Supporting Information

A series of entangled Zn^{II}/Cd^{II} coordination polymers constructed from 1,3,5-benzenetricarboxylate acid and triazole ligands

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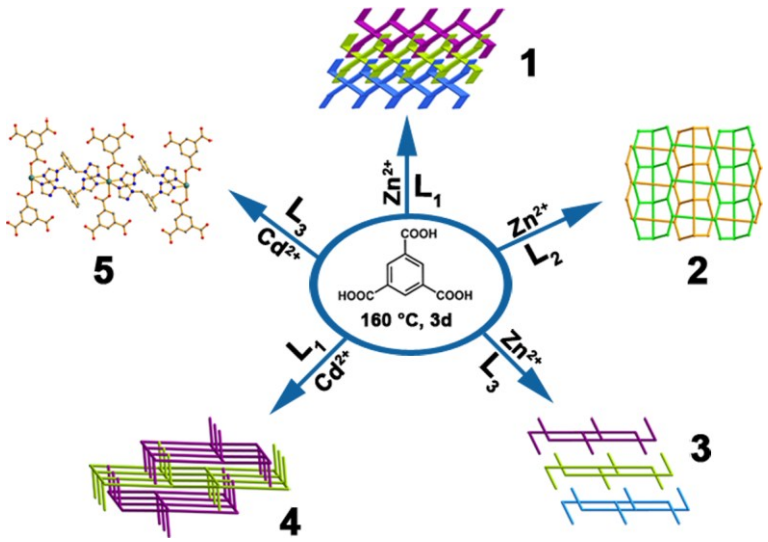
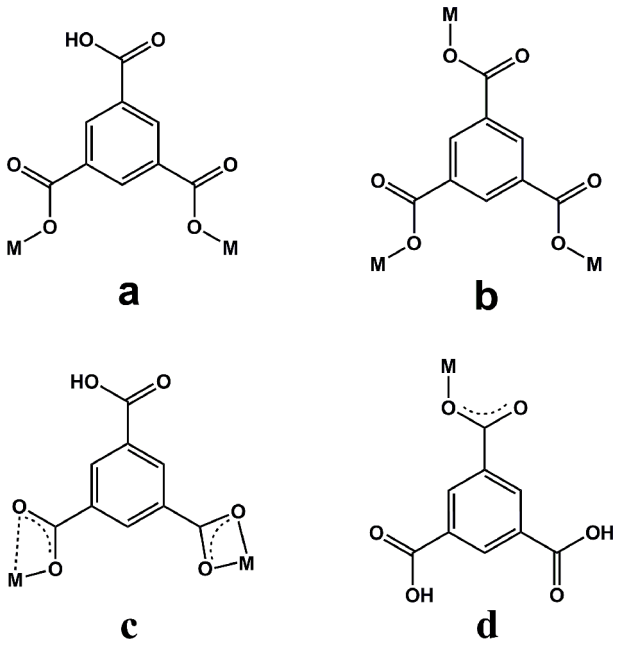
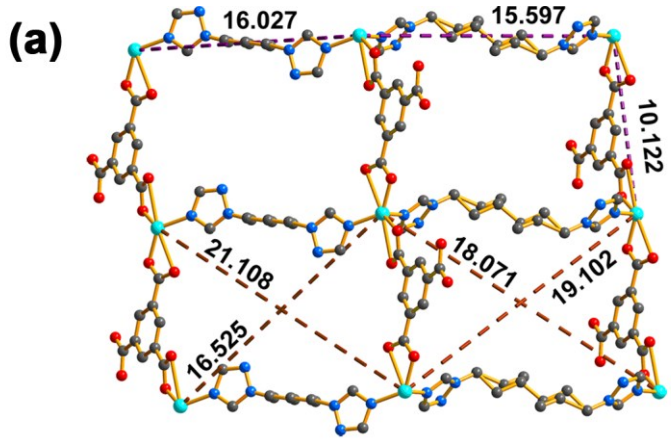


Scheme S1. Synthetic route of the title compounds.

Scheme S2. Coordination modes of H_3BTC in **1**-**5**, model a for **1** and **3**, model b for **2**, model c for **4** and model d for **5**.





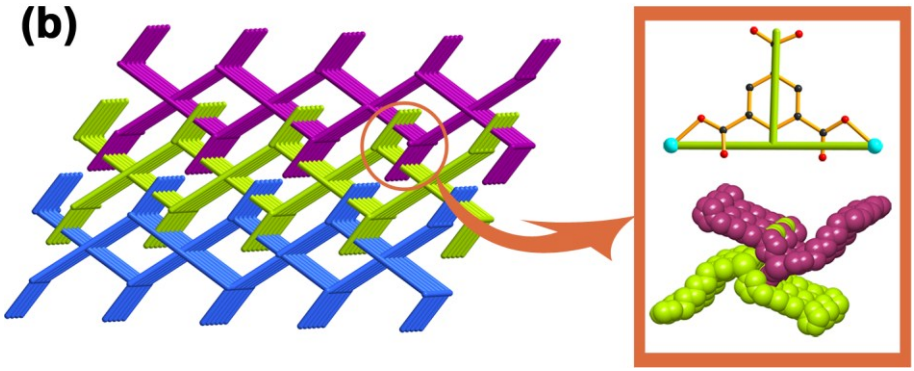


Fig. S1 (a) View of 4^4-**sql** layer of **1**. Zn···Zn distances (Å) are shown in dashed line. (b) Schematic description of 2D→3D interdigitated structure of **1**.

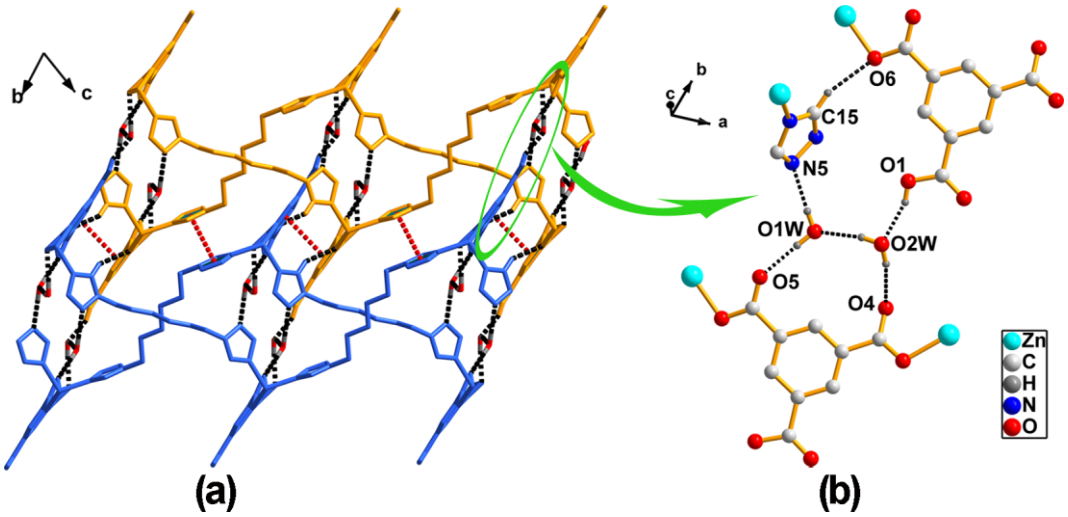


Fig. S2 (a) 2D layers of **1** are further linked into a 3D supramolecular structure by hydrogen-bonding interactions (dashed black lines) and $\pi\cdots\pi$ interactions (dashed red lines). (b) A partial schematic view of hydrogen bonds of **1**.

