the experimental data are 51.97 %, 62.86 %, 33.63 %, 18.06 %, 43.68 %, 47.95 %, and 40.03 % at 800 °C, respectively. The final decomposition products are not metallic oxides, and there are still some organic compositions left even at 800 °C.

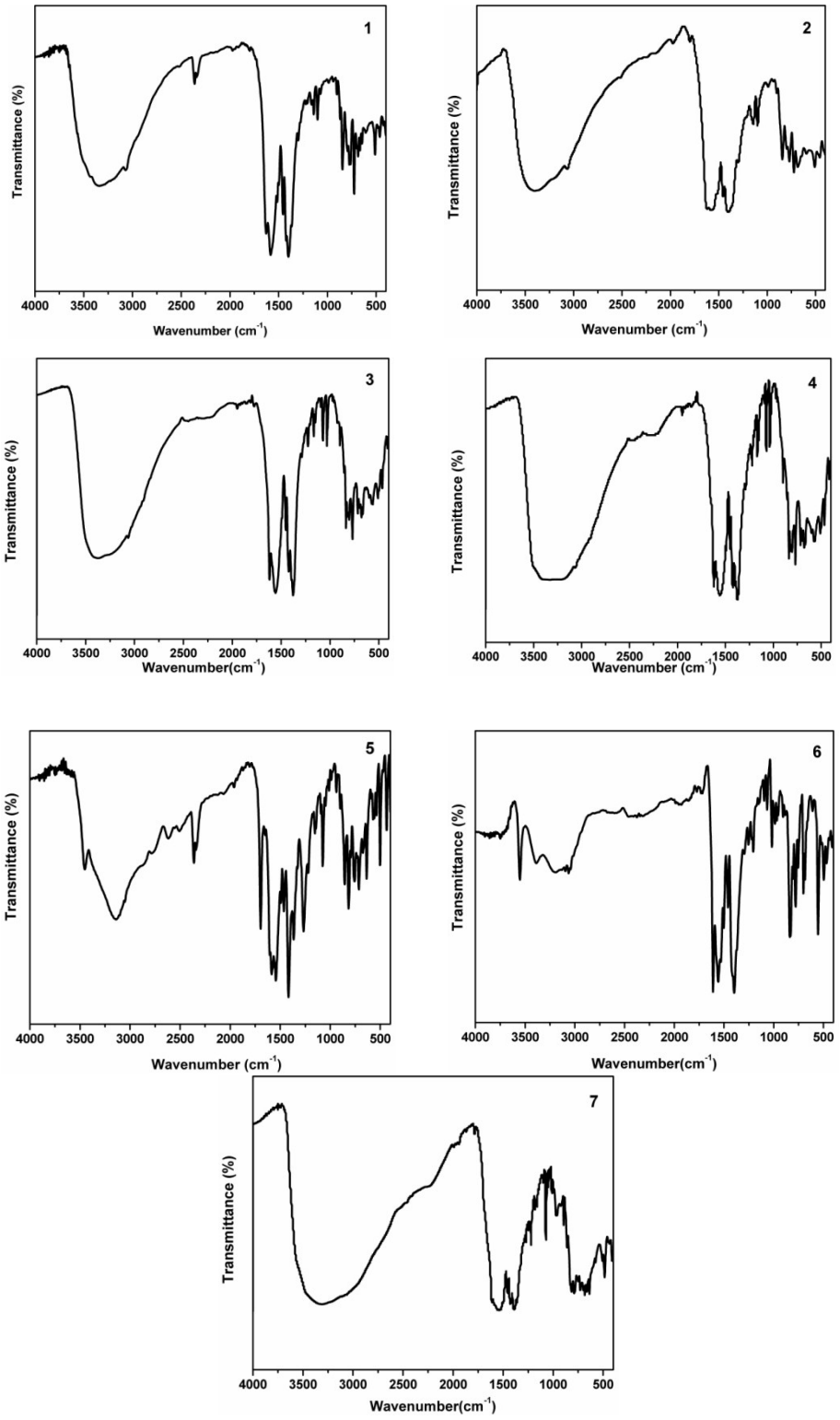

Fig. S6. Infrared spectra of **1-7**.

