Electronic Supplementary Information (ESI) for B818567K

Structural diversity and modulation of metal-organic coordination frameworks with a flexible V-shaped dicarboxyl building block

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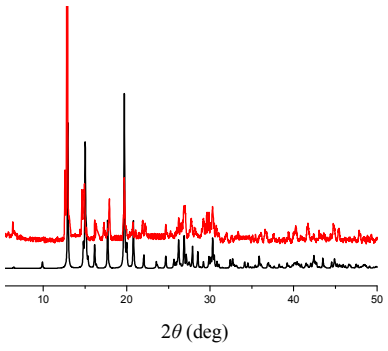
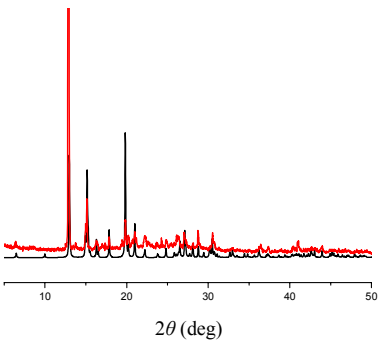


(*a*)



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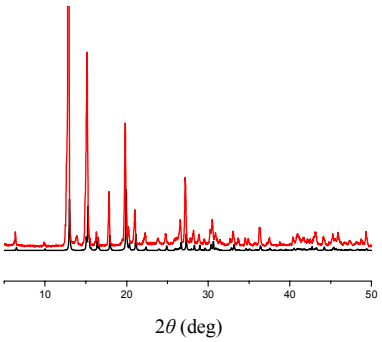

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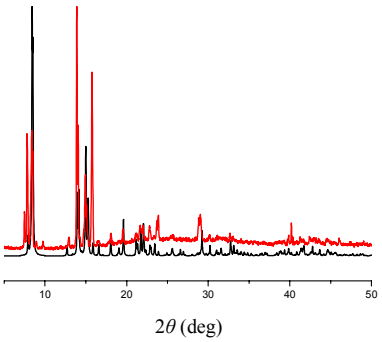

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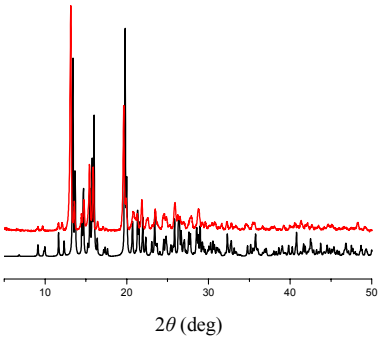

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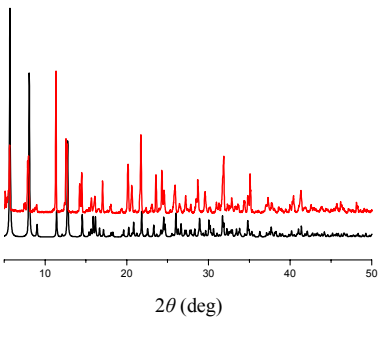
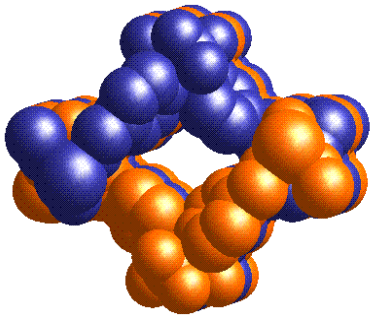


(*f*)

Fig. S1 Experimental (red) and calculated (black) PXRD patterns for 1–6 (from *a* to *f*).



