Electronic Supplementary Information (ESI)

Syntheses, crystal structures and properties of transition metal coordination polymers based on isophthalic acid and flexible bis(pyridyl) ligand with unsymmetrical spacer: influence of metal cations, ligand conformations and coordination modes†

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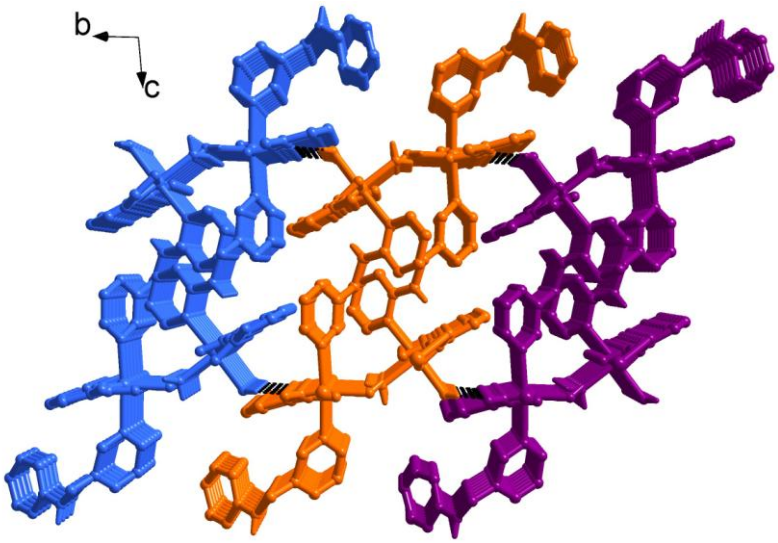


Fig. S1 3-D hydrogen-bonding supramolecular network.

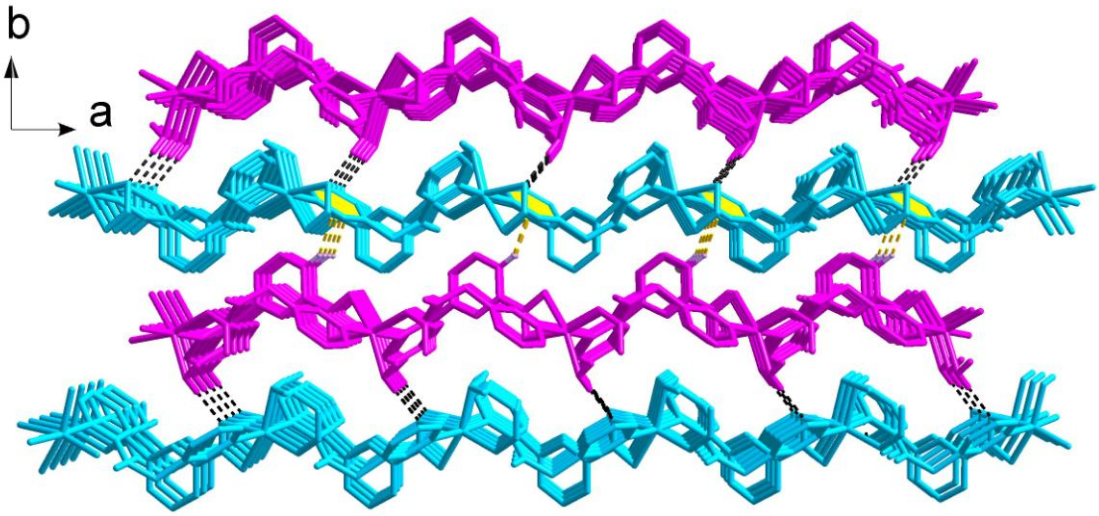


Fig. S2 3-D network extended by the C-H···π interactions (yellow dashed lines).

