Electronic supplementary information

A family of coordination polymers assembled with a flexible hexacarboxylate ligand and auxiliary N-donor ligands: syntheses, structures, and physical properties

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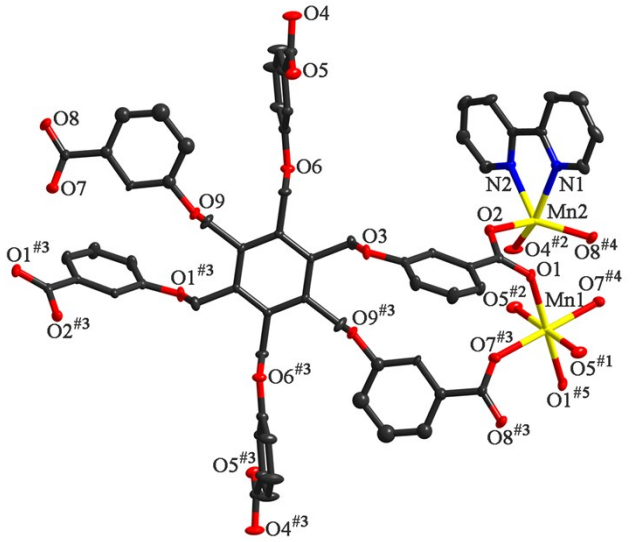

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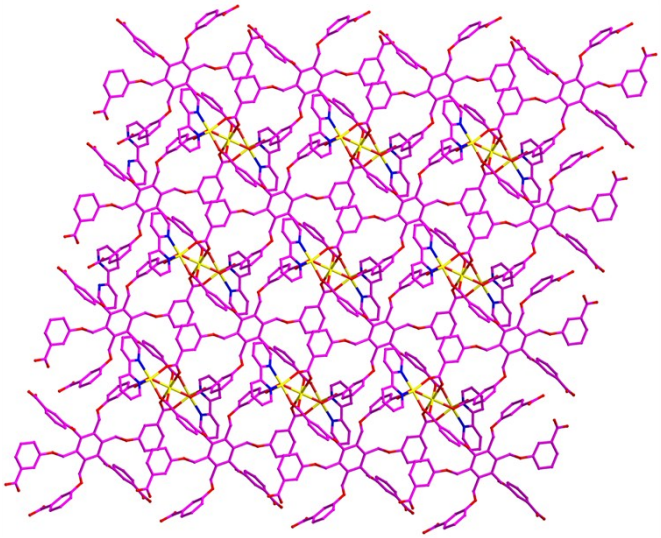

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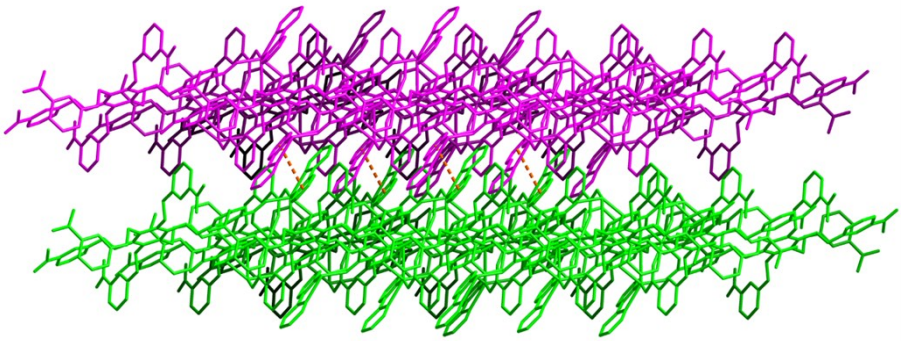
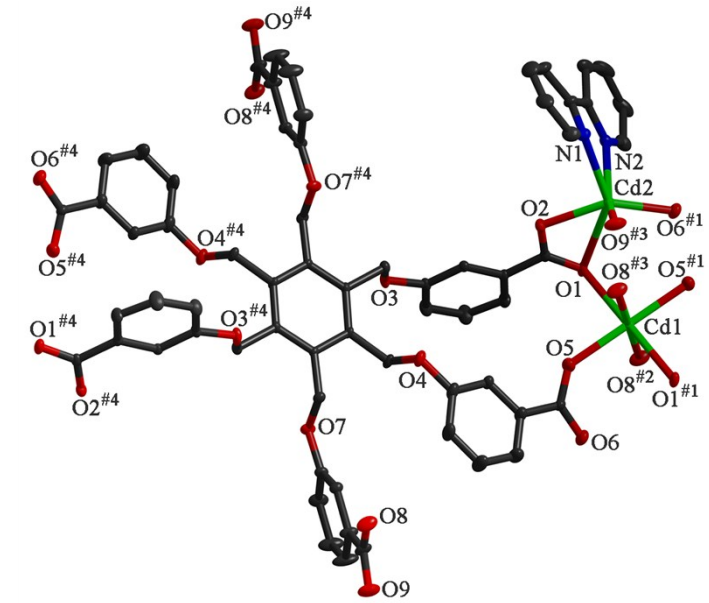