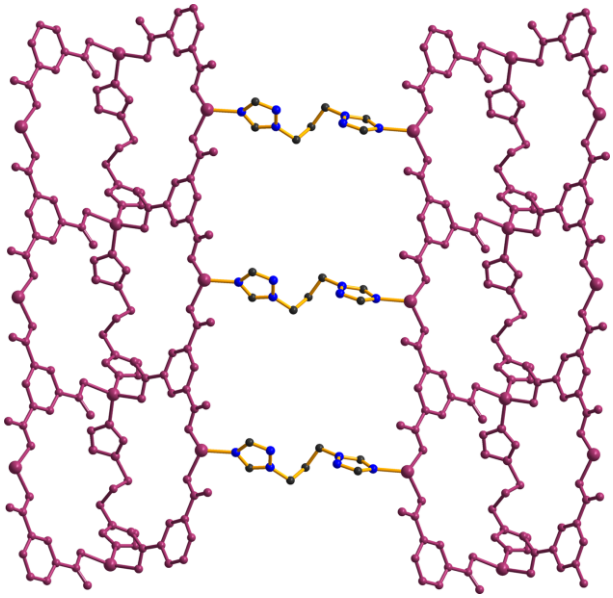


Fig. S3 The pentalene-like units enhance into 1D chain through edge-sharing (showing in purple), and the chains are further linked into 2D wave-shaped layer by L_2 ligands.

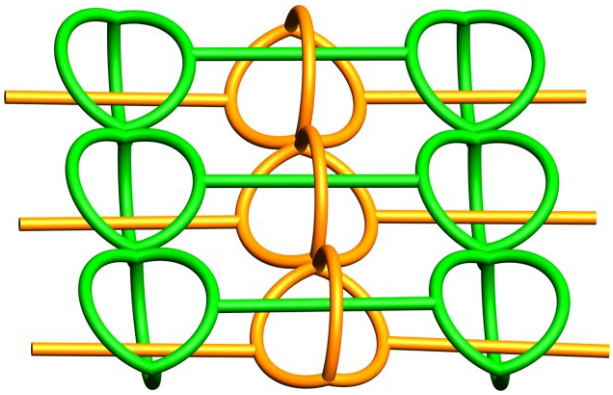


Fig. S4 Schematic description of 2D→2D entangled structure of **2** with the coexistence of polycatenation and polythreading.

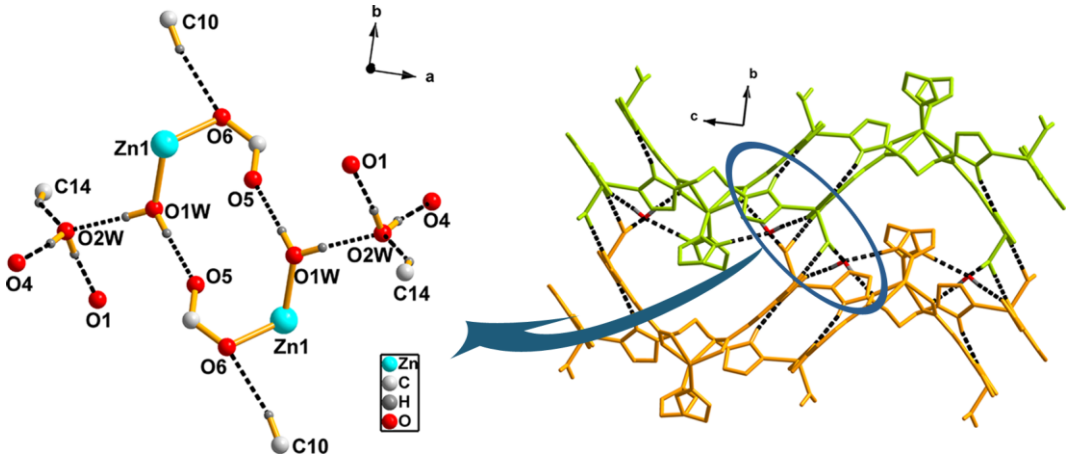


Fig. S5 A partial schematic view of hydrogen bonds in **2**.

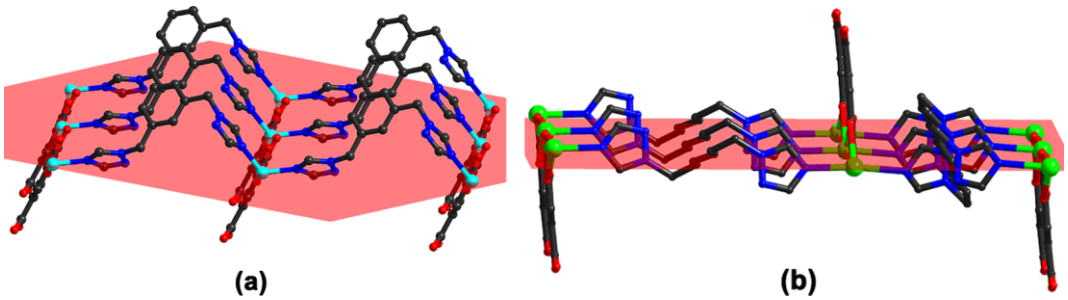


Fig. S6 (a) The Zn atoms in each independent layer of **3** nearly lie in the same horizontal plane. (b) The Cd atoms in each independent layer of **4** nearly lie in the same horizontal plane.