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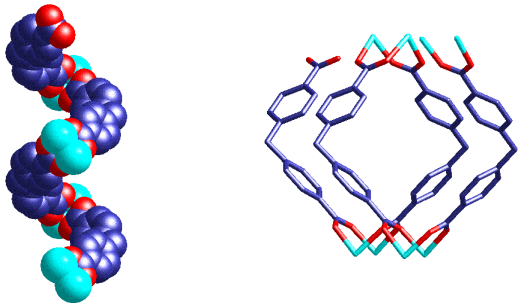
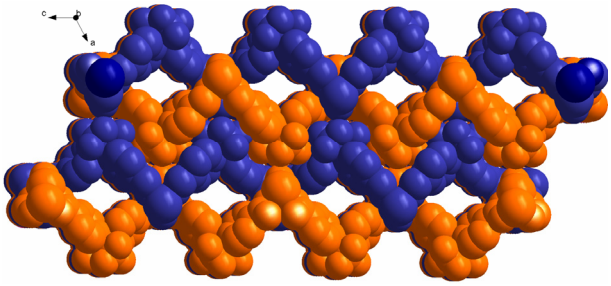
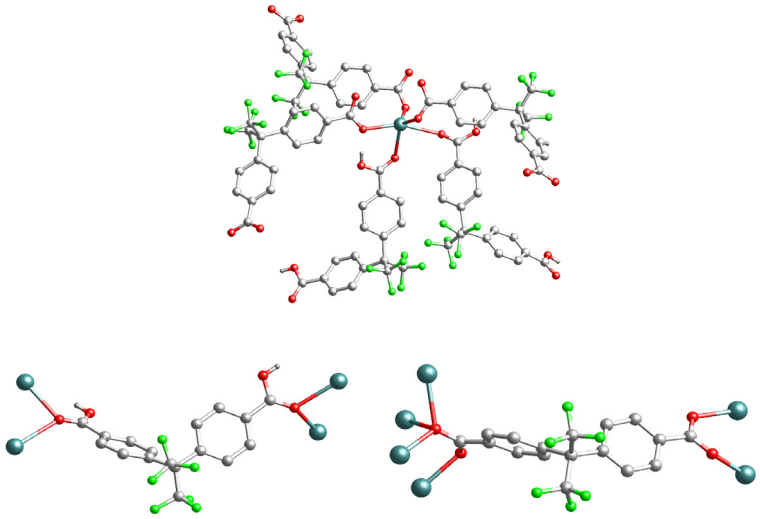


(*b*)

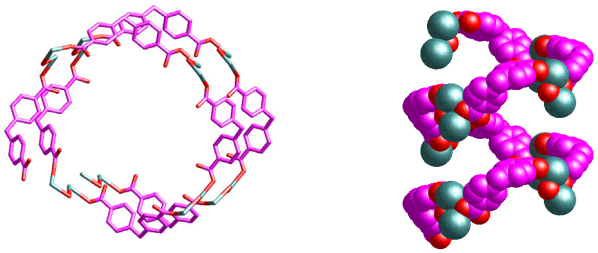


(*c*)

Fig. S2 Views of 4. (*a*) Tubular channel within the 2-fold interpenetrating array. (*b*) Infinite helical chain: (left) side view in space-filling model and (right) perspective view along the 2_1 axis. (*c*) 3-D microporous supramolecular framework in space-filling model (the adjacent 2-D coordination layers are shown in different colors).



(*a*)