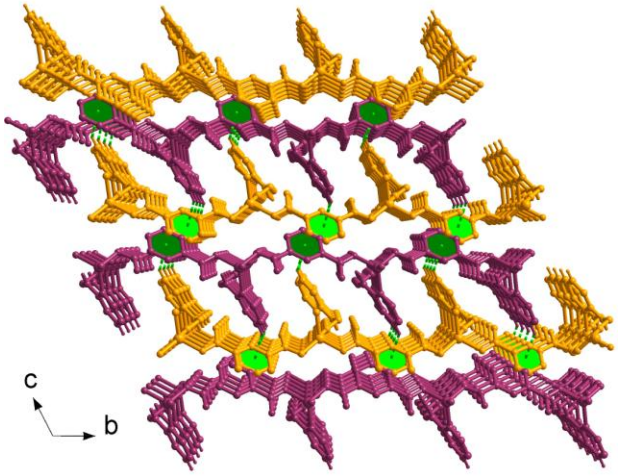


Fig. S3 3-D network linked by the interlayer C-H···π interactions with adjacent sheets packed in an

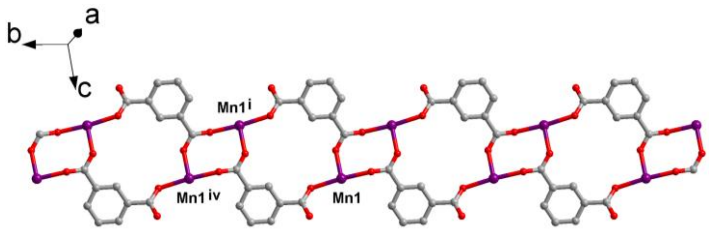


Fig. S4 1-D double chain along the [010] direction formed by the carboxyl groups linking Mn(II) cations.

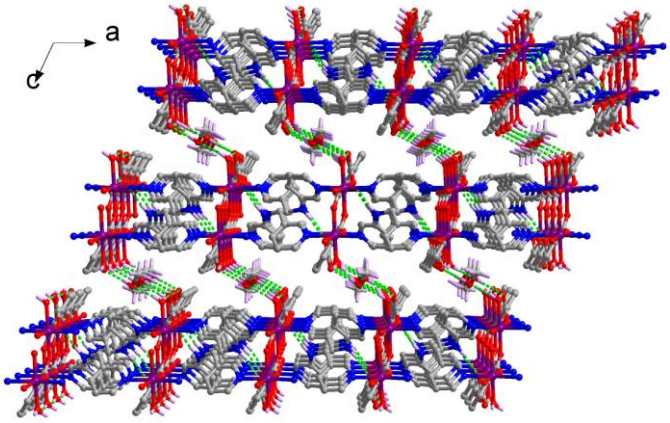


Fig. S5 3-D network linked by the interlayer O-H···O hydrogen bonds.