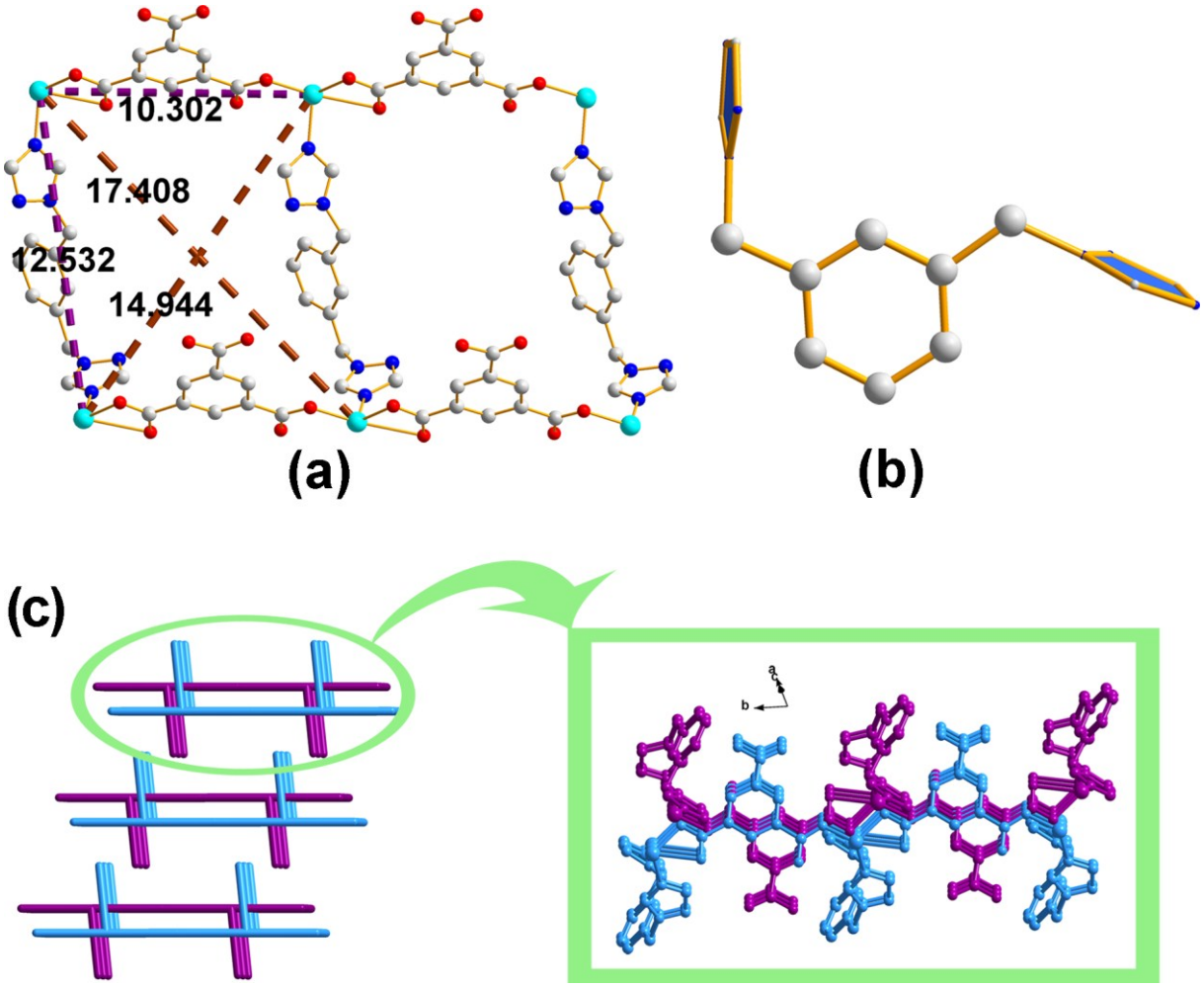


Fig. S7 (a) The bridged Zn···Zn distances (Å) in **3**. (b) View of *anti*-coordination model of L_3 ligand. (c) View of 2D→2D polythreaded network of **3**.

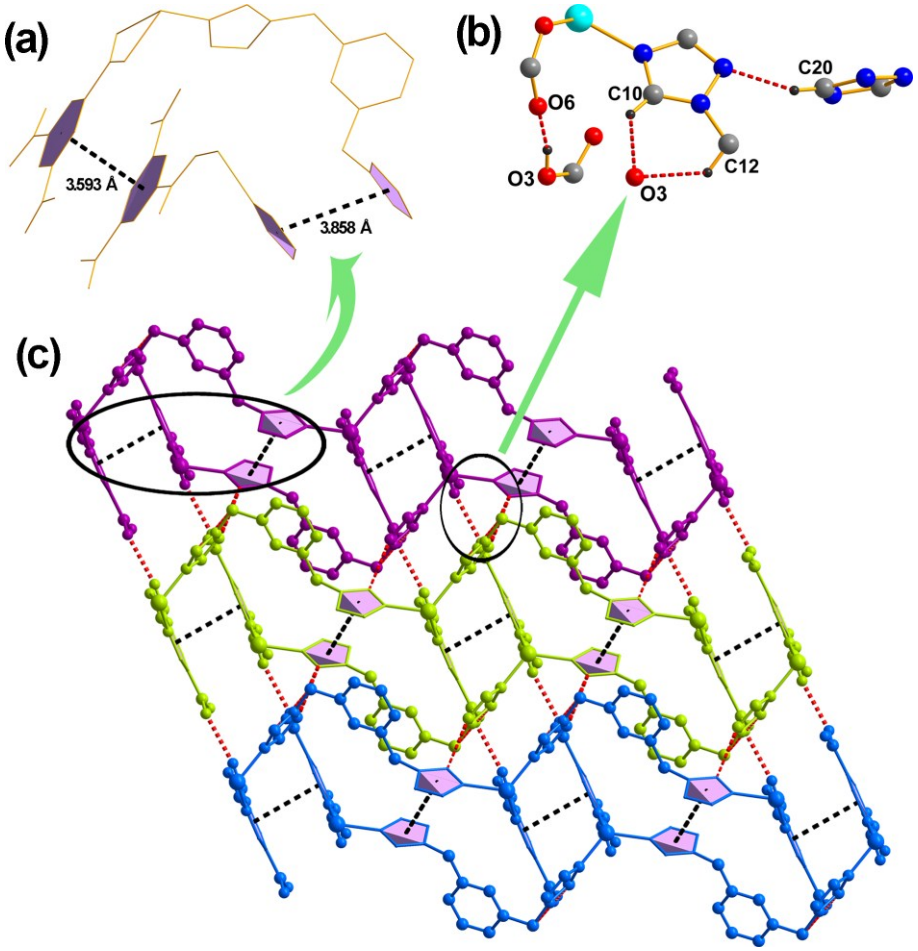


Fig. S8 (a) A partial schematic view of $\pi\cdots\pi$ interactions in **3**. (b) A partial schematic view of hydrogen bonds in **3**. (c) 3D supramolecular architecture based on hydrogen-bonding interactions and $\pi\cdots\pi$ interactions.