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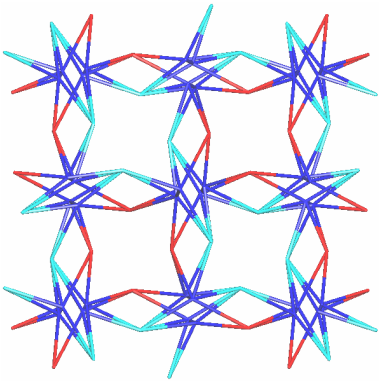
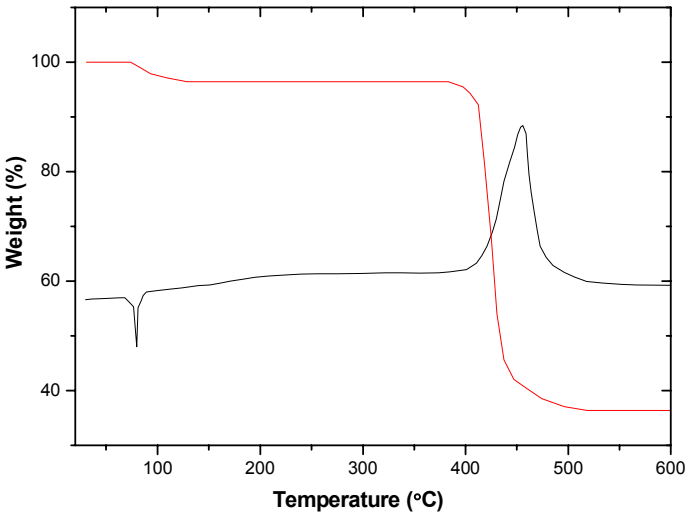


(*c*)

Fig. S3 Views of 6. (*a*) Connectivity of (above) Ag1 and (below) H_2L/L in the 3-D network, indicating 5-, 4-, and 6-connected nodes, respectively. (*b*) Infinite helical chain: (left) perspective view along the 4_2 axis and (right) side view in space-filling model. (*c*) A schematic illustration of the (4,5,6)-connected net topology (red for H_2L, blue for Ag^I, and cyan for L).


Weight (%)
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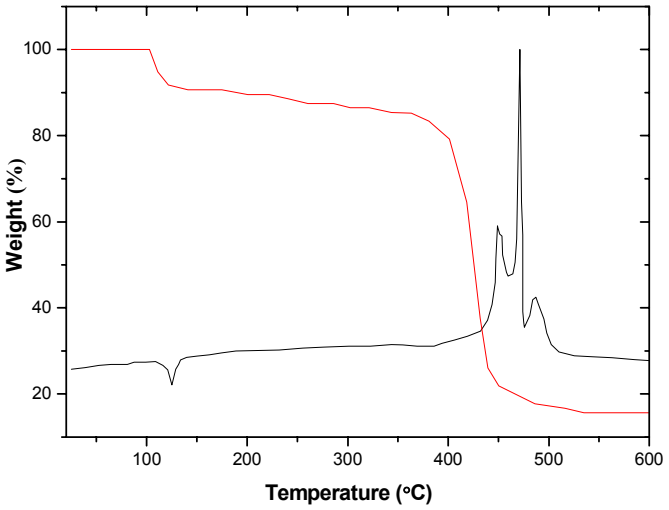
80
60
40
100
200
300
400
500
600
Temperature (°C)

(*a*)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500
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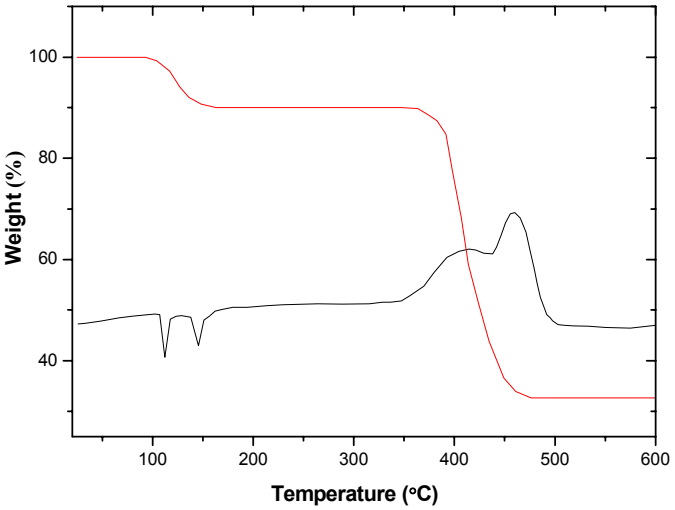
Temperature (°C)