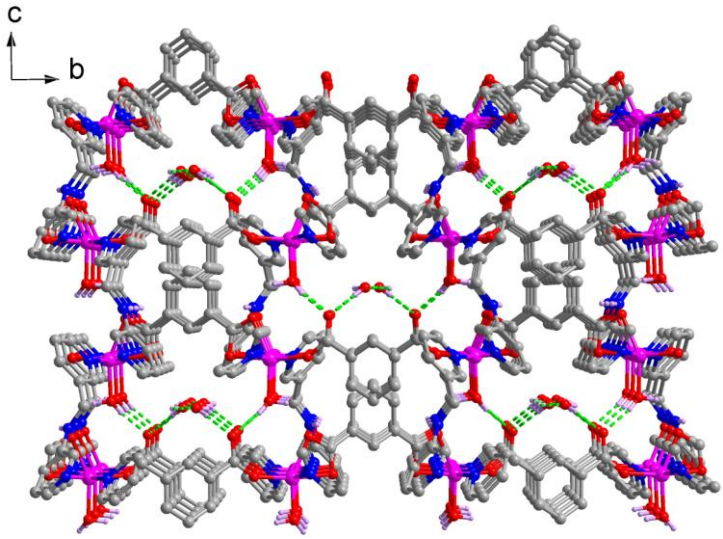


Fig. S6 The 3-D network of complex **6** along the [100] direction with the

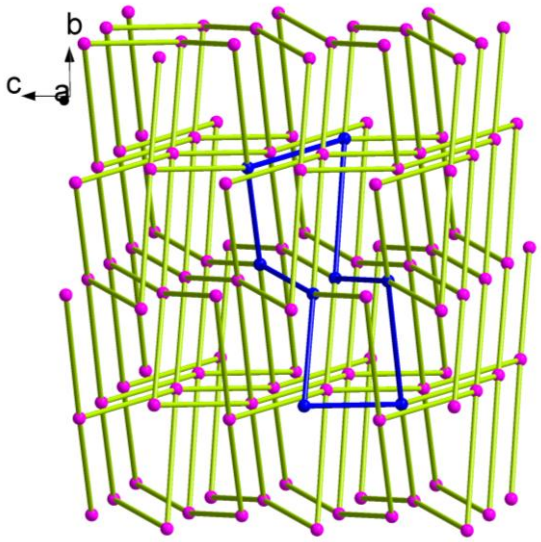


Fig. S7 Schematic illustrating of the **tcb** topology of complex **6** with the shortest six-membered rings denoted as blue lines and balls.

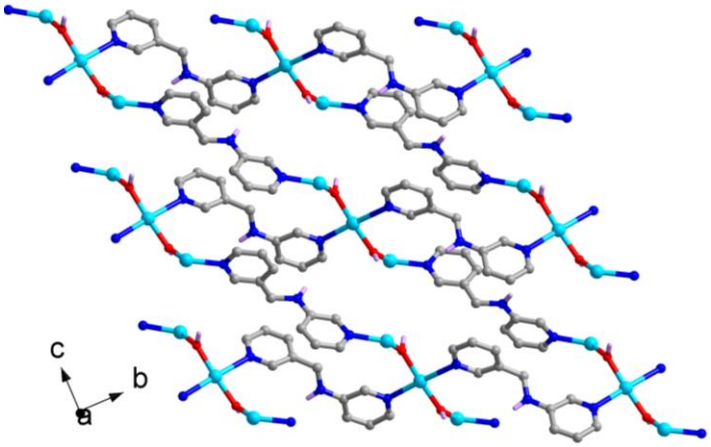
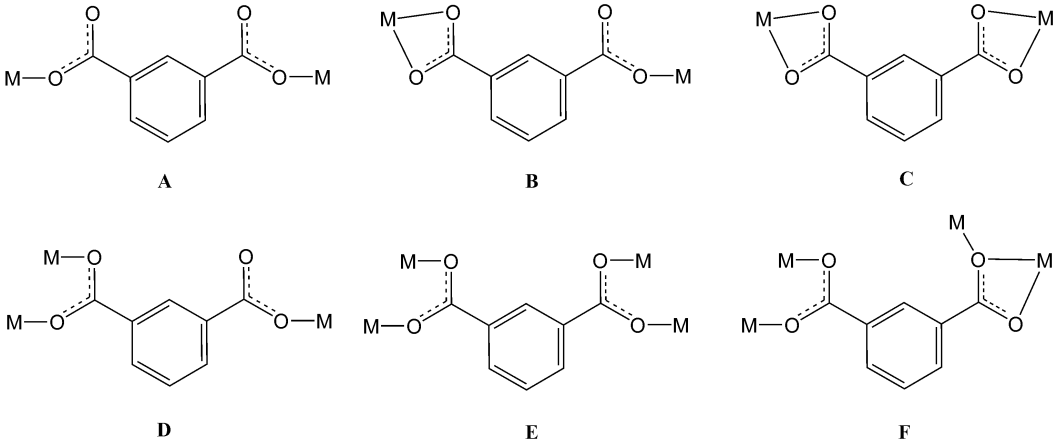


Fig. S8 2-D Layer motif in complex **8** formed by the **L2** molecules linking $[Zn_3(OH)_2]$ clusters.