The absence of the ν(C=O) absorption band in the area of 1700 cm^{-1} indicates full deprotonation of carboxylate groups in complex **1**, **2**, **3**, **4**, **6** and **7**, which are consistent with the results of sing-crystal X-ray analysis. In **5**, the presence of the ν(C=O) absorption because carboxylate groups are partially deprotonated.

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

Bond	Distance	Bond	Distance
Co(1)-O(8)#1	2.016(2)	Co(2)-O(6)#3	2.014(3)
Co(1)-O(3)#2	2.072(2)	Co(2)-O(9)	2.050(3)
Co(1)-N(2)	2.1047(12)	Co(2)-O(7)#1	2.064(2)
Co(1)-N(1)	2.1335(11)	Co(2)-O(4)#2	2.080(2)
Co(1)-O(2)	2.175(2)	Co(2)-O(2)	2.134(2)
Co(1)-O(1)	2.234(2)	Co(2)-O(10)	2.1703(12)
Moiety	Angle	Moiety	Angle
O(8)#1-Co(1)-O(3)#2	97.35(10)	O(6)#3-Co(2)-O(9)	99.1(2)
O(8)#1-Co(1)-N(2)	101.92(8)	O(6)#3-Co(2)-O(7)#1	88.13(12)
O(3)#2-Co(1)-N(2)	93.13(7)	O(9)-Co(2)-O(7)#1	161.89(15)
O(8)#1-Co(1)-N(1)	86.55(7)	O(6)#3-Co(2)-O(4)#2	169.39(13)
O(3)#2-Co(1)-N(1)	78.6	O(9)-Co(2)-O(4)#2	88.78(19)
N(2)-Co(1)-N(1)	171.47(8)	O(7)#1-Co(2)-O(4)#2	86.39(11)
O(8)#1-Co(1)-O(2)	106.32(9)	O(6)#3-Co(2)-O(2)	85.00(11)
O(3)#2-Co(1)-O(2)	89.91(9)	O(9)-Co(2)-O(2)	96.38(13)
N(2)-Co(1)-O(2)	150.95(7)	O(7)#1-Co(2)-O(2)	100.79(9)
N(1)-Co(1)-O(2)	96.29(7)	O(4)#2-Co(2)-O(2)	87.12(10)
O(8)#1-Co(1)-O(1)	164.59(10)	O(6)#3-Co(2)-O(10)	99.01(10)
O(3)#2-Co(1)-O(1)	88.06(10)	O(9)-Co(2)-O(10)	84.47(12)
N(2)-Co(1)-O(1)	92.12(7)	O(7)#1-Co(2)-O(10)	77.99(7)
N(1)-Co(1)-O(1)	90.10(7)	O(4)#2-Co(2)-O(10)	88.73(8)
O(2)-Co(1)-O(1)	59.09(9)	O(2)-Co(2)-O(10)	175.74(7)

Symmetry transformations used to generate equivalent atoms:

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

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

#5 -y+3/2, x-1/2, -z+5/2 #6 -y+3/2, x-1/2, -z+3/2

Table S2. Main bond lengths [Å] and angles [°] for **2**.