(*b*)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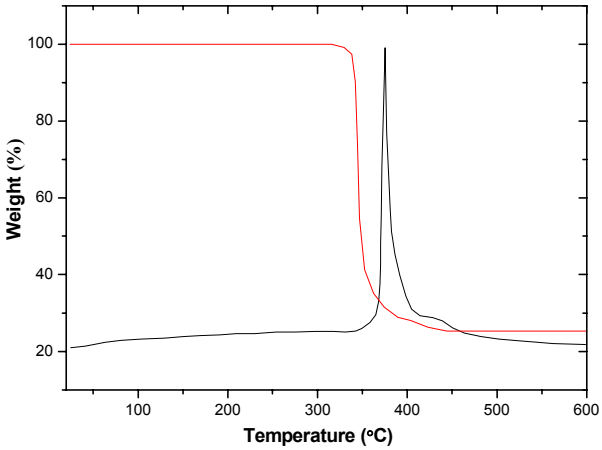
Temperature (°C)

(*c*)



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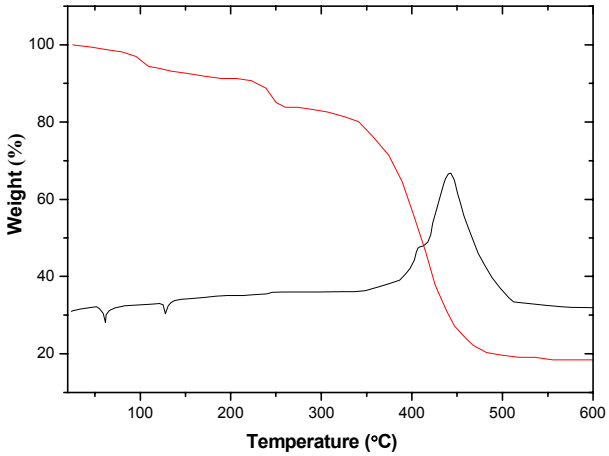
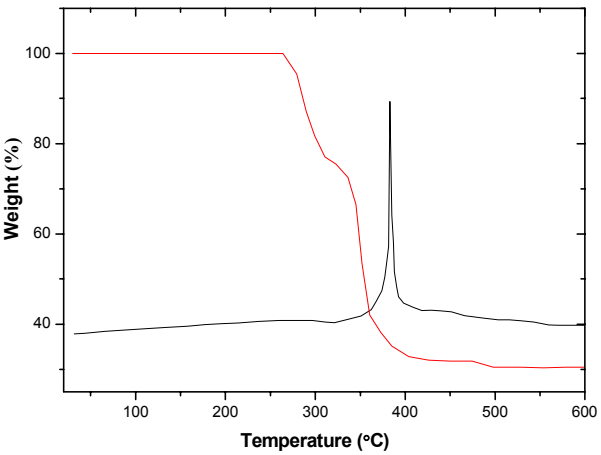


(*e*)



(*f*)

Fig. S4 TG-DTA curves for complexes 1–6 (from *a* to *f*).