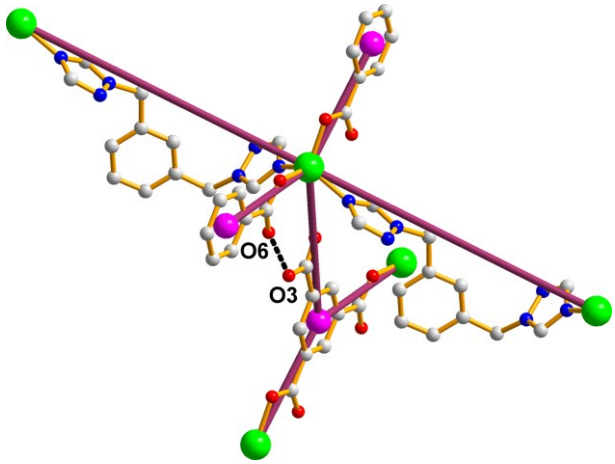


Fig. S9 For **3**, when O3−H3···O6 hydrogen bond is taken into consideration, the ZnO_2N_2 tetrahedral geometry can be seen as a 5-connected node (big green ball), and the $HBTC^{2-}$ ligand can be considered as a 3-connected node (big pink ball).

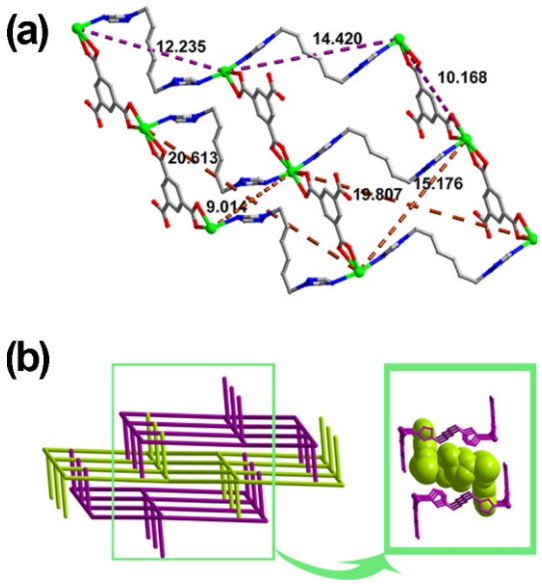


Fig. S10 (a) View of 4^4-**sql** layer of **4**. The Cd···Cd distances (Å) are shown in dashed line. (b) Schematic description of 2D→3D interdigitation.

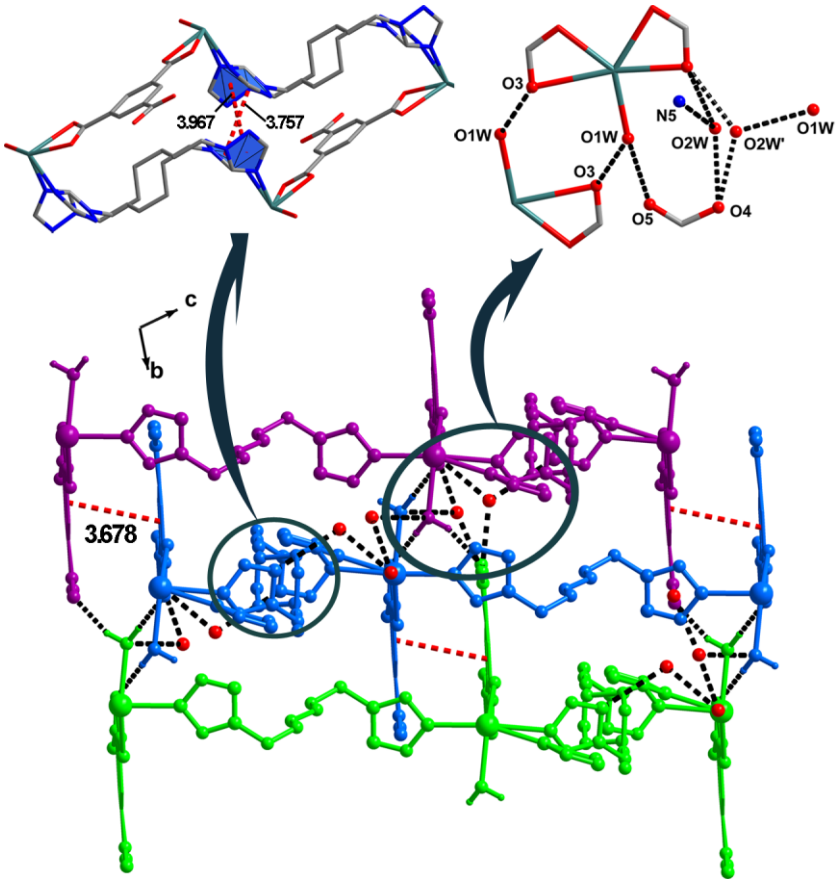


Fig. S11 Partial schematic view of hydrogen bonds (dashed black line) and $\pi\cdots\pi$ interactions (dashed red line) in **4**.

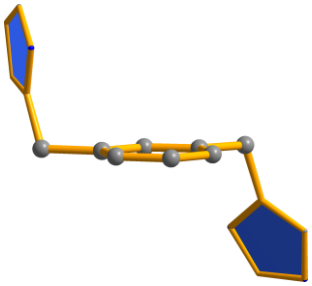


Fig. S12 View of *anti*-coordination model of L_3 ligand in **5**.

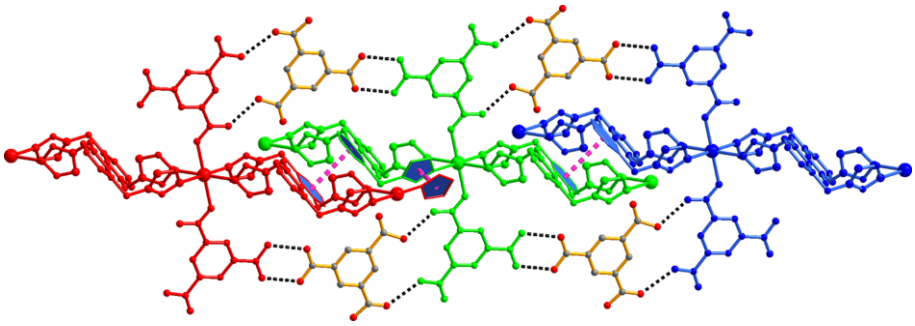


Fig. S13 1D chains of **5** are connected into 2D layer by noncovalent interactions (hydrogen-bonding interactions are shown in dashed black line and $\pi\cdots\pi$ interactions are shown in dashed pink line).