Bond	Distance	Bond	Distance
Mn(1)-O(8)#1	2.078(4)	Mn(2)-O(6)#3	2.083(5)
Mn(1)-O(3)#2	2.136(4)	Mn(2)-O(9)	2.160(6)
Mn(1)-O(2)	2.213(4)	Mn(2)-O(4)#2	2.159(4)
Mn(1)-N(2)	2.227(5)	Mn(2)-O(7)#1	2.164(4)
Mn(1)-N(1)	2.259(5)	Mn(2)-O(2)	2.214(4)
Mn(1)-O(1)	2.425(5)	Mn(2)-O(10)	2.267(6)
Moiety	Angle	Moiety	Angle
O(8)#1-Mn(1)-O(3)#2	100.45(18)	O(6)#3-Mn(2)-O(9)	103.1(4)
O(8)#1-Mn(1)-O(2)	109.55(18)	O(6)#3-Mn(2)-O(4)#2	169.1(2)
O(3)#2-Mn(1)-O(2)	90.30(16)	O(9)-Mn(2)-O(4)#2	84.9(3)
O(8)#1-Mn(1)-N(2)	103.95(19)	O(6)#3-Mn(2)-O(7)#1	89.3(2)
O(3)#2-Mn(1)-N(2)	94.61(18)	O(9)-Mn(2)-O(7)#1	157.8(3)
O(2)-Mn(1)-N(2)	144.62(17)	O(4)#2-Mn(2)-O(7)#1	85.60(19)
O(8)#1-Mn(1)-N(1)	88.14(18)	O(6)#3-Mn(2)-O(2)	86.4(2)
O(3)#2-Mn(1)-N(1)	166.81(18)	O(9)-Mn(2)-O(2)	98.5(2)
O(2)-Mn(1)-N(1)	96.27(17)	O(4)#2-Mn(2)-O(2)	85.03(17)
N(2)-Mn(1)-N(1)	73.5(2)	O(7)#1-Mn(2)-O(2)	100.59(16)
O(8)#1-Mn(1)-O(1)	163.74(18)	O(6)#3-Mn(2)-O(10)	100.0(3)
O(3)#2-Mn(1)-O(1)	88.17(17)	O(9)-Mn(2)-O(10)	83.1(3)
O(2)-Mn(1)-O(1)	56.19(15)	O(4)#2-Mn(2)-O(10)	88.2(2)
N(2)-Mn(1)-O(1)	88.92(17)	O(7)#1-Mn(2)-O(10)	76.6(2)
N(1)-Mn(1)-O(1)	86.04(16)	O(2)-Mn(2)-O(10)	172.9(2)

Symmetry transformations used to generate equivalent atoms:

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

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

#5 -y+1/2, x+1/2, -z-1/2 #6 -y+1/2, x+1/2, -z+1/2

Table S3. Main bond lengths [Å] and angles [°] for **3**.

Bond	Distance	Bond	Distance
Co(1)-O(1)	2.079(3)	Co(2)-O(7)	2.027(3)
Co(1)-O(11)	2.094(3)	Co(2)-N(2)#2	2.079(4)
Co(1)-N(1)	2.103(3)	Co(2)-O(13)	2.097(4)
Co(1)-O(10)	2.111(3)	Co(2)-O(15)	2.126(3)
Co(1)-O(6)#1	2.115(3)	Co(2)-O(12)	2.136(4)
Co(1)-O(9)	2.162(3)	Co(2)-O(14)	2.184(3)
Moiety	Angle	Moiety	Angle
O(1)-Co(1)-O(11)	98.21(13)	O(7)-Co(2)-N(2)#2	175.56(13)
O(1)-Co(1)-N(1)	93.41(12)	O(7)-Co(2)-O(13)	90.86(14)
O(11)-Co(1)-N(1)	94.07(13)	N(2)#2-Co(2)-O(13)	93.51(15)
O(1)-Co(1)-O(10)	172.33(13)	O(7)-Co(2)-O(15)	84.54(12)
O(11)-Co(1)-O(10)	88.76(14)	N(2)#2-Co(2)-O(15)	91.05(13)
N(1)-Co(1)-O(10)	89.28(13)	O(13)-Co(2)-O(15)	174.77(14)
O(1)-Co(1)-O(6)#1	82.18(11)	O(7)-Co(2)-O(12)	89.37(14)
O(11)-Co(1)-O(6)#1	179.13(11)	N(2)#2-Co(2)-O(12)	90.95(15)
N(1)-Co(1)-O(6)#1	86.68(13)	O(13)-Co(2)-O(12)	95.79(16)
O(10)-Co(1)-O(6)#1	90.82(13)	O(15)-Co(2)-O(12)	86.68(14)
O(1)-Co(1)-O(9)	87.65(12)	O(7)-Co(2)-O(14)	85.88(13)
O(11)-Co(1)-O(9)	85.83(13)	N(2)#2-Co(2)-O(14)	93.39(14)
N(1)-Co(1)-O(9)	178.94(14)	O(13)-Co(2)-O(14)	89.47(14)
O(10)-Co(1)-O(9)	89.67(13)	O(15)-Co(2)-O(14)	87.71(12)
O(6)#1-Co(1)-O(9)	93.41(12)	O(12)-Co(2)-O(14)	172.97(14)