(c)

Fig. S1 (a) Coordination environments of Mn(II) ions in **3**. (b) The 2D layer built by L anions, 2,2'-bpy ligands and Mn(II) ions. (c) The 3D supramolecular architecture formed by π-π stackings.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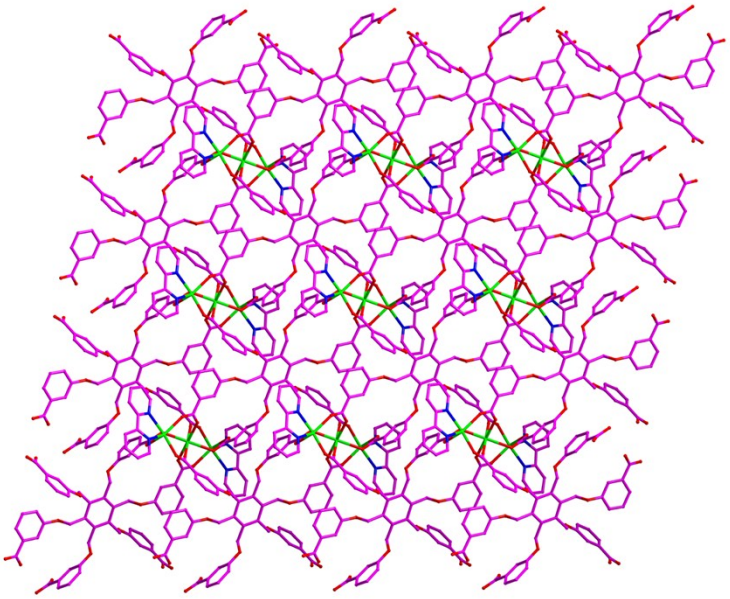

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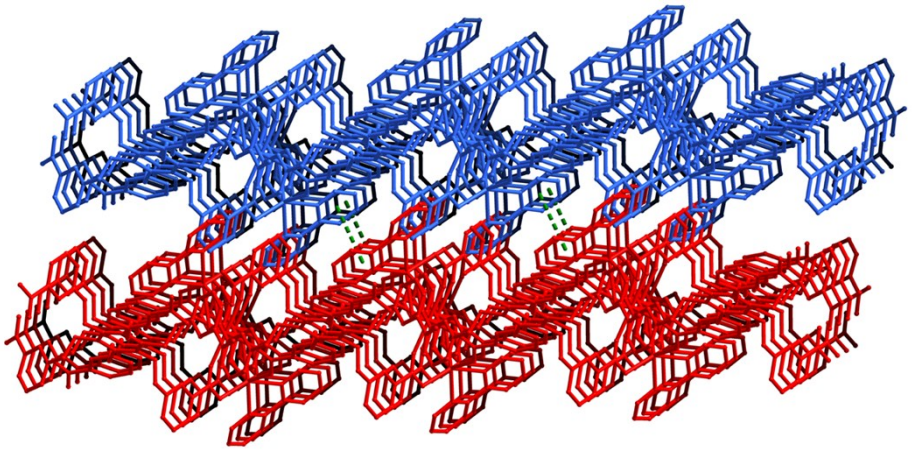
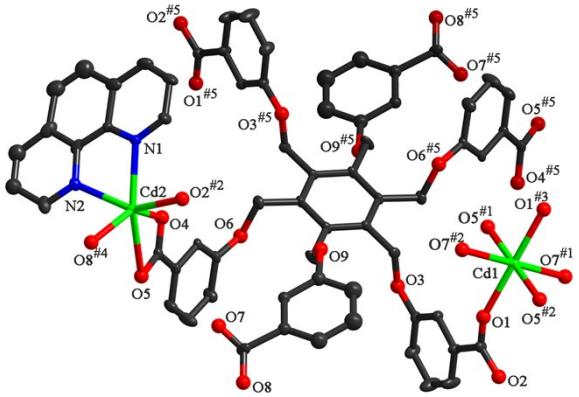