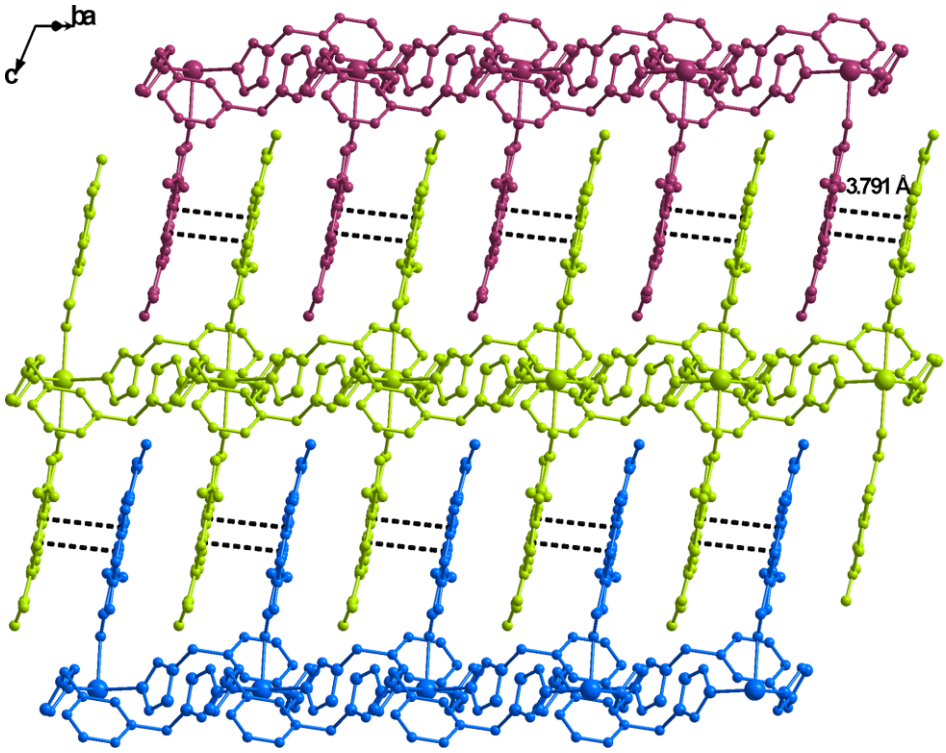


Fig. S14 View of 3D supramolecular architecture of **5**. The dashed black lines indicate $\pi\cdots\pi$ interactions of Cg(3)>Cg(4): 3.791(12) Å (Cg(3): C2, C3, C4, C5, C6, C7; Cg(4): C13, C14, C15, C16, C17, C18).

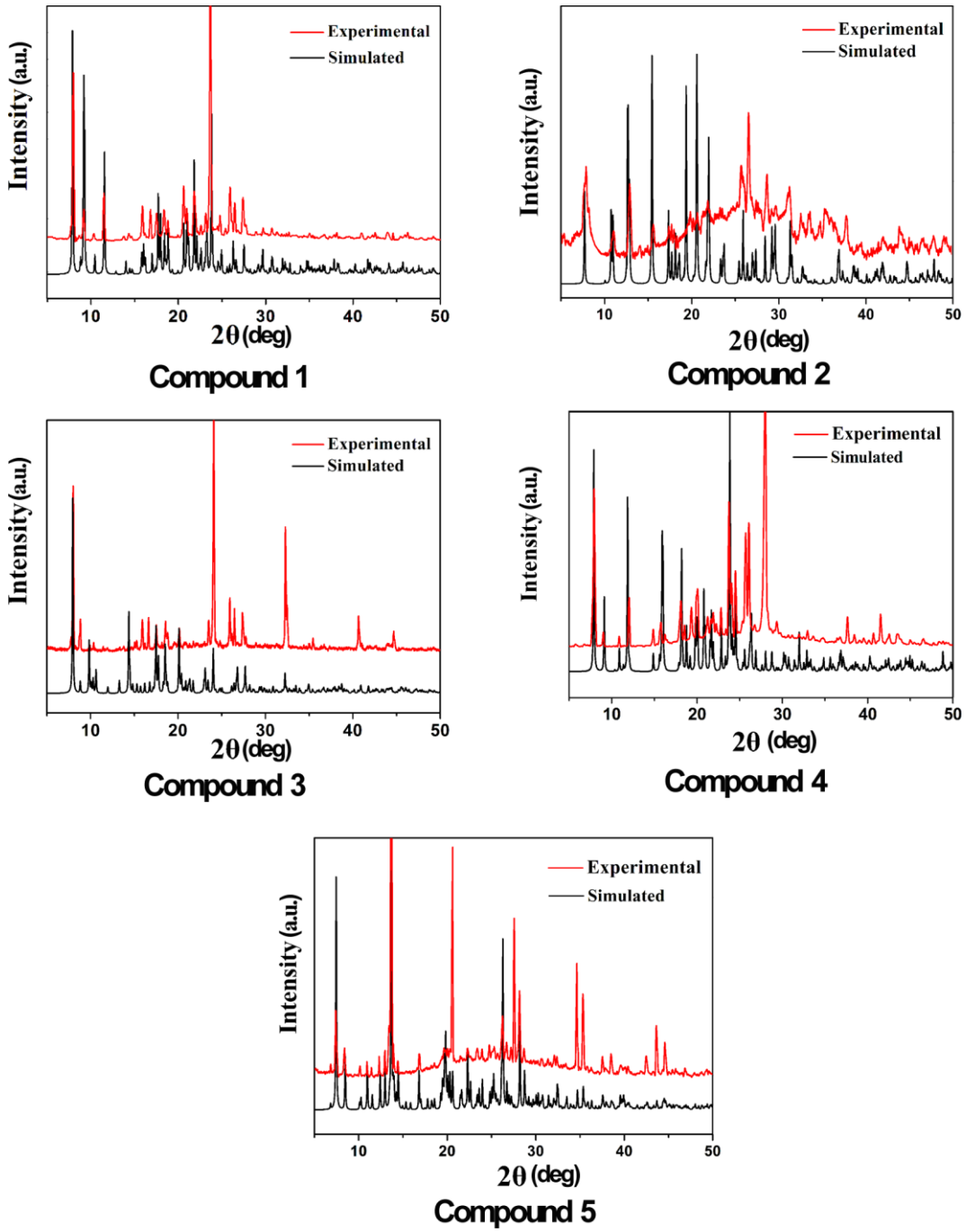


Fig. S15 The PXRD patterns of **1**-**5**.