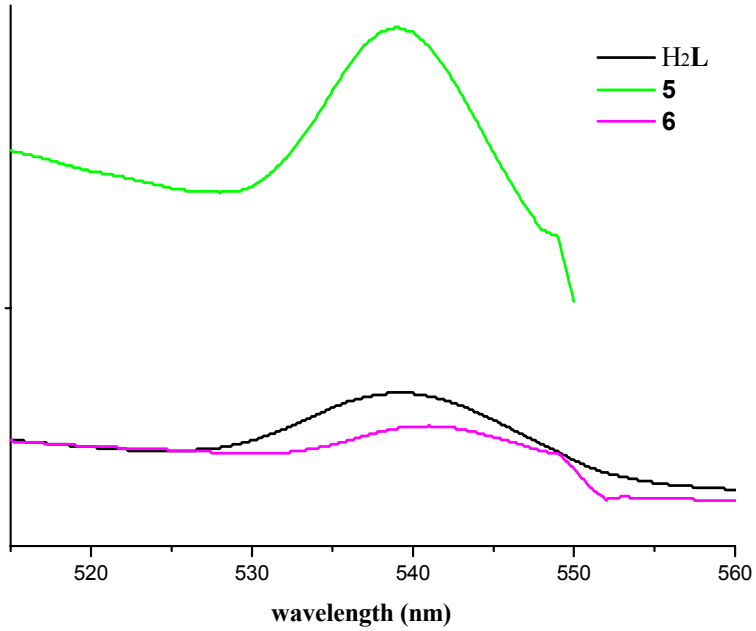


Fig. S5 Solid-state fluorescence emission spectra for H_2L, 5, and 6.

Table S1. Selective bond lengths (Å) and angles (°) for complexes **1**–**6**

1

Mn(1)–O(5)	2.152(2)	Mn(1)–O(6)	2.160(2)
Mn(1)–O(1)	2.193(2)	Mn(2)–O(3)	2.157(2)
Mn(2)–O(7)	2.169(2)	Mn(2)–O(8)	2.173(2)
O(1)–C(4)	1.249(3)	O(2)–C(4)	1.263(3)
O(3)–C(17)	1.249(3)	O(4)–C(17)	1.272(3)
O(5)–Mn(1)–O(6)	89.07(8)	O(5A)–Mn(1)–O(6)	90.93(8)
O(5)–Mn(1)–O(1)	93.17(7)	O(5A)–Mn(1)–O(1)	86.83(7)
O(6)–Mn(1)–O(1)	93.33(7)	O(6A)–Mn(1)–O(1)	86.67(7)
O(3)–Mn(2)–O(7)	88.34(8)	O(3B)–Mn(2)–O(7)	91.66(8)
O(3)–Mn(2)–O(8)	88.20(7)	O(3B)–Mn(2)–O(8)	91.80(7)
O(7)–Mn(2)–O(8)	88.70(9)	O(7B)–Mn(2)–O(8)	91.30(9)

2

Co(1)–O(5)	2.054(3)	Co(1)–O(6)	2.069(2)
Co(1)–O(2)	2.135(2)	Co(2)–O(7)	2.068(3)
Co(2)–O(8)	2.083(2)	Co(2)–O(3)	2.102(2)
O(1)–C(1)	1.276(4)	O(2)–C(1)	1.246(4)
O(3)–C(17)	1.252(4)	O(4)–C(17)	1.278(4)
O(5)–Co(1)–O(6)	88.4(1)	O(5A)–Co(1)–O(6)	91.6(1)
O(5)–Co(1)–O(2)	93.3(1)	O(5A)–Co(1)–O(2)	86.7(1)
O(6)–Co(1)–O(2)	92.30(9)	O(6A)–Co(1)–O(2)	87.70(9)
O(7)–Co(2)–O(8)	88.5(1)	O(7B)–Co(2)–O(8)	91.5(1)
O(7)–Co(2)–O(3)	88.0(1)	O(7B)–Co(2)–O(3)	92.1(1)

O(8)–Co(2)–O(3)	88.7(1)	O(8B)–Co(2)–O(3)	91.4(1)