(b)

3

Fig. S2 (a) Coordination environments of Cd(II) ions in **4**. (b) The 2D layer built by L anions, 2,2'-bpy ligands and Cd(II) ions in **4**. (c) The 3D supramolecular architecture formed by π-π stackings.



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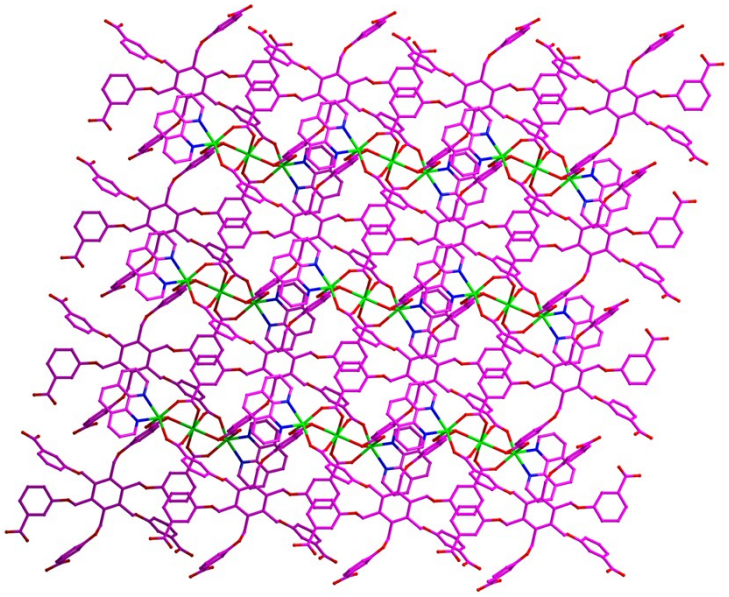

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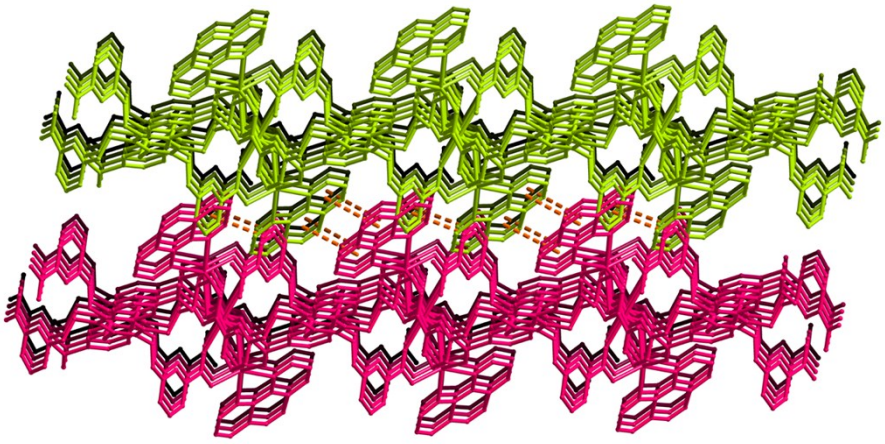

(c)

Fig. S3 (a) Coordination environments of Cd(II) ions in **5**. (b) View of the 2D layer built through L anions, phen ligands and Cd(II) ions. (c) View of the 3D supramolecular architecture formed by π-π stackings.

Table S1 Selected bond distances (Å) and angles (°) for **1**.