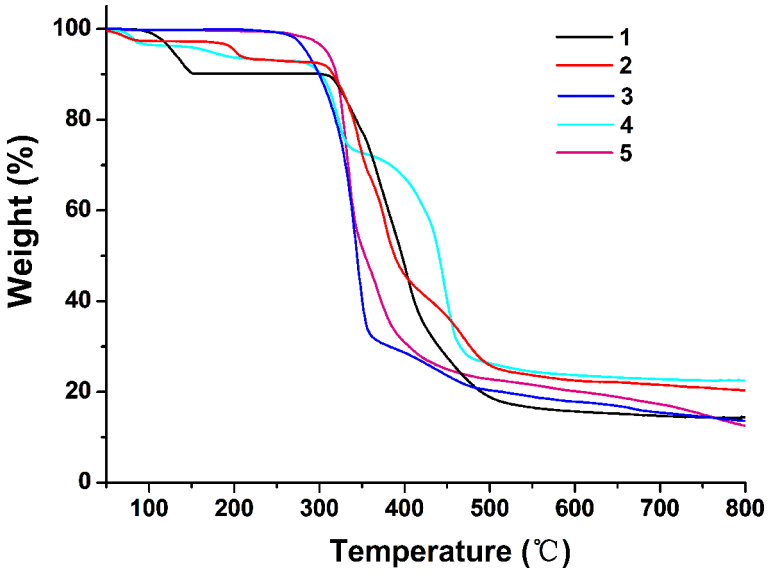


Fig. S16 Thermogravimetric analysis curves of **1-5**.

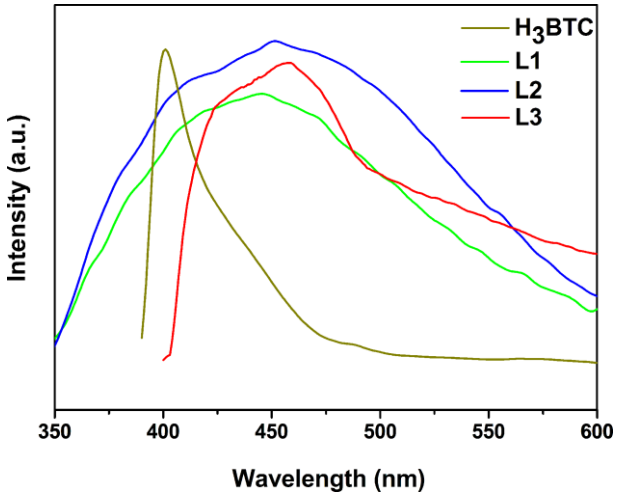


Fig. S17 Emission spectra of free ligands.

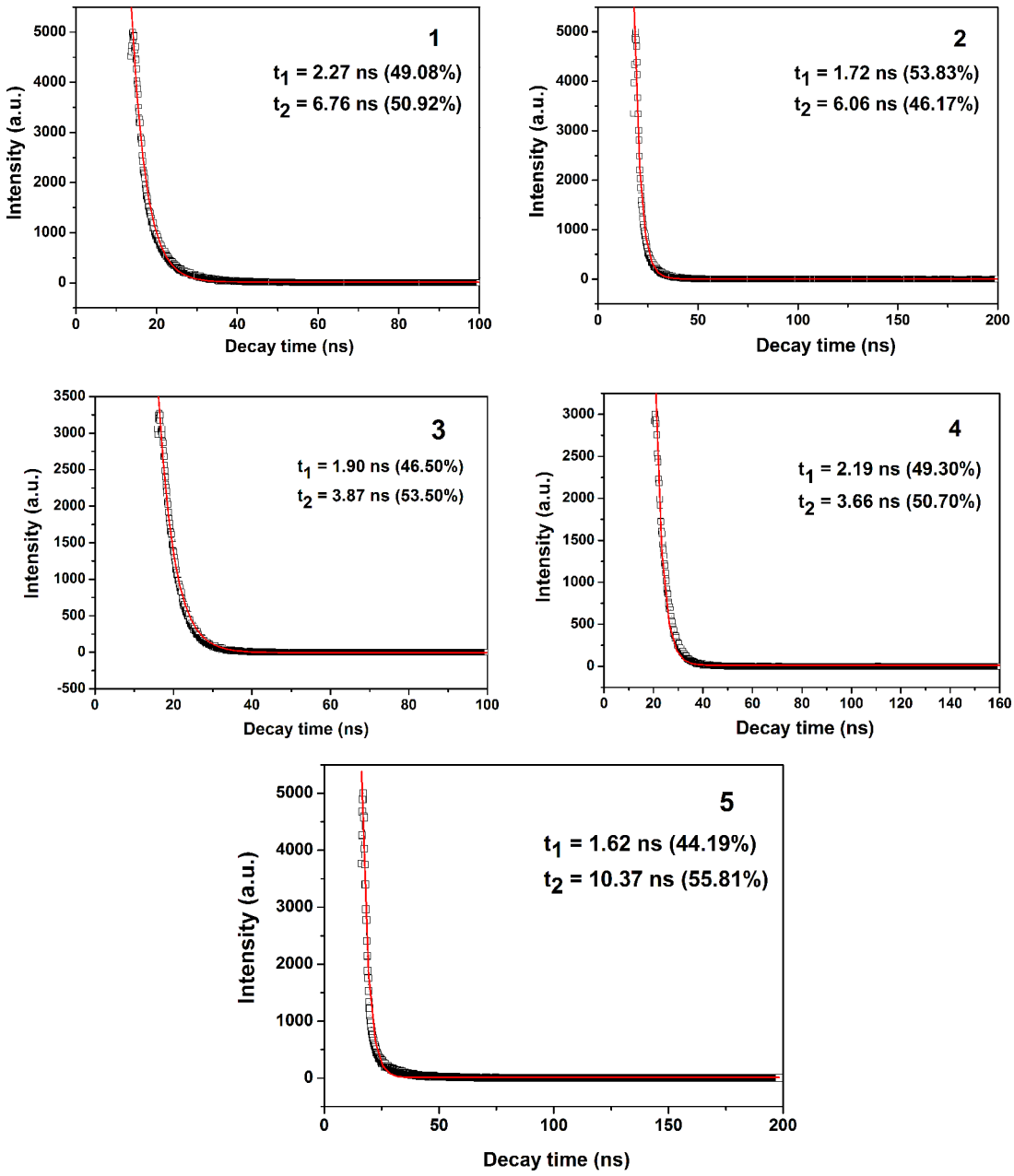


Fig. S18 Fitted decay curves for **1-5**. The black circles represent experimental data, and the solid red lines represent fitting results.