3

Ni(1)–O(6)	2.034(2)	Ni(1)–O(5)	2.037(2)
Ni(1)–O(1)	2.048(2)	Ni(2)–O(8)	2.030(2)
Ni(2)–O(7)	2.033(2)	Ni(2)–O(3)	2.077(2)
O(1)–C(7)	1.247(3)	O(2)–C(7)	1.271(3)
O(3)–C(17)	1.249(3)	O(4)–C(17)	1.264(3)
O(6)–Ni(1)–O(5)	89.2(1)	O(6A)–Ni(1)–O(5)	90.8(1)
O(6)–Ni(1)–O(1)	90.15(9)	O(6A)–Ni(1)–O(1)	89.85(9)
O(5)–Ni(1)–O(1)	91.5(1)	O(5A)–Ni(1)–O(1)	88.5(1)
O(8)–Ni(2)–O(7)	88.7(1)	O(8B)–Ni(2)–O(7)	91.3(1)
O(8)–Ni(2)–O(3)	88.96(8)	O(8B)–Ni(2)–O(3)	91.04(8)
O(7)–Ni(2)–O(3)	87.0(1)	O(7B)–Ni(2)–O(3)	93.0(1)

4

Cu(1)–O(4A)	1.951(2)	Cu(1)–O(1)	1.959(2)
Cu(1)–O(3B)	1.963(2)	Cu(1)–O(2C)	1.973(2)
Cu(1)–O(5)	2.141(2)	O(1)–C(7)	1.249(3)
O(2)–C(7)	1.261(3)	O(3)–C(17)	1.260(3)
O(4)–C(17)	1.252(3)		
O(4A)–Cu(1)–O(1)	91.20(7)	O(4A)–Cu(1)–O(3B)	168.87(7)
O(1)–Cu(1)–O(3B)	89.41(8)	O(4A)–Cu(1)–O(2C)	89.35(8)
O(1)–Cu(1)–O(2C)	168.77(7)	O(3B)–Cu(1)–O(2C)	87.90(8)
O(4A)–Cu(1)–O(5)	96.87(7)	O(1)–Cu(1)–O(5)	100.88(7)
O(3B)–Cu(1)–O(5)	93.92(7)	O(2C)–Cu(1)–O(5)	90.18(7)

5

Zn(1)–O(3A)	1.964(3)	Zn(1)–O(10)	1.983(3)
Zn(1)–O(9)	1.992(3)	Zn(1)–O(2)	1.992(3)
Zn(2)–O(7A)	1.912(3)	Zn(2)–O(5)	1.928(3)
Zn(2)–O(12)	1.968(3)	Zn(2)–O(11)	1.973(3)
O(1)–C(4)	1.252(4)	O(2)–C(4)	1.269(5)
O(3)–C(15)	1.267(5)	O(4)–C(15)	1.250(5)
O(5)–C(21)	1.268(5)	O(6)–C(21)	1.229(5)
O(7)–C(32)	1.268(5)	O(8)–C(32)	1.246(5)
O(3A)–Zn(1)–O(10)	111.6(1)	O(3A)–Zn(1)–O(9)	96.8(1)
O(10)–Zn(1)–O(9)	97.7(1)	O(3A)–Zn(1)–O(2)	135.1(1)
O(10)–Zn(1)–O(2)	100.8(1)	O(9)–Zn(1)–O(2)	109.1(1)
O(7A)–Zn(2)–O(5)	121.4(1)	O(7A)–Zn(2)–O(12)	112.3(1)
O(5)–Zn(2)–O(12)	106.1(1)	O(7A)–Zn(2)–O(11)	102.3(1)
O(5)–Zn(2)–O(11)	114.7(1)	O(12)–Zn(2)–O(11)	97.6(2)

6

Ag(1)–O(3A)	2.333(3)	Ag(1)–O(2)	2.376(3)
Ag(1)–O(4B)	2.431(3)	Ag(1)–O(5)	2.606(3)
Ag(1)–O(7F)	2.714(4)	Ag(2)–O(1)	2.215(3)
Ag(2)–O(4A)	2.278(3)	Ag(2)–O(4C)	2.581(3)
Ag(2)–O(7D)	2.614(3)	Ag(2)–O(5E)	2.725(3)
O(1)–C(1)	1.265(5)	O(2)–C(1)	1.257(5)
O(3)–C(15)	1.248(6)	O(4)–C(15)	1.297(5)
O(5)–C(18)	1.233(6)	O(6)–C(18)	1.315(6)
O(7)–C(34)	1.220(6)	O(8)–C(34)	1.323(5)