Scheme S1 Coordination modes of ip dianions in the eight complexes.

PXRD Analysis. Powder X-ray diffraction (PXRD) patterns for solid samples of complexes **1-8** are measured at room temperature as illustrated in Fig. S9. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples.

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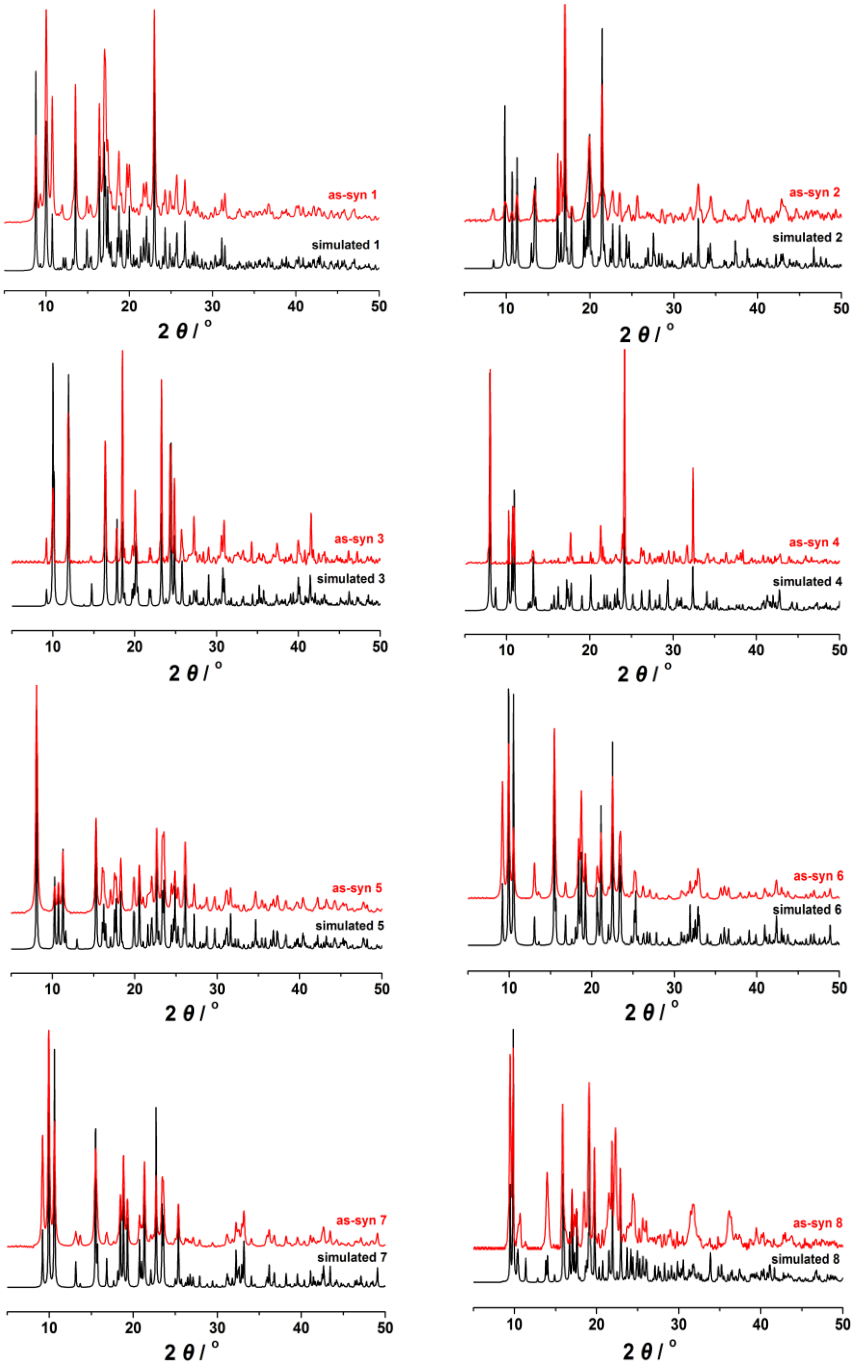

Fig. S9 PXRD patterns for complexes **1**-**8**.