Table S1. Hydrogen-bonding geometry parameters for **1**

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O1–H1···O2W	0.82	1.84	2.593(10)	152
O1W–H1WA···O5	0.85	1.86	2.710(10)	178
O1W–H1WB···N5	0.85	2.01	2.857(12)	178
O2W–H2WA···O4	0.85	1.99	2.828(10)	167
O2W–H2WB···O1W	0.85	1.99	2.826(11)	167
C15–H15···O6	0.93	2.43	3.259(11)	148

Table S2. $\pi\cdots\pi$ interactions in **1**[a]

Two rings	Symmetry code	Cg-Cg (Å)	Alpha (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(4)>Cg(4)	*1-x,–y,2-z*	3.607(6)	0	17.61	3.439(4)	3.439(4)
Cg(6)>Cg(6)	*–x,1-y,1-z*	3.864(5)	0	24.63	–3.512(3)	–3.512(3)

[a] Cg(4): N(1)>C(10)>N(3)>N(2)>C(11); Cg(6): C(1)>C(2)>C(3)>C(4)>C(5)>C(6); Alpha = Dihedral Angle between Planes I and J; Gamma = Angle Cg(I)>Cg(J) vector and normal to plane J; Cg-Cg = Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I.

Table S3. Hydrogen-bonding geometry parameters for **2**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O1W–H1WA···O5	0.85	1.84	2.686(49)	178
O1W–H1WB···O2W	0.85	1.82	2.671(51)	178
O2W–H2WA···O4	0.85	1.87	2.718(53)	173
O2W–H2WB···O1	0.85	1.93	2.781(51)	173
C10–H10···O6	0.93	2.47	3.384(60)	167
C14–H14···O2W	0.93	2.36	3.223(103)	154

Table S4. C–H···π interactions in **2**[a]

C–H···π	Symmetry code	H–C(g) (Å)	X–H···C(g) (°)	X···C(g) (Å)
C(16)–H(16)>Cg(8)	*1/2-x,1/2+y,1/2-z*	2.86	132	3.579(4)

[a]Cg(8):C(4)>C(5)>C(6)>C(7)>C(8)>C(9)

Table S5. π···π interactions in **2**[a]

Two rings	Symmetry code	Cg-Cg (Å)	Alpha (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(8)>Cg(8)	*1-x,2-y,2-z*	3.839(6)	0	27.15	3.416(2)	3.418(2)

[a]Cg(5): C(4)>C(5)>C(6)>C(7)>C(8)>C(9); Alpha = Dihedral Angle between Planes I and J; Gamma = Angle Cg(I)>Cg(J) vector and normal to plane J; Cg-Cg = Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I.

Table S6. Hydrogen-bonding geometry parameters for **3**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O3–H3···O6	0.82	1.82	2.602(3)	158
C10–H10···O3	0.93	2.43	3.158(3)	135
C12–H12A···O3	0.97	2.56	3.187(3)	123
C20–H204···N3	0.93	2.33	3.219(4)	160

Table S7. C–H···π interactions in **3**[a].

C–H···π	Symmetry code	H–C(g) (Å)	X–H···C(g) (°)	X···C(g) (Å)

C(15)–H(15)>Cg(4)	*x,1+y, –1+z*	2.84	138	3.583(3)

[a]Cg(4): C(4)>C(5)>C(6)>C(7)>C(8)>C(9)

Table S8. $\pi\cdots\pi$ interactions in **3**[a].

Two rings	Symmetry code	Cg-Cg (Å)	Alpha (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(3)>Cg(3)	*–x,1-y,2-z*	3.858(14)	0	21.12	3.599(10)	3.599(10)
Cg(4)>Cg(4)	*1-x,–y,1-z*	3.593(12)	0	14.54	3.478(8)	3.478(8)

[a]Cg(3): N(4)>C(20)>N(5)>N(6)>C(21); Cg(4): C(4)>C(5)>C(6)>C(7)>C(8)>C(9); Alpha = Dihedral Angle between Planes I and J; Gamma = Angle Cg(I)>Cg(J) vector and normal to plane J; Cg-Cg = Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I.

Table S9. Hydrogen-bonding geometry parameters for **4**.

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O1W–H1WA···O3	0.86	1.83	2.688(6)	177
O1W–H1WB···O5	0.86	1.94	2.764(7)	161
O4–H4···O2W	0.82	1.77	2.517(7)	150

Table S10. $\pi\cdots\pi$ interactions in **4**[a].

Two rings	Symmetry code	Cg-Cg (Å)	Alpha (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(2)>Cg(2)	*1-x,1-y,2-z*	3.757(10)	0	28.52	–3.427(3)	–3.427(3)
Cg(3)>Cg(3)	*1-x,1-y,2-z*	3.967(7)	0	29.02	–3.469(5)	–3.469(5)
Cg(4)>Cg(4)	*1-x,–y,1-z*	3.678(3)	0	17.48	–3.508(18)	–3.508(18)

[a]Cg(2): N(4)>C(15)>N(6)>N(5)>C(16); Cg(3): N(4')>C(15)>N(6')>N(5')>C(16'); Cg(4): C(2)>C(3)>C(4)>C(6)>C(7)>C(9); Alpha = Dihedral Angle between Planes I and J; Gamma = Angle Cg(I)>Cg(J) vector and normal to plane J; Cg-Cg = Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I.

Table S11. Hydrogen-bonding geometry parameters for **5**.

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O3–H3A···O7	0.82	1.92	2.669(2)	152
O6–H6···O10	0.82	1.84	2.659(3)	173
O8–H8···N2	0.82	1.92	2.727(2)	169
O9–H9···O5	0.82	1.81	2.625 (3)	171
O12–H12···O2	0.82	1.76	2.550(2)	163
C3–H3···O12	0.93	2.29	3.190(3)	162'
C14–H14···O3	0.93	2.37	3.273(3)	164
C21–H21A···O11	0.97	2.36	3.282(3)	158

C30–H30···O4	0.93	2.4	3.225(3)	149

Table S12. $\pi\cdots\pi$ interactions in **5**[a].

Two rings	Symmetry code	Cg-Cg (Å)	Alpha (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(1)>Cg(1)	*2-x,1-y,1-z*	3.731(12)	0.02	31.11	3.194(8)	3.194(8)
Cg(3)>Cg(4)	*1-x,–y,–z*	3.791(12)	0.93	26.79	3.385(8)	3.361(9)
Cg(5)>Cg(5)	*2-x,–y,1–z*	3.635(13)	0.02	15.16	3.509(9)	3.509(9)

[a]Cg(1): N(1)>C(19)>N(3)>N(2)>C(20); Cg(3): C(2)>C(3)>C(4)>C(5)>C(6)>C(7); Cg(4): C(13)>C(14)>C(15)>C(16)>C(17)>C(18); Cg(5): C(22)>C(23)>C(24)>C(25)>C(27)>C(26); Alpha = Dihedral Angle between Planes I and J; Gamma = Angle Cg(I)>Cg(J) vector and normal to plane J; Cg-Cg = Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I.