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Main bond lengths [Å] and angles [°] for **4**.

Bond	Distance	Bond	Distance
Ni(1)-O(1)	1.981(5)	Ni(2)-O(5)	2.046(5)
Ni(1)-N(1)	2.029(6)	Ni(2)-N(2)#1	2.054(6)
Ni(1)-O(9)	2.052(5)	Ni(2)-O(14)	2.058(5)
Ni(1)-O(11)	2.079(6)	Ni(2)-O(15)	2.065(5)
Ni(1)-O(12)	2.111(5)	Ni(2)-O(3)#2	2.075(5)
Ni(1)-O(10)	2.154(5)	Ni(2)-O(13)	2.113(5)
Moiety	Angle	Moiety	Angle
O(5)-Ni(2)-N(2)#1	93.0(2)	O(1)-Ni(1)-N(1)	175.1(2)
O(5)-Ni(2)-O(14)	97.7(2)	O(1)-Ni(1)-O(9)	91.2(2)
N(2)#1-Ni(2)-O(14)	92.3(2)	N(1)-Ni(1)-O(9)	93.6(2)
O(5)-Ni(2)-O(15)	173.7(2)	O(1)-Ni(1)-O(11)	89.1(2)
N(2)#1-Ni(2)-O(15)	89.5(2)	N(1)-Ni(1)-O(11)	91.2(2)
O(14)-Ni(2)-O(15)	88.0(2)	O(9)-Ni(1)-O(11)	96.4(2)
O(5)-Ni(2)-O(3)#2	82.21(19)	O(1)-Ni(1)-O(12)	84.4(2)
N(2)#1-Ni(2)-O(3)#2	87.1(2)	N(1)-Ni(1)-O(12)	90.7(2)
O(14)-Ni(2)-O(3)#2	179.4(2)	O(9)-Ni(1)-O(12)	174.9(2)
O(15)-Ni(2)-O(3)#2	92.2(2)	O(11)-Ni(1)-O(12)	86.1(2)
O(5)-Ni(2)-O(13)	87.4(2)	O(1)-Ni(1)-O(10)	86.1(2)
N(2)#1-Ni(2)-O(13)	179.4(2)	N(1)-Ni(1)-O(10)	93.2(2)
O(14)-Ni(2)-O(13)	87.2(2)	O(9)-Ni(1)-O(10)	88.8(2)
O(15)-Ni(2)-O(13)	90.2(2)	O(11)-Ni(1)-O(10)	172.9(2)
O(3)#2-Ni(2)-O(13)	93.4(2)	O(12)-Ni(1)-O(10)	88.3(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Main bond lengths [Å] and angles [°] for **5**.