Mn(1)-O(1)	2.101(5)	Mn(1)-O(17)$^{\#2}$	2.195(5)
Mn(1)-O(4)	2.324(4)	Mn(2)-O(2)	2.044(5)
Mn(2)-O(8)$^{\#4}$	2.081(6)	Mn(2)-O(16)$^{\#3}$	2.088(7)
Mn(2)-O(11)$^{\#5}$	2.108(6)	Mn(2)-O(5)$^{\#1}$	2.214(4)
Mn(2)-O(4)$^{\#1}$	2.445(4)	Mn(3)-O(7)$^{\#6}$	2.110(5)
Mn(3)-O(13)$^{\#7}$	2.131(4)	Mn(3)-O(10)	2.148(6)
Mn(3)-O(14)	2.176(5)	Mn(3)-O(1W)	2.256(8)
Mn(3)-O(5)$^{\#8}$	2.279(4)	O(1)-Mn(1)-O(17)$^{\#2}$	86.7(2)
O(1)$^{\#1}$-Mn(1)-O(17)$^{\#2}$	93.3(2)	O(1)-Mn(1)-O(17)$^{\#3}$	93.3(2)
O(1)-Mn(1)-O(4)$^{\#1}$	91.36(17)	O(17)$^{\#2}$-Mn(1)-O(4)$^{\#1}$	83.22(19)
O(1)-Mn(1)-O(4)	88.64(17)	O(17)$^{\#2}$-Mn(1)-O(4)	96.78(19)
O(2)-Mn(2)-O(8)$^{\#4}$	92.8(3)	O(2)-Mn(2)-O(16)$^{\#3}$	91.1(2)
O(8)$^{\#4}$-Mn(2)-O(16)$^{\#3}$	95.4(4)	O(2)-Mn(2)-O(11)$^{\#5}$	93.0(2)
O(8)$^{\#4}$-Mn(2)-O(11)$^{\#5}$	92.1(3)	O(16)$^{\#3}$-Mn(2)-O(11)$^{\#5}$	171.3(3)
O(2)-Mn(2)-O(5)$^{\#1}$	149.51(19)	O(8)$^{\#4}$-Mn(2)-O(5)$^{\#1}$	117.7(2)
O(16)$^{\#3}$-Mn(2)-O(5)$^{\#1}$	84.6(2)	O(11)$^{\#5}$-Mn(2)-O(5)$^{\#1}$	87.9(2)
O(2)-Mn(2)-O(4)$^{\#1}$	93.87(18)	O(8)$^{\#4}$-Mn(2)-O(4)$^{\#1}$	173.3(2)
O(16)$^{\#3}$-Mn(2)-O(4)$^{\#1}$	83.7(2)	O(11)$^{\#5}$-Mn(2)-O(4)$^{\#1}$	88.3(2)
O(5)$^{\#1}$-Mn(2)-O(4)$^{\#1}$	55.67(14)	O(7)$^{\#6}$-Mn(3)-O(13)$^{\#7}$	170.4(2)
O(7)$^{\#6}$-Mn(3)-O(10)	92.1(2)	O(13)$^{\#7}$-Mn(3)-O(10)	90.9(2)
O(7)$^{\#6}$-Mn(3)-O(14)	94.7(2)	O(13)$^{\#7}$-Mn(3)-O(14)	94.28(17)
O(10)-Mn(3)-O(14)	93.5(2)	O(7)$^{\#6}$-Mn(3)-O(1W)	86.3(3)
O(13)$^{\#7}$-Mn(3)-O(1W)	91.6(2)	O(10)-Mn(3)-O(1W)	174.5(3)

O(14)-Mn(3)-O(1W)	81.4(3)	O(7)$^{\#6}$-Mn(3)-O(5)$^{\#8}$	83.51(18)
O(13)$^{\#7}$-Mn(3)-O(5)$^{\#8}$	87.07(16)	O(10)-Mn(3)-O(5)$^{\#8}$	96.32(19)
O(14)-Mn(3)-O(5)$^{\#8}$	170.04(19)	O(1W)-Mn(3)-O(5)$^{\#8}$	88.7(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y,-z+1; $^{\#2}$ -x+1,-y+1,-z+1; $^{\#3}$ x, y-1, z; $^{\#4}$ x+1, -y, z+1/2; $^{\#5}$ x+1, -y+1, z+1/2; $^{\#6}$ x, y+1, z; $^{\#7}$ -x, y, -z+1/2; $^{\#8}$ -x, y+1, -z+1/2.