Table S13. Selected bond lengths and angles of **1**[a].

Zn(1)-O(6)	1.984(5)	Zn(1)-N(4)	2.006(8)
Zn(1)-O(3)#1	2.006(5)	Zn(1)-N(1)	2.020(7)
O(6)-Zn(1)-O(3)#1	96.05(18)	O(6)-Zn(1)-N(1)	117.3(2)
O(6)-Zn(1)-N(4)	112.9(2)	O(3)#1-Zn(1)-N(1)	127.3(2)
O(3)#1-Zn(1)-N(4)	98.1(2)	N(4)-Zn(1)-N(1)	103.9(3)

[a]Symmetry code: #1, x+1, y, z.

Table S14. Selected bond lengths and angles of **2**[a].

Zn(1)-O(3)	1.971(3)	Zn(2)-O(1)#2	1.994(4)
Zn(1)-O(6)#1	1.978(3)	Zn(2)-N(4)#2	2.037(6)
Zn(1)-O(1W)	1.984(4)	Zn(2)-N(4)	2.037(6)
Zn(1)-N(1)	2.012(4)	Zn(2)-O(1)	1.994(4)
O(3)-Zn(1)-O(6)#1	100.11(13)	O(1)-Zn(2)-O(1)#2	123.3(2)
O(3)-Zn(1)-O(1W)	104.38(15)	O(1)-Zn(2)-N(4)#2	105.27(19)
O(6)#1-Zn(1)-O(1W)	105.88(14)	O(1)#2-Zn(2)-N(4)#2	112.7(2)
O(3)-Zn(1)-N(1)	113.23(16)	O(1)-Zn(2)-N(4)	112.7(2)
O(6)#1-Zn(1)-N(1)	118.71(16)	O(1)#2-Zn(2)-N(4)	105.27(19)
O(1W)-Zn(1)-N(1)	112.88(17)	N(4)#2-Zn(2)-N(4)	93.7(4)

[a]Symmetry code: #1, x+1, y, z; #2, -x+1, y, -z+3/2.

Table S15. Selected bond lengths and angles of **3**[a].

Zn(1)-O(5)#1	1.9718(15)	Zn(1)-N(1)	2.0093(18)
Zn(1)-O(2)	2.0047(15)	Zn(1)-N(4)	2.0355(18)
O(5)#1-Zn(1)-O(2)	106.17(6)	O(5)#1-Zn(1)-N(4)	101.41(7)
O(5)#1-Zn(1)-N(1)	107.87(7)	O(2)-Zn(1)-N(4)	110.16(7)
O(2)-Zn(1)-N(1)	108.95(7)	N(1)-Zn(1)-N(4)	121.08(7)

[a]Symmetry code: #1, x, y+1, z.

Table S16. Selected bond lengths and angles of **4**[a].

Cd(1)-N(4')	2.244(14)	Cd(1)-O(2)	2.380(3)
Cd(1)-O(6)#1	2.284(3)	Cd(1)-N(4)	2.394(13)
Cd(1)-N(1)	2.284(4)	Cd(1)-O(1)	2.413(3)
Cd(1)-O(1W)	2.348(3)	Cd(1)-O(3)#1	2.696(3)
N(4')-Cd(1)-O(6)#1	97.1(2)	O(2)-Cd(1)-N(4)	91.2(3)
N(4')-Cd(1)-N(1)	161.5(4)	N(4')-Cd(1)-O(1)	105.4(4)
O(6)#1-Cd(1)-N(1)	90.24(13)	O(6)#1-Cd(1)-O(1)	82.28(10)
N(4')-Cd(1)-O(1W)	77.8(3)	N(1)-Cd(1)-O(1)	92.37(13)
O(6)#1-Cd(1)-O(1W)	139.58(12)	O(1W)-Cd(1)-O(1)	138.00(13)
N(1)-Cd(1)-O(1W)	85.62(15)	O(2)-Cd(1)-O(1)	54.16(10)
N(4')-Cd(1)-O(2)	85.2(3)	N(4)-Cd(1)-O(1)	99.0(3)
O(6)#1-Cd(1)-O(2)	134.88(10)	N(4')-Cd(1)-O(3)#1	86.7(3)
N(1)-Cd(1)-O(2)	101.59(13)	O(6)#1-Cd(1)-O(3)#1	51.52(9)
O(1W)-Cd(1)-O(2)	85.13(12)	N(1)-Cd(1)-O(3)#1	84.62(12)
N(4')-Cd(1)-N(4)	14.0(3)	O(1W)-Cd(1)-O(3)#1	88.06(12)
O(6)#1-Cd(1)-N(4)	83.9(3)	O(2)-Cd(1)-O(3)#1	170.38(10)
N(1)-Cd(1)-N(4)	166.4(3)	N(4)-Cd(1)-O(3)#1	82.1(3)
O(1W)-Cd(1)-N(4)	90.9(3)	O(1)-Cd(1)-O(3)#1	133.59(9)

[a]Symmetry code: #1, x-1, y, z.

Table S17. Selected bond lengths and angles of **5**[a].

Cd(1)-O(1)#1	2.3087(13)	Cd(1)-N(4)#1	2.3538(16)
Cd(1)-O(1)	2.3087(13)	Cd(1)-N(1)#1	2.3798(16)
Cd(1)-N(4)	2.3538(16)	Cd(1)-N(1)	2.3798(16)
O(1)#1-Cd(1)-O(1)	180	N(4)-Cd(1)-N(1)#1	96.36(6)
O(1)#1-Cd(1)-N(4)	94.42(6)	N(4)#1-Cd(1)-N(1)#1	83.64(6)
O(1)-Cd(1)-N(4)	85.58(6)	O(1)#1-Cd(1)-N(1)	101.69(5)
O(1)#1-Cd(1)-N(4)#1	85.58(6)	O(1)-Cd(1)-N(1)	78.31(5)
O(1)-Cd(1)-N(4)#1	94.42(6)	N(4)-Cd(1)-N(1)	83.64(6)
N(4)-Cd(1)-N(4)#1	180	N(4)#1-Cd(1)-N(1)	96.36(6)
O(1)#1-Cd(1)-N(1)#1	78.31(5)	N(1)#1-Cd(1)-N(1)	180.000(1)
O(1)-Cd(1)-N(1)#1	101.69(5)		

[a]Symmetry code: #1, -x+1, -y+2, -z+1.