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Thermogravimetric analysis

To examine the thermal stability of the complexes, in this study, their stabilities were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 900 ℃ at a rate of 10 °C min^{-1}, under N_2 atmosphere. As shown in Fig. S10, the TGA curve indicates that complex **1** loses the lattice and coordinated water molecules from 50 to 157 °C with the observed weight loss of 8.24% (calcd 8.18%). The following gradually weigh losses correspond to the loss of the organic components occurs in the temperature range 265-870 °C. The remaining component corresponds to Mn_2O_3 (obsd 17.64%, calcd 17.93%). The weight loss corresponding to the release of the coordinated water molecules is observed from 70 to 180 °C (obsd 4.01%, calcd 4.23%) in complex **2**. The following weight loss completes at 468 °C, leading to the formation of CoO as the residue (obsd 17.21%, calcd 17.58%). Complex **3** exhibits nearly one step loss with the decomposing of organic components occuring in the temperature range 230-650 °C, and the final remaining component is ZnO (obsd 19.82%, calcd 19.62%). The decomposing of organic components in complex **4** occurs between 304 and 730 °C with the remaining component being CdO (obsd 34.58%, calcd 34.79%). Complex **5** loses the free methanol and coordinated water molecules from 54 to 185 °C with the observed weight loss of 11.14% (calcd 11.02%). Then, the following weight loss with the decomposing of organic components occurs in the temperature range 348-864 °C, and the final remaining component is Mn_2O_3 (obsd 17.16%, calcd 17.37%). Complexes **6** and **7** exhibit the similar loss steps. The first step corresponds to the loss of lattice and coordinated water molecules in the temperature range 58-192 °C for **6** and 58-192 °C for **7** (obsd 8.01% for **6** and 8.08% for **7**, calcd 8.11% for **6** and **7**). Then, the following weight loss with the decomposing of organic components occurs in the temperature range 360-464 °C (complex **6**) and 380-473 °C (complex **7**), and the final remaining component corresponds to CoO (obsd 16.63%, calcd 16.86%) and NiO (obsd 17.06%, calcd 16.82%), respectively. Complex **8** also exhibits nearly one step loss with the decomposing of organic components occuring in the temperature range 202-524 °C, and the final remaining component is ZnO (obsd 26.37%, calcd 26.29%).