Bond	Distance	Bond	Distance
Co(1)-O(3)#1	2.008(3)	Co(2)-O(7)	2.056(3)
Co(1)-O(9)	2.035(3)	Co(2)-O(7)#2	2.056(3)
Co(1)-O(1)	2.041(3)	Co(2)-O(10)	2.130(4)
Co(1)-N(1)	2.073(4)	Co(2)-O(10)#2	2.130(4)
Co(1)-O(4)#1	2.385(3)	Co(2)-N(2)#3	2.156(4)
		Co(2)-N(2)#4	2.156(4)
Moiety	Angle	Moiety	Angle
O(3)#1-Co(1)-O(9)	102.54(15)	O(7)-Co(2)-O(10)#2	94.76(15)
O(3)#1-Co(1)-O(1)	104.42(13)	O(7)#2-Co(2)-O(10)#2	85.24(15)
O(9)-Co(1)-O(1)	94.11(13)	O(10)-Co(2)-O(10)#2	179.998(1)
O(3)#1-Co(1)-N(1)	136.75(15)	O(7)-Co(2)-N(2)#3	89.95(15)
O(9)-Co(1)-N(1)	99.15(15)	O(7)#2-Co(2)-N(2)#3	90.05(15)
O(1)-Co(1)-N(1)	110.84(14)	O(10)-Co(2)-N(2)#3	92.06(15)
O(3)#1-Co(1)-O(4)#1	58.92(12)	O(10)#2-Co(2)-N(2)#3	87.94(15)
O(9)-Co(1)-O(4)#1	79.45(13)	O(7)-Co(2)-N(2)#4	90.05(15)
O(1)-Co(1)-O(4)#1	159.50(12)	O(7)#2-Co(2)-N(2)#4	89.95(15)
N(1)-Co(1)-O(4)#1	89.48(13)	O(10)-Co(2)-N(2)#4	87.94(15)
O(7)-Co(2)-O(7)#2	179.998(1)	O(10)#2-Co(2)-N(2)#4	92.06(15)
O(7)-Co(2)-O(10)	85.24(15)	N(2)#3-Co(2)-N(2)#4	180.0(2)
O(7)#2-Co(2)-O(10)	94.76(15)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S6. Main bond lengths [Å] and angles [°] for **6**.

Bond	Distance	Bond	Distance
Co(1)-O(1)	2.036(2)	Co(1)-O(8)#1	2.197(2)
Co(1)-N(1)	2.112(3)	Co(2)-O(5)#2	1.966(2)
Co(1)-O(9)	2.137(3)	Co(2)-O(6)#3	2.008(3)
Co(1)-N(2)	2.142(3)	Co(2)-O(4)	2.018(3)
Co(1)-O(7)#1	2.180(2)	Co(2)-N(3)	2.039(3)
Moiety	Angle	Moiety	Angle
O(1)-Co(1)-N(1)	97.16(11)	O(7)#1-Co(1)-O(8)#1	60.15(9)
O(1)-Co(1)-O(9)	90.88(10)	O(1)-Co(1)-C(14)#1	137.06(11)
N(1)-Co(1)-O(9)	85.45(11)	N(1)-Co(1)-C(14)#1	125.77(12)
O(1)-Co(1)-N(2)	84.56(10)	O(9)-Co(1)-C(14)#1	91.54(11)
N(1)-Co(1)-N(2)	106.28(12)	N(2)-Co(1)-C(14)#1	84.23(11)
O(9)-Co(1)-N(2)	167.83(11)	O(7)#1-Co(1)-C(14)#1	30.25(10)
O(1)-Co(1)-O(7)#1	107.35(10)	O(8)#1-Co(1)-C(14)#1	29.94(10)
N(1)-Co(1)-O(7)#1	154.21(11)	O(5)#2-Co(2)-O(6)#3	103.50(11)
O(9)-Co(1)-O(7)#1	86.24(10)	O(5)#2-Co(2)-O(4)	137.81(11)
N(2)-Co(1)-O(7)#1	84.37(10)	O(6)#3-Co(2)-O(4)	97.12(11)
O(1)-Co(1)-O(8)#1	165.94(9)	O(5)#2-Co(2)-N(3)	110.16(11)
N(1)-Co(1)-O(8)#1	96.24(11)	O(6)#3-Co(2)-N(3)	101.14(11)
O(9)-Co(1)-O(8)#1	94.42(10)	O(4)-Co(2)-N(3)	101.21(12)
N(2)-Co(1)-O(8)#1	87.60(11)		

Symmetry transformations used to generate equivalent atoms:

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

#4 x-1,y,z #5 x-1,y+1,z #6 -x+1,-y+3,-z

#7 -x,-y+1,-z #8 -x-1,-y+4,-z+1

Table S7. Main bond lengths [Å] and angles [°] for **7**.