Table S2 Selected bond distances (Å) and angles (°) for **2**.

Mn(1)-O(4)$^{\#1}$	2.046(3)	Mn(1)-O(8)$^{\#2}$	2.092(3)
Mn(1)-O(6)	2.092(4)	Mn(1)-N(2)	2.301(4)
Mn(1)-N(1)	2.305(4)	Mn(2)-O(7)	2.104(4)
Mn(2)-O(5)$^{\#1}$	2.141(3)	Mn(2)-O(9)$^{\#2}$	2.288(3)
O(4)$^{\#1}$-Mn(1)-O(8)$^{\#2}$	134.16(16)	O(4)$^{\#1}$-Mn(1)-O(6)	102.26(18)
O(8)$^{\#2}$-Mn(1)-O(6)	100.60(15)	O(4)$^{\#1}$-Mn(1)-N(2)	125.91(14)
O(8)$^{\#2}$-Mn(1)-N(2)	95.57(14)	O(6)-Mn(1)-N(2)	83.84(14)
O(4)$^{\#1}$-Mn(1)-N(1)	85.22(15)	O(8)$^{\#2}$-Mn(1)-N(1)	91.86(12)
O(6)-Mn(1)-N(1)	153.06(15)	N(2)-Mn(1)-N(1)	71.15(14)
O(7)-Mn(2)-O(5)$^{\#1}$	92.67(16)	O(7)-Mn(2)-O(5)$^{\#8}$	87.33(16)
O(7)-Mn(2)-O(9)$^{\#9}$	91.58(13)	O(5)$^{\#1}$-Mn(2)-O(9)$^{\#9}$	90.46(12)
O(7)-Mn(2)-O(9)$^{\#2}$	88.42(13)	O(5)$^{\#1}$-Mn(2)-O(9)$^{\#2}$	89.54(12)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, y-1, z; $^{\#2}$ x, y, z-1; $^{\#8}$ -x+2, -y+1, -z+1; $^{\#9}$ -x+2, -y, -z+2.

Table S3 Selected bond distances (Å) and angles (°) for **3**.

Mn(1)-O(5)$^{\#1}$	2.102(4)	Mn(1)-O(7)$^{\#3}$	2.131(4)
Mn(1)-O(1)	2.266(4)	Mn(2)-O(8)$^{\#4}$	2.035(4)
Mn(2)-O(4)$^{\#2}$	2.062(4)	Mn(2)-O(2)	2.075(4)
Mn(2)-N(1)	2.278(5)	Mn(2)-N(2)	2.294(4)
O(5)$^{\#1}$-Mn(1)-O(7)$^{\#3}$	92.14(18)	O(5)$^{\#1}$-Mn(1)-O(7)$^{\#4}$	87.86(18)
O(5)$^{\#1}$-Mn(1)-O(1)	91.21(16)	O(5)$^{\#2}$-Mn(1)-O(1)	88.79(16)
O(7)$^{\#3}$-Mn(1)-O(1)	90.15(15)	O(7)$^{\#4}$-Mn(1)-O(1)	89.85(15)

O(8)$^{\#4}$-Mn(2)-O(4)$^{\#2}$	100.9(2)	O(8)$^{\#4}$-Mn(2)-O(2)	133.04(18)
O(4)$^{\#2}$-Mn(2)-O(2)	100.1(2)	O(8)$^{\#4}$-Mn(2)-N(1)	86.02(19)
O(4)$^{\#2}$-Mn(2)-N(1)	152.44(17)	O(2)-Mn(2)-N(1)	94.05(17)
O(8)$^{\#4}$-Mn(2)-N(2)	125.35(18)	O(4)$^{\#2}$-Mn(2)-N(2)	84.49(17)
O(2)-Mn(2)-N(2)	98.09(17)	N(1)-Mn(2)-N(2)	70.11(18)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1, -y+1, -z-1; $^{\#2}$ x, y, z+1; $^{\#3}$ -x+1, -y+2, -z-1; $^{\#4}$ x, y-1, z+1.