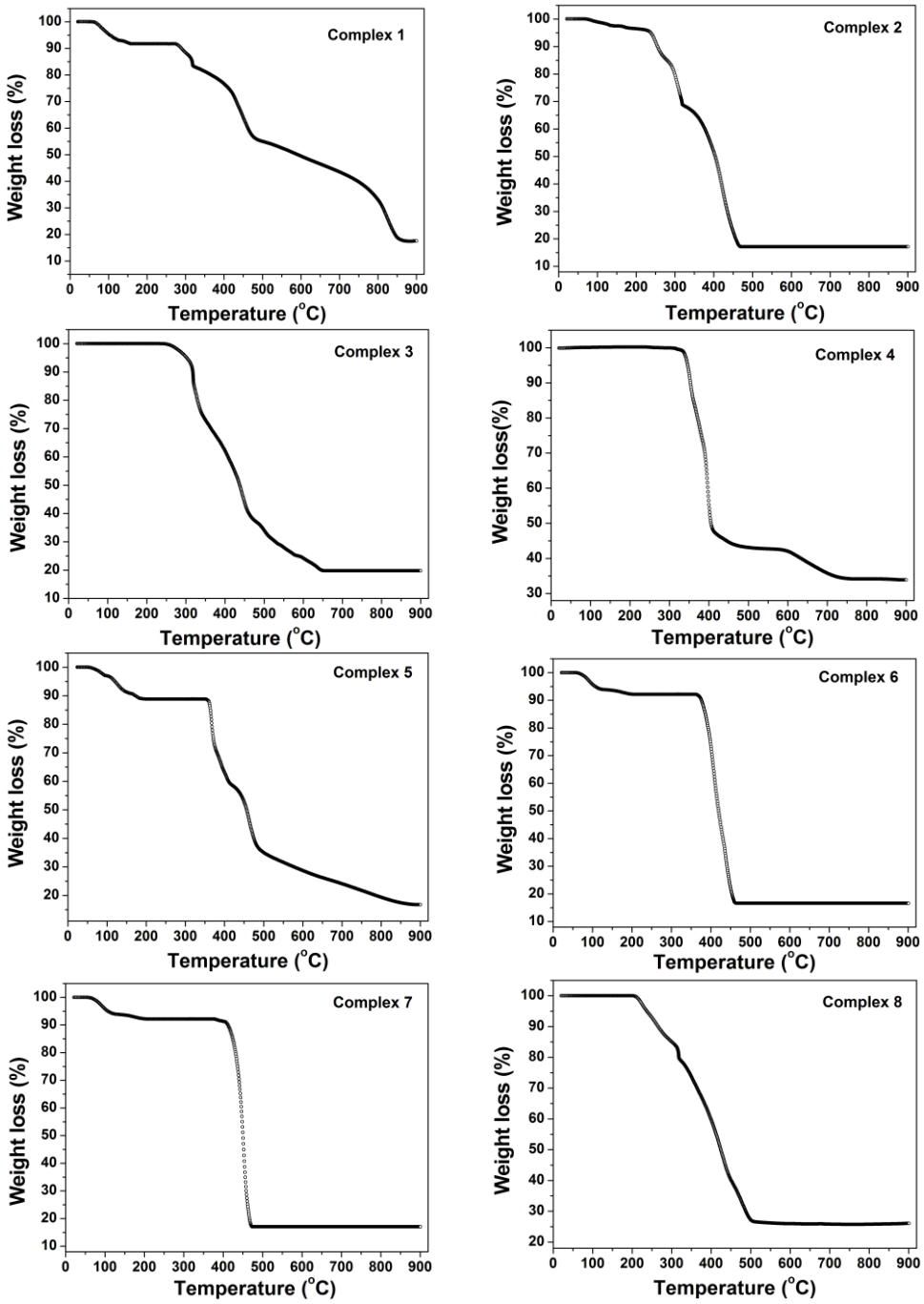

Fig. S10 TG curves of complexes **1-8**.

Table S1 Selected bond lengths (Å) data of complexes **1-8**[a]

		Complex 1	
Mn(1)-O(1)	2.127(5)	Mn(2)-O(5)	2.119(5)
Mn(1)-O(2W)	2.160(5)	Mn(2)-O(3W)	2.123(5)
Mn(1)-O(1W)	2.196(4)	Mn(2)-N(3)	2.204(6)
Mn(1)-O(4)^{i}	2.269(5)	Mn(2)-O(8)^{ii}	2.240(5)
Mn(1)-N(1)	2.273(7)	Mn(2)-N(4)	2.269(6)
Mn(1)-O(3)^{i}	2.324(5)	Mn(2)-O(7)^{ii}	2.325(5)
		Complex 2	
Co(1)-O(3)^{i}	2.089(6)	Co(2)-O(8)^{i}	2.044(6)
Co(1)-O(1W)	2.087(6)	Co(2)-O(2W)	2.081(8)
Co(1)-O(1)	2.130(6)	Co(2)-O(6)	2.111(6)
Co(1)-O(2)	2.166(6)	Co(2)-N(4)	2.199(8)
Co(1)-N(3)^{ii}	2.186(8)	Co(2)-N(6)^{ii}	2.200(7)
Co(1)-N(1)	2.240(7)	Co(2)-O(5)	2.208(6)
		Complex 3	
Zn(1)-O(3)^{i}	1.983(2)	Zn(1)-N(3)^{ii}	2.010(2)
Zn(1)-O(1)	1.9882(19)	Zn(1)-N(1)	2.054(2)
		Complex 4	
Cd(1)-O(1)	2.240(3)	Cd(2)-O(6)	2.234(3)
Cd(1)-O(3)^{i}	2.248(3)	Cd(2)-O(8)^{i}	2.254(3)
Cd(1)-O(5)	2.317(3)	Cd(2)-O(4)^{iii}	2.307(3)
Cd(1)-O(7)^{ii}	2.342(3)	Cd(2)-O(2)	2.316(3)
Cd(1)-N(1)	2.405(4)	Cd(2)-N(3)^{iv}	2.360(4)
Cd(1)-O(4)^{i}	2.540(3)	Cd(2)-O(7)^{i}	2.583(3)
		Complex 5	
Mn(1)-O(4)^{i}	2.129(2)	Mn(1)-N(1)	2.244(3)
Mn(1)-O(3)^{ii}	2.146(2)	Mn(1)-O(1)	2.262(2)
Mn(1)-O(1W)	2.214(2)	Mn(1)-N(3)^{iii}	2.277(3)
		Complex 6	
Co(1)-O(3)	1.995(2)	Co(1)-O(2)	2.155(2)
Co(1)-O(1W)	2.026(3)	Co(1)-N(1)	2.167(3)