Bond	Distance	Bond	Distance
Ni(1)-O(12)	2.041(3)	Ni(3)-O(10)	2.011(3)
Ni(1)-O(1)	2.056(3)	Ni(3)-O(12)	2.050(3)
Ni(1)-O(10)	2.057(3)	Ni(3)-N(3)	2.066(3)
Ni(1)-N(2)#1	2.060(3)	Ni(3)-O(11)	2.084(3)
Ni(1)-O(9)	2.065(3)	Ni(3)-O(5)#2	2.089(3)
Ni(1)-O(13)	2.113(3)	Ni(3)-O(7)#2	2.113(3)
Ni(2)-O(10)	2.025(3)	Ni(4)-O(9)	2.040(3)
Ni(2)-O(9)	2.042(3)	Ni(4)-O(12)	2.044(3)
Ni(2)-O(11)	2.074(3)	Ni(4)-O(11)	2.057(3)
Ni(2)-O(2)	2.090(3)	Ni(4)-N(1)	2.080(3)
Ni(2)-O(14)	2.090(4)	Ni(4)-O(16)	2.081(3)
Ni(2)-N(4)	2.094(3)	Ni(4)-O(15)	2.113(4)
Moiety	Angle	Moiety	Angle
O(12)-Ni(1)-O(1)	166.53(11)	O(10)-Ni(2)-Ni(1)	43.31(7)
O(12)-Ni(1)-O(10)	81.44(11)	O(9)-Ni(2)-Ni(1)	43.57(8)
O(1)-Ni(1)-O(10)	87.82(11)	O(11)-Ni(2)-Ni(1)	85.33(8)
O(12)-Ni(1)-N(2)#1	98.49(12)	O(2)-Ni(2)-Ni(1)	79.55(8)
O(1)-Ni(1)-N(2)#1	92.67(12)	O(14)-Ni(2)-Ni(1)	129.59(10)
O(10)-Ni(1)-N(2)#1	176.93(14)	N(4)-Ni(2)-Ni(1)	142.50(10)
O(12)-Ni(1)-O(9)	80.06(12)	O(10)-Ni(3)-O(12)	82.33(11)
O(1)-Ni(1)-O(9)	90.80(11)	O(10)-Ni(3)-N(3)	92.48(12)
O(10)-Ni(1)-O(9)	83.96(11)	O(12)-Ni(3)-N(3)	173.80(13)
N(2)#1-Ni(1)-O(9)	99.05(12)	O(10)-Ni(3)-O(11)	79.56(12)
O(12)-Ni(1)-O(13)	92.70(13)	O(12)-Ni(3)-O(11)	81.21(11)
O(1)-Ni(1)-O(13)	95.09(13)	N(3)-Ni(3)-O(11)	94.56(12)
O(10)-Ni(1)-O(13)	88.26(12)	O(10)-Ni(3)-O(5)#2	169.33(11)
N(2)#1-Ni(1)-O(13)	88.68(13)	O(12)-Ni(3)-O(5)#2	87.44(11)
O(9)-Ni(1)-O(13)	170.07(12)	N(3)-Ni(3)-O(5)#2	97.54(12)
O(12)-Ni(1)-Ni(2)	86.30(8)	O(11)-Ni(3)-O(5)#2	95.93(12)
O(1)-Ni(1)-Ni(2)	80.29(8)	O(10)-Ni(3)-O(7)#2	93.38(12)
O(10)-Ni(1)-Ni(2)	42.47(8)	O(12)-Ni(3)-O(7)#2	90.31(11)
N(2)#1-Ni(1)-Ni(2)	140.59(10)	N(3)-Ni(3)-O(7)#2	93.39(13)
O(9)-Ni(1)-Ni(2)	42.97(7)	O(11)-Ni(3)-O(7)#2	169.58(11)
O(13)-Ni(1)-Ni(2)	130.37(9)	O(5)#2-Ni(3)-O(7)#2	89.69(12)
O(10)-Ni(2)-O(9)	85.36(11)	O(9)-Ni(4)-O(12)	80.58(11)
O(10)-Ni(2)-O(11)	79.50(12)	O(9)-Ni(4)-O(11)	80.95(10)
O(9)-Ni(2)-O(11)	80.49(10)	O(12)-Ni(4)-O(11)	82.00(11)
O(10)-Ni(2)-O(2)	85.77(11)	O(9)-Ni(4)-N(1)	94.47(12)
O(9)-Ni(2)-O(2)	92.07(10)	O(12)-Ni(4)-N(1)	96.16(13)
O(11)-Ni(2)-O(2)	163.95(12)	O(11)-Ni(4)-N(1)	175.27(13)
O(10)-Ni(2)-O(14)	172.87(12)	O(9)-Ni(4)-O(16)	168.19(12)