Table S4 Selected bond distances (Å) and angles (°) for **4**.

Cd(1)-O(5)	2.208(5)	Cd(1)-O(8)$^{\#2}$	2.212(5)
Cd(1)-O(1)	2.384(4)	Cd(2)-O(6)$^{\#1}$	2.188(4)
Cd(2)-O(9)$^{\#3}$	2.201(5)	Cd(2)-O(2)	2.211(4)
Cd(2)-N(2)	2.348(5)	Cd(2)-N(1)	2.400(5)
O(5)-Cd(1)-O(8)$^{\#2}$	91.5(2)	O(5)-Cd(1)-O(8)$^{\#3}$	88.5(2)
O(5)$^{\#1}$-Cd(1)-O(1)	91.19(16)	O(5)-Cd(1)-O(1)	88.81(16)
O(8)$^{\#2}$-Cd(1)-O(1)	91.75(17)	O(8)$^{\#3}$-Cd(1)-O(1)	88.25(17)
O(6)$^{\#1}$-Cd(2)-O(9)$^{\#3}$	104.6(2)	O(6)$^{\#1}$-Cd(2)-O(2)	137.49(19)
O(9)$^{\#3}$-Cd(2)-O(2)	100.4(2)	O(6)$^{\#1}$-Cd(2)-N(2)	82.86(18)
O(9)$^{\#3}$-Cd(2)-N(2)	146.15(19)	O(2)-Cd(2)-N(2)	94.98(16)
O(6)$^{\#1}$-Cd(2)-N(1)	123.82(19)	O(9)$^{\#3}$-Cd(2)-N(1)	81.70(19)
O(2)-Cd(2)-N(1)	93.23(17)	N(2)-Cd(2)-N(1)	67.39(19)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+2, -y, -z+2; $^{\#2}$ x, y+1, z; $^{\#3}$ -x+2, -y-1, -z+2.

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

Cd(1)-O(7)$^{\#1}$	2.208(6)	Cd(1)-O(1)	2.212(6)
Cd(1)-O(5)$^{\#1}$	2.403(5)	Cd(2)-O(8)$^{\#4}$	2.186(6)
Cd(2)-O(2)$^{\#2}$	2.205(6)	Cd(2)-O(4)	2.215(5)
Cd(2)-N(2)	2.370(6)	Cd(2)-N(1)	2.389(6)
O(7)$^{\#1}$-Cd(1)-O(1)	92.6(3)	O(7)$^{\#2}$-Cd(1)-O(1)	87.4(3)
O(7)$^{\#1}$-Cd(1)-O(5)$^{\#1}$	88.64(19)	O(1)-Cd(1)-O(5)$^{\#1}$	92.3(2)

O(7)$^{\#1}$-Cd(1)-O(5)$^{\#2}$	91.36(19)	O(1)-Cd(1)-O(5)$^{\#2}$	87.7(2)
O(8)$^{\#4}$-Cd(2)-O(2)$^{\#2}$	105.4(3)	O(8)$^{\#4}$-Cd(2)-O(4)	135.5(2)
O(2)$^{\#2}$-Cd(2)-O(4)	101.7(3)	O(8)$^{\#4}$-Cd(2)-N(2)	82.4(3)
O(2)$^{\#2}$-Cd(2)-N(2)	147.1(2)	O(4)-Cd(2)-N(2)	93.4(2)
O(8)$^{\#4}$-Cd(2)-N(1)	125.7(2)	O(2)$^{\#2}$-Cd(2)-N(1)	81.2(2)
O(4)-Cd(2)-N(1)	92.7(2)	N(2)-Cd(2)-N(1)	68.9(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, y+1, z; $^{\#2}$ -x, -y+1, -z+2; $^{\#4}$ -x, -y, -z+2.