Co(1)-N(3)^{i}	2.134(3)	Co(1)-O(1)	2.201(3)
		Complex 7	
Ni(1)-O(3)	1.987(3)	Ni(1)-N(3)^{i}	2.112(3)
Ni(1)-O(1W)	2.019(4)	Ni(1)-O(2)	2.149(2)
Ni(1)-N(1)	2.145(3)	Ni(1)-O(1)	2.195(3)
		Complex 8	
Zn(1)-O(9)	1.873(4)	Zn(2)-O(2)	2.128(4)
Zn(1)-O(5)	1.966(4)	Zn(2)-N(4)	2.318(5)
Zn(1)-O(1)	1.996(4)	Zn(2)-N(6)^{i}	2.517(6)
Zn(1)-N(1)	2.062(5)	Zn(3)-O(10)	1.873(4)
Zn(1)-O(6)	2.728(5)^{b}	Zn(3)-O(3)^{ii}	1.956(4)
Zn(2)-O(9)	1.976(4)	Zn(3)-O(8)	1.981(4)
Zn(2)-O(10)	1.987(4)	Zn(3)-N(3)^{iii}	2.082(5)
Zn(2)-O(7)	2.119(4)		

^{a} Symmetry operations: **For 1**, i x+1,y,z; ii x-1,y,z. **For 2**, i x-1,y,z-1; ii x+1,y,z. **For 3**, i x,y+1,z; ii x+1,y,z. **For 4**, i x+1/2,-y+1/2,z+1/2; ii -x+1,-y,-z+1; iii -x+1,-y+1,-z+1; iv x+1,y,z. **For 5**, i -x+1,-y+1,-z; ii x,y-1,z; iii x+1,y+1,z. **For 6**, i x-1,-y+3/2,z-1/2. **For 7**, i x-1,-y+3/2,z-1/2. **For 8**, i -x+3/2,y+1/2,z-1/2; ii x+1/2,-y+3/2,z+1/2; iii -x+3/2,y-1/2,z+3/2.

^{b} Zn(1)-O(6) is a longer contact, which also has been indicated in the main text.