O(9)-Ni(2)-O(14)	87.60(13)	O(12)-Ni(4)-O(16)	92.55(14)
O(11)-Ni(2)-O(14)	100.40(16)	O(11)-Ni(4)-O(16)	88.62(12)
O(2)-Ni(2)-O(14)	93.42(16)	N(1)-Ni(4)-O(16)	95.82(14)
O(10)-Ni(2)-N(4)	100.00(12)	O(9)-Ni(4)-O(15)	96.24(13)
O(9)-Ni(2)-N(4)	173.30(13)	O(12)-Ni(4)-O(15)	173.47(13)
O(11)-Ni(2)-N(4)	96.45(12)	O(11)-Ni(4)-O(15)	91.89(13)
O(2)-Ni(2)-N(4)	92.33(12)	N(1)-Ni(4)-O(15)	89.75(15)
O(14)-Ni(2)-N(4)	87.10(14)	O(16)-Ni(4)-O(15)	89.60(15)
Ni(4)-O(9)-Ni(2)	99.71(11)	Ni(4)-O(11)-Ni(2)	98.10(11)
Ni(4)-O(9)-Ni(1)	99.13(12)	Ni(4)-O(11)-Ni(3)	96.55(12)
Ni(2)-O(9)-Ni(1)	93.46(11)	Ni(2)-O(11)-Ni(3)	98.25(12)
Ni(3)-O(10)-Ni(2)	102.35(13)	Ni(1)-O(12)-Ni(4)	99.78(13)
Ni(3)-O(10)-Ni(1)	97.75(11)	Ni(1)-O(12)-Ni(3)	97.03(11)
Ni(2)-O(10)-Ni(1)	94.22(11)	Ni(4)-O(12)-Ni(3)	98.06(12)

Symmetry transformations used to generate equivalent atoms:

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

#3 y+1/4,-x+1/4,z+1/4 #4 -x+0,-y+1/2,z+0

Table S8. Parameters of hydrogen bonds (Å, °) for **3** and **4**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
3					
O9-H9A	0.844	2.538	143.75	3.257	O3 [-x+2, -y, -z]
O10-H10B	0.851	1.927	159.32	2.740	O5 [-x+2, -y, -z+1]
O10-H10C	0.856	1.867	164.21	2.700	O4 [-x+2, -y, -z]
O11-H11A	0.847	1.907	162.66	2.727	O2
O11-H11B	0.851	1.963	156.38	2.763	O3 [-x+2, -y, -z]
O12-H12A	0.847	1.888	165.80	2.717	O16 [-x+2, -y-1, -z+1]
O13-H13A	0.860	2.084	161.86	2.913	O4 [x-1, y, z+1]
O14-H14A	0.853	2.118	159.11	2.930	O3 [-x+2, -y, -z+1]
O14-H14B	0.842	2.098	165.18	2.920	O6
O15-H15B	0.844	1.853	159.62	2.660	O16 [x, y, z+1]
O15-H15C	0.824	2.013	172.41	2.831	O5
O16-H16B	0.835	2.370	132.05	2.994	O5 [-x+2, -y-1, -z+1]
O16-H16C	0.843	1.787	178.30	2.629	O2
C19-H19A	0.930	2.524	139.73	3.289	O8 [-x+1, -y, -z+1]
C27-H27A	0.930	2.469	153.89	3.329	O5 [x-1, y+1, z]
4					
O9-H9A	0.842	1.981	147.77	2.730	O2
O9-H9B	0.842	2.079	158.60	2.879	O7 [x+1, y, z-1]
O10-H10A	0.843	2.107	163.63	2.925	O3
O10-H10B	0.847	2.132	167.53	2.964	O8 [-x+1, -y+1, -z]
O11-H11A	0.850	1.955	146.24	2.703	O16 [-x+1, -y+2, -z]
O11-H11B	0.853	2.357	125.61	2.936	O7 [-x+1, -y+2, -z]
O12-H12A	0.841	1.918	142.97	2.639	O16 [x, y, z-1]
O12-H12B	0.828	2.223	138.91	2.898	O13 [-x+1, -y+1, -z]
O13-H13A	0.847	2.092	158.98	2.898	O12 [-x+1, -y+1, -z]
O13-H13B	0.851	2.307	135.55	2.974	O6 [-x+1, -y+1, -z+1]
O14-H14B	0.832	1.881	172.20	2.707	O6
O14-H14C	0.887	1.921	162.45	2.780	O8 [-x+1, -y+1, -z+1]
O15-H15B	0.845	1.900	158.60	2.704	O7 [-x+1, -y+1, -z+1]
O15-H15C	0.858	1.935	155.01	2.737	O4 [-x+1, -y+1, -z]
O16-H16C	0.847	1.816	155.31	2.610	O6
O16-H16B	0.838	2.288	137.09	2.957	O4 [-x+1, -y+2, -z]
C17-H17A	0.930	2.444	152.13	3.295	O4 [-x+1, -y+2, -z-1]
C17-H17A	0.930	2.444	152.13	3.295	O4 [-x+1, -y+2, -z-1]
C25-H25A	0.930	2.499	138.09	3.251	O2 [x, y, z-1]
C28-H28A	0.930	2.632	115.59	3.148	O5 [-x+2, -y+1, -z-1]

There are typical strong O−H···O and weak C−H···O hydrogen bonding interactions within and between the chains of **3**: The coordinated water molecules (O9, O10, O11, O13, O14 and O15) are involved in stronger intrachain hydrogen bonds with the uncoordinated carboxylate oxygen atoms (O2, O3, O4, O5 and O8) with O···O separations between 2.629 and 2.930 Å, and the carboxylate

oxygen atom (O6) with O···O separation is 2.920 Å; the interchain O−H···O hydrogen bonds exist between the coordinated water molecules (O9, O10, O11, O12 and O15) and uncoordinated carboxylate oxygen atoms (O2, O3, O4) with O···O separations varying from 2.660 to 3.257 Å, which extend 1D chains into a 3D supramolecular network. Meanwhile, the lattice water molecules (O16) are intercalated between chains, forming O−H···O hydrogen bonds with the carboxylate O atoms (O2 and O5) and coordination water molecules (O12 and O15) and with each other, as indicated by the H···O and O···O distances in the ranges of 1.787−2.370 and 2.629−2.994 Å. The interchain C−H···O hydrogen bonds exist between the bpea ligand (C19 and C27) and uncoordinated carboxylate oxygen atoms (O8 and O5) with C···O separations varying from 3.148 to 3.329 Å.

Table S9. The comparison of the dihedral angles for **1-7**.

Complex	The dihedral angle of four carboxylate groups (˚)				The dihedral angle between the two phenyl rings (˚)	N-donor ligands	Dimension
	2	3	3'	4'			
1,2	70.33	37.51	62.17	36.11	60.04	phen	1D
3,4	69.36	35.33	76.10	20.66	49.54	bpea	1D
5	89.02	5.21	65.53	33.87	54.09	bipy	3D
6	78.05	30.78	77.62	9.77	48.48	bpee	3D
7	73.30	33.89	88.98	37.27	56.92	bipy	3D