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

Co(1)-O(18)$^{\#1}$	2.005(3)	Co(1)-O(16)	2.083(2)
Co(1)-O(7)$^{\#2}$	2.098(3)	Co(1)-N(4)	2.100(4)
Co(1)-N(3)	2.158(3)	Co(1)-O(8)$^{\#2}$	2.385(4)
Co(2)-O(15)	2.049(3)	Co(2)-O(14)$^{\#1}$	2.049(3)
Co(2)-N(2)	2.123(3)	Co(2)-N(1)	2.127(3)
Co(2)-O(10)$^{\#3}$	2.130(3)	Co(2)-O(9)$^{\#3}$	2.258(3)
Na(1)-O(11)	2.246(4)	Na(1)-O(17)$^{\#4}$	2.292(3)
Na(1)-O(8)$^{\#5}$	2.304(3)	Na(1)-O(16)$^{\#6}$	2.365(3)
Na(1)-O(9)	2.432(3)	Na(1)-O(14)$^{\#4}$	2.506(3)
O(18)$^{\#1}$-Co(1)-O(16)	98.69(12)	O(18)$^{\#1}$-Co(1)-O(7)$^{\#2}$	95.48(13)
O(16)-Co(1)-O(7)$^{\#2}$	141.71(13)	O(18)$^{\#1}$-Co(1)-N(4)	92.08(14)
O(16)-Co(1)-N(4)	119.57(13)	O(7)$^{\#2}$-Co(1)-N(4)	95.11(14)
O(18)$^{\#1}$-Co(1)-N(3)	168.94(14)	O(16)-Co(1)-N(3)	83.99(11)
O(7)$^{\#2}$-Co(1)-N(3)	88.80(12)	N(4)-Co(1)-N(3)	77.36(14)
O(18)$^{\#1}$-Co(1)-O(8)$^{\#2}$	99.34(13)	O(16)-Co(1)-O(8)$^{\#2}$	85.06(11)
O(7)$^{\#2}$-Co(1)-O(8)$^{\#2}$	57.53(11)	N(4)-Co(1)-O(8)$^{\#2}$	151.04(12)
N(3)-Co(1)-O(8)$^{\#2}$	91.57(13)	O(15)-Co(2)-O(14)$^{\#1}$	97.77(11)
O(15)-Co(2)-N(2)	103.81(12)	O(14)$^{\#1}$-Co(2)-N(2)	98.40(12)

O(15)-Co(2)-N(1)	83.12(12)	O(14)$^{\#1}$-Co(2)-N(1)	176.12(12)
N(2)-Co(2)-N(1)	77.73(13)	O(15)-Co(2)-O(10)$^{\#3}$	156.50(11)
O(14)$^{\#1}$-Co(2)-O(10)$^{\#3}$	92.48(12)	N(2)-Co(2)-O(10)$^{\#3}$	95.48(12)
N(1)-Co(2)-O(10)$^{\#3}$	88.07(12)	O(15)-Co(2)-O(9)$^{\#3}$	99.27(10)
O(14)$^{\#1}$-Co(2)-O(9)$^{\#3}$	88.08(10)	N(2)-Co(2)-O(9)$^{\#3}$	154.88(12)
N(1)-Co(2)-O(9)$^{\#3}$	95.51(11)	O(10)$^{\#3}$-Co(2)-O(9)$^{\#3}$	59.86(10)
O(11)-Na(1)-O(17)$^{\#4}$	93.46(13)	O(11)-Na(1)-O(8)$^{\#5}$	104.60(13)
O(17)$^{\#4}$-Na(1)-O(8)$^{\#5}$	94.42(14)	O(11)-Na(1)-O(16)$^{\#6}$	173.08(13)
O(17)$^{\#4}$-Na(1)-O(16)$^{\#6}$	81.76(12)	O(8)$^{\#5}$-Na(1)-O(16)$^{\#6}$	80.86(12)
O(11)-Na(1)-O(9)	90.45(12)	O(17)$^{\#4}$-Na(1)-O(9)	166.79(14)
O(8)$^{\#5}$-Na(1)-O(9)	96.80(12)	O(16)$^{\#6}$-Na(1)-O(9)	93.13(10)
O(11)-Na(1)-O(14)$^{\#4}$	91.07(12)	O(17)$^{\#4}$-Na(1)-O(14)$^{\#4}$	92.55(12)
O(8)$^{\#5}$-Na(1)-O(14)$^{\#4}$	162.40(13)	O(16)$^{\#6}$-Na(1)-O(14)$^{\#4}$	84.17(10)
O(9)-Na(1)-O(14)$^{\#4}$	74.75(9)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1/2, y+1/2, -z+3/2; $^{\#2}$ -x, -y, -z+1; $^{\#3}$ x, y, z-1; $^{\#4}$ -x+1/2, y+1/2, -z+5/2; $^{\#5}$ -x, -y, -z+2; $^{\#6}$ x, y, z+1.