Table 2 Hydrogen bond parameters for complexes **1-8**[a]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
	Complex 1			
O(1W)-H(1W1)...O(8)^{iii}	0.82	2.09	2.838(6)	152.1
O(1W)-H(1W2)...O(5)^{iv}	0.82	2.00	2.744(7)	151.5
O(2W)-H(2W1)...O(7)^{v}	0.82	2.24	3.047(6)	169.4
O(2W)-H(2W2)...N(6)^{vi}	0.82	1.94	2.750(8)	168.9
O(3W)-H(3W1)...O(2)^{vii}	0.82	1.92	2.736(7)	178.7
O(3W)-H(3W2)...O(4W)	0.82	1.86	2.684(7)	177.3
O(4W)-H(4W1)...O(4)^{vii}	0.82	1.84	2.661(7)	177.9
O(4W)-H(4W2)...O(6)	0.82	1.89	2.711(8)	177.9
N(2)-H(2N)...O(1)	0.86(9)	2.12(9)	2.976(9)	175(8)
N(5)-H(5N)...O(6)^{viii}	0.86(9)	2.50(5)	3.245(10)	145(7)
O(1W)-H(1W1)...O(8)^{iii}	0.82	2.09	2.838(6)	152.1
	Complex 2			
O(1W)-H(1W1)...O(4)^{i}	0.82	1.84	2.661(8)	174.1
O(1W)-H(1W1)...O(3)^{i}	0.82	2.49	3.022(9)	123.6
O(1W)-H(1W2)...O(5)^{iv}	0.82	2.00	2.818(9)	174.4
O(2W)-H(2W1)...O(7)^{i}	0.85(5)	1.82(4)	2.629(9)	157(9)
O(2W)-H(2W2)...N(4)	0.85(5)	2.61(10)	3.010(10)	110(8)
N(2)-H(2N)...O(3)^{i}	0.86	2.11	2.897(11)	152.6
N(5)-H(5N)...O(8)^{i}	0.86	2.11	2.873(11)	147.8
	Complex 3			
N(2)-H(2N)...O(1)	0.854(10)	2.170(12)	3.011(3)	168(3)
	Complex 4			
N(2)-H(2N)...O(7)^{ii}	0.86	2.23	3.075(6)	168.2
	Complex 5			
N(2)-H(2N)...O(1)^{vi}	0.86(4)	2.340(16)	3.172(4)	162(3)
O(1W)-H(1W1)...O(2)	0.85(3)	1.766(13)	2.599(3)	166(4)
O(1W)-H(1W2)...O(5)^{vii}	0.86(4)	1.941(12)	2.790(4)	173(4)

O(5)-H(5O)...O(2)^{viii}	0.86(5)	2.052(12)	2.906(5)	176(6)
Complex 6				
O(1W)-H(1W2)...O(1)^{v}	0.85(4)	2.07(6)	2.643(4)	124(5)
O(1W)-H(1W1)...O(4)^{v}	0.85(4)	1.83(4)	2.653(4)	162(5)
O(2W)-H(2W2)...O(2)	0.85	2.16	2.994(9)	169.1
O(2W)-H(2W1)...O(4)^{v}	0.85	2.19	3.031(9)	169.1
Complex 7				
O(1W)-H(1W1)...O(1)^{v}	0.85	1.79	2.639(4)	173.4
O(1W)-H(1W2)...O(4)^{v}	0.85	1.79	2.640(5)	173.1
O(2W)-H(2W1)...O(2)	0.85	2.14	2.977(9)	169.2
O(2W)-H(2W2)...O(4)^{v}	0.85	2.17	3.006(10)	169.3
Complex 8				
O(9)-H(9O)...O(4)^{ix}	0.85(4)	2.06(4)	2.826(6)	150(6)
O(10)-H(10O)...O(6)^{x}	0.85(4)	2.08(3)	2.858(6)	152(6)

[a] Symmetry operations: **For 1**, iii -x+2,-y+1,-z+1; iv -x+1,-y+1,-z+1; v -x+2,-y,-z+1; vi x+1,y-1,z-1; vii -x+1,-y,-z+1; viii -x+1,-y+1,-z+2. **For 2**, i x-1,y,z-1; iv x-1,y,z. **For 4**, ii -x+1,-y,-z+1. **For 5**, vi -x,-y,-z; vii x+1,y,z; viii -x+1,-y+1,-z+1. **For 6**, v x,-y+3/2,z+1/2. **For 7**, v x,-y+3/2,z+1/2. **For 8**, ix x+1/2,-y+3/2,z-1/2; x x,y,z+1.