O(3A)–Ag(1)–O(2)	114.3(1)	O(3A)–Ag(1)–O(4B)	130.6(1)
O(2)–Ag(1)–O(4B)	105.0(1)	O(3A)–Ag(1)–O(5)	133.4(1)
O(2)–Ag(1)–O(5)	79.2(1)	O(4B)–Ag(1)–O(5)	81.1(1)
O(3A)–Ag(1)–O(7F)	77.6(1)	O(2)–Ag(1)–O(7F)	157.8(1)
O(4B)–Ag(1)–O(7F)	76.8(1)	O(5)–Ag(1)–O(7F)	79.3(1)
O(1)–Ag(2)–O(4A)	147.2(1)	O(1)–Ag(2)–O(4C)	111.2(1)
O(4A)–Ag(2)–O(4C)	94.2(1)	O(1)–Ag(2)–O(7D)	82.7(1)
O(4A)–Ag(2)–O(7D)	81.5(1)	O(4C)–Ag(2)–O(7D)	80.0(1)
O(1)–Ag(2)–O(5E)	88.2(1)	O(4A)–Ag(2)–O(5E)	118.8(1)
O(4C)–Ag(2)–O(5E)	76.3(1)	O(7D)–Ag(2)–O(5E)	149.5(1)

Symmetry codes: A = $-x + 1, -y, -z + 1$, B = $-x + 1, -y + 1, -z + 1$ for **1**, **2**, and **3**; A = $x, -y + 1, z - 1/2$, B = $-x, y + 1, -z + 1/2$, C = $-x, -y + 2, -z$ for **4**; A = $x, y, z - 1$ for **5**; A = $y, -x + 1/2, -z + 5/2$, B = $-y + 1, x + 1/2, z - 1/2$, C = $-y + 1, x + 1/2, z + 1/2$, D = $-y + 1, x + 1/2, z + 3/2$, E = $x, y, z + 1$, F = $y, -x + 1/2, -z + 1/2$ for **6**.

Table S2. Hydrogen-bonding parameters (Å, °) in the structures of complexes **1**–**6**

D–H···A	D···A	H···A	D–H···A	Symmetry codes
1				
O(5)–H(5A)···O(2)	2.762(3)	1.93	168	$x + 1, y, z$
O(5)–H(5B)···O(4)	2.740(3)	1.92	162	$x + 1/2, -y + 1/2, z + 1/2$
O(7)–H(7A)···O(4)	2.788(3)	1.94	174	$-x, -y + 1, -z + 1$
O(7)–H(7B)···O(2)	2.776(3)	2.00	150	$-x + 1/2, y + 1/2, -z + 3/2$
O(6)–H(6A)···O(2)	2.680(3)	1.87	158	$-x + 1, -y, -z + 1$
O(8)–H(8A)···O(4)	2.683(3)	1.91	151	
2				
O(5)–H(5A)···O(1)	2.779(4)	1.94	168	$x - 1, y, z$
O(5)–H(5B)···O(4)	2.743(4)	1.92	162	$x - 1/2, -y + 1/2, z + 1/2$
O(6)–H(6A)···O(1)	2.666(3)	1.87	155	$-x + 1, -y, -z + 1$
O(7)–H(7A)···O(4)	2.798(4)	1.95	174	$-x + 2, -y + 1, -z + 1$
O(7)–H(7B)···O(1)	2.781(4)	2.00	152	$-x + 3/2, y + 1/2, -z + 3/2$
O(8)–H(8A)···O(4)	2.656(4)	1.83	163	
3				
O(5)–H(5A)···O(2)	2.811(3)	1.97	172	$x + 1, y, z$
O(5)–H(5B)···O(4)	2.794(3)	2.03	150	$x + 1/2, -y + 1/2, z - 1/2$
O(6)–H(6')···O(2)	2.621(3)	1.81	158	$-x + 1, -y, -z + 1$
O(7)–H(7A)···O(2)	2.749(3)	1.94	160	$-x + 1/2, y + 1/2, -z + 1/2$
O(7)–H(7B)···O(4)	2.787(3)	1.98	158	$-x, -y + 1, -z + 1$
O(8)–H(8')···O(4)	2.624(3)	1.82	157	