Table S7 Selected bond distances (Å) and angles (°) for **7**.

Co(1)-O(8)$^{\#2}$	2.047(3)	Co(1)-O(4)$^{\#4}$	2.117(4)
Co(1)-O(2)	2.123(3)	Co(2)-O(7)$^{\#2}$	1.952(4)
Co(2)-O(5)$^{\#4}$	1.963(4)	Co(2)-O(1)	2.021(3)
Co(2)-N(1)	2.072(4)	Co(2)-O(2)	2.237(3)
O(8)$^{\#2}$-Co(1)-O(4)$^{\#4}$	92.31(14)	O(8)$^{\#2}$-Co(1)-O(4)$^{\#3}$	87.69(14)
O(8)$^{\#2}$-Co(1)-O(2)	92.84(13)	O(8)$^{\#1}$-Co(1)-O(2)	87.16(13)
O(4)$^{\#4}$-Co(1)-O(2)	90.59(13)	O(4)$^{\#3}$-Co(1)-O(2)	89.41(13)
O(7)$^{\#2}$-Co(2)-O(5)$^{\#4}$	125.46(16)	O(7)$^{\#2}$-Co(2)-O(1)	116.99(18)
O(5)$^{\#4}$-Co(2)-O(1)	112.13(16)	O(7)$^{\#2}$-Co(2)-N(1)	84.83(16)
O(5)$^{\#4}$-Co(2)-N(1)	105.94(16)	O(1)-Co(2)-N(1)	103.25(15)
O(7)$^{\#2}$-Co(2)-O(2)	92.81(14)	O(5)$^{\#4}$-Co(2)-O(2)	91.35(14)

O(1)-Co(2)-O(2)	60.55(13)	N(1)-Co(2)-O(2)	160.33(16)

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

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

Cu(1)-N(2)	2.033(10)	Cu(1)-N(4)	2.046(8)
Cu(1)-N(3)	2.060(8)	Cu(1)-N(1)	2.039(10)
N(2)-Cu(1)-N(4)	110.7(5)	N(2)-Cu(1)-N(3)	110.5(5)
N(4)-Cu(1)-N(3)	106.0(5)	N(2)-Cu(1)-N(1)	104.1(5)
N(4)-Cu(1)-N(1)	113.3(5)	N(3)-Cu(1)-N(1)	112.3(6)

Table S9a Selected bond distances (Å) and angles (°) for **9**.

Cu(1)-N(2)	1.928(3)	Cu(1)-O(1)	1.935(3)
Cu(1)-N(1)	2.008(3)	Cu(1)-N(3)	2.020(3)
Cu(1)-O(8)#1	2.141(2)	N(2)-Cu(1)-O(1)	157.41(11)
N(2)-Cu(1)-N(1)	79.72(12)	O(1)-Cu(1)-N(1)	94.91(12)
N(2)-Cu(1)-N(3)	79.44(12)	O(1)-Cu(1)-N(3)	103.21(12)
N(1)-Cu(1)-N(3)	158.94(13)	N(2)-Cu(1)-O(8)#1	111.52(11)
O(1)-Cu(1)-O(8)#1	90.94(11)	N(1)-Cu(1)-O(8)#1	99.03(11)
N(3)-Cu(1)-O(8)#1	91.39(11)		

Table S9b Hydrogen bonds for **9** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(10)-H(10)...O(8)	0.82	2.09	2.839(4)	151.5
O(1W)-H(1A)...O(2)	0.914(10)	2.03(3)	2.898(6)	159(8)
O(6)-H(6)...O(9)#4	0.96(7)	1.62(7)	2.548(5)	161(6)
O(1W)-H(1B)...O(5)#5	0.911(10)	2.029(19)	2.924(6)	167(7)

Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z; #4 x+1, y+1, z; #5 -x+1, -y+1, -z.