4

O(5)–H(5A)···O(2)	2.968(2)	2.17	155	$x, y + 1, z$
O(5)–H(5A)···O(3)	3.085(2)	2.45	132	$x, -y + 2, z - 1/2$
O(5)–H(5B)···F(1)	3.006(2)	2.26	146	$-x + 1, y + 1, -z + 1/2$

5

O(9)–H(9A)···O(14)	2.755(5)	2.02	145	$x, y + 1, z$
O(9)–H(9B)···O(4)	2.614(5)	1.85	149	$-x, y + 1/2, -z + 2$
O(10)–H(10A)···O(6)	2.711(4)	1.90	158	$-x, y + 1/2, -z + 1$
O(10)–H(10B)···O(13)	2.701(5)	1.86	171	$-x, y + 1/2, -z + 1$
O(11)–H(11A)···O(16)	2.664(5)	1.83	165	
O(11)–H(11B)···O(8)	2.700(4)	1.91	155	$-x + 1, y + 1/2, -z + 2$
O(12)–H(12A)···O(1)	2.739(4)	1.98	148	$-x + 1, y - 1/2, -z + 1$
O(12)–H(12B)···O(14)	2.728(5)	1.99	139	$-x + 1, y + 1/2, -z + 1$
O(13)–H(13A)···O(8)	2.883(4)	2.44	111	$-x + 1, y + 1/2, -z + 2$
O(13)–H(13B)···O(1)	2.805(5)	1.98	164	
O(14)–H(14)···O(15)	2.714(6)	1.91	167	
O(15)–H(15B)···O(6)	2.882(5)	2.09	150	

6

O(6)–H(6)···O(2)	2.538(5)	1.72	173	
O(8)–H(8)···O(1)	2.668(4)	1.85	175	$y - 1/2, -x + 1, z - 3/2$

Table S3. A comparison of the structural parameters for all related complexes

Complex	Space group	φ (°)*	Helicity	Reference
$[Cu(\mathbf{L})(H_2\mathbf{L})_{0.5}]_n$	$P2/n$	73.8	2_1	21*b*,*e*
$[Zn\mathbf{L}]_n$	$P6_422$	70.2	$6_4/2_1$	21*d*
$[Ln_2(\mathbf{L})_3]_n$	$Pnan$	72.8/63.9	2_1	21*h*
$[Eu_2(\mathbf{L})_3]_n$	$P2_1/n$	61.3/69.4	2_1	21*i*
$[In(OH)(\mathbf{L})]_n$	$Fddd$	79.8	—	21*g*
$[Mn(\mathbf{L})(CH_3OH)_2(H_2O)_2]_n$	$P2_1/n$	77.9	—	this work
$[Co(\mathbf{L})(CH_3OH)_2(H_2O)_2]_n$	$P2_1/n$	78.9	—	this work
$[Ni(\mathbf{L})(CH_3OH)_2(H_2O)_2]_n$	$P2_1/n$	79.8	—	this work
$\{[Zn(\mathbf{L})(H_2O)]_2(CH_3OH)(H_2O)_3\}_n$	$P2_1$	72.1/75.5	—	this work
$[Cu(\mathbf{L})(H_2O)]_n$	$P2/c$	70.7	2_1	this work
$[Ag_2(H_2\mathbf{L})(\mathbf{L})]_n$	$P4_2/n$	64.6/68.8	4_2	this work

* The dihedral angle between two phenyl rings of the ligand.