

Table S1 Selected bond lengths (Å) of complexes 1 and 3–8^[a]

1							
Zn(1)-O(1)	1.953(3)	Zn(1)-Zn(1)#1	2.962(2)	Zn(1)-O(3)#2	2.031(3)	Zn(2)-O(2)	1.955(4)
Zn(1)-O(6)#1	2.024(4)	Zn(2)-O(7)	1.951(4)	Zn(1)-O(4)#3	2.044(3)	Zn(1)-O(5)	2.076(3)
3							
Zn(1)-O(8)#1	1.896(7)	Zn(2)-O(2)	2.021(7)	Zn(1)-O(3)#3	1.931(6)	Zn(2)-O(4)#3	2.003(6)
Zn(1)-O(1)	1.937(7)	Zn(2)-O(4)#1	2.118(7)	Zn(1)-O(5)	1.936(5)	Zn(2)-O(7)#2	2.016(6)
Zn(1)-O(5)	1.966(6)	Zn(2)-N(2)	2.118(8)	Zn(1)-O(1)	1.950(6)	Zn(2)-N(2)	2.123(8)
Zn(1)-N(1)#2	2.020(7)	Zn(2)-O(3)#1	2.191(7)	Zn(1)-N(1)#4	2.035(7)	Zn(2)-O(8)#2	2.366(6)
Zn(2)-O(7)#1	2.007(7)	Zn(2)-O(5)	2.423(6)	Zn(2)-O(6)	1.992(6)	Zn(2)-O(1)	2.436(7)
5							
Zn(1)-O(7)#1	2.036(2)	Zn(1)-O(6)	2.343(3)	Cd(1)-N(1)	2.298(3)		
Zn(1)-O(4)#2	2.038(2)	Zn(2)-O(8)#1	1.926(2)	Cd(1)-O(1)	2.312(3)		
Zn(1)-O(5)	2.045(2)	Zn(2)-O(3)#2	1.947(2)	Cd(1)-O(2)	2.350(4)		
Zn(1)-N(1)#3	2.113(3)	Zn(2)-O(1)	1.978(2)				
Zn(1)-O(1)	2.256(2)	Zn(2)-N(2)	2.014(3)				
7							
Cd(1)-O(1)	2.255(3)	Cd(1)-O(5)#2	2.388(3)	Cd(1)-O(5)	2.292(7)	N(3)-Cd(2)#2	2.297(9)
Cd(1)-O(2)	2.283(3)	Cd(1)-O(4)#2	2.400(3)	Cd(1)-N(2)	2.334(9)	N(4)-Cd(2)#3	2.327(8)
Cd(1)-N(1)	2.354(4)	Cd(1)-O(3)	2.642(3)	Cd(1)-N(1)	2.336(9)	O(8)-Cd(2)#5	2.331(8)
Cd(1)-N(2)#1	2.369(4)	Cd(2)-O(6)	2.234(3)	Cd(1)-O(3)#1	2.372(9)	O(5)-Cd(2)	2.405(7)
Cd(2)-O(13)#3	2.309(3)	Cd(2)-N(4)#1	2.347(4)	Cd(1)-O(1)	2.382(7)	Cd(2)-O(7)#6	2.406(8)
Cd(2)-O(3)	2.362(3)	Cd(2)-O(14)#3	2.510(3)	Cd(1)-O(2)	2.439(7)	O(6)-Cd(2)	2.474(7)
Cd(2)-N(3)	2.373(4)	Cd(3)-O(8)	2.225(4)	Cd(2)-O(4)#2	2.315(8)		
Cd(3)-O(7)#4	2.242(4)	Cd(3)-O(10)	2.302(4)				
Cd(3)-O(11)	2.295(4)	Cd(3)-O(12)	2.342(4)				
Cd(3)-O(9)	2.554(4)						

[a] Symmetry codes: **1** #1 -x+1/2,-y+1/2,-z+1; #2 x,-y,z+1/2; #3 -x+1/2,y+1/2,-z+1/2. **3**: #1 x,-y+1,z-1/2; #2 x+1,y,z+1. **4**: #2 -x+1,-y+2,-z+1; #3 -x,-y+1,-z; #4 x,y-1,z-1. **5**: #1 -x+1,-y+1,-z; #2 -x+2,-y+2,-z+1; #3 x,y-1,z-1. **7**: #1 x+1,y+1,z; #2 -x+1,-y+1,-z+1; #3 -x+1,-y+1,-z+2; #4 x-1,y,z. **8**: #1 -x,y-1/2,-z+3/2; #2 x+1,y,z; #3 -x+1,y+1/2,-z+3/2; #5 -x+1,y+1/2,-z+3/2; #6 -x+1,y-1/2,-z+3/2.

(°) of complexes 1 and 3–8^[a]

O(1)-Zn(1)-O(5)	89.55(14)	O(7)#4-Zn(2)-O(7)	106.4(2)
O(6)#1-Zn(1)-O(5)	159.39(14)	O(7)#4-Zn(2)-O(2)	103.77(17)
O(3)#2-Zn(1)-O(4)#3	159.20(15)	O(2)-Zn(2)-O(2)#4	102.0(2)
O(6)#1-Zn(1)-O(4)#3	88.91(15)	O(7)-Zn(2)-O(2)#4	103.77(17)
O(4)#1-Zn(2)-O(3)#1	60.4(3)	O(7)#1-Zn(2)-O(2)	103.6(3)
N(2)-Zn(2)-O(3)#1	89.4(3)	O(2)-Zn(2)-O(3)#1	98.4(3)
O(7)#1-Zn(2)-O(5)	93.8(3)	O(3)#1-Zn(2)-O(5)	84.0(2)
O(2)-Zn(2)-O(5)	86.8(2)		
O(4)#1-Zn(2)-O(5)	87.0(2)		
N(2)-Zn(2)-O(5)	172.2(3)		
5			
O(7)#1-Zn(1)-O(4)#2	111.35(10)	O(4)#2-Zn(1)-O(6)	93.92(9)
O(7)#1-Zn(1)-O(5)	95.50(10)	O(5)-Zn(1)-O(6)	59.46(9)
O(4)#2-Zn(1)-O(5)	152.41(10)	N(1)#3-Zn(1)-O(6)	87.97(10)
O(7)#1-Zn(1)-N(1)#3	92.42(10)	O(1)-Zn(1)-O(6)	94.25(8)
O(4)#2-Zn(1)-N(1)#3	87.98(10)	O(8)#1-Zn(2)-O(3)#2	117.97(10)
O(5)-Zn(1)-N(1)#3	97.43(10)	O(8)#1-Zn(2)-O(1)	111.24(10)
O(7)#1-Zn(1)-O(1)	88.80(9)	O(3)#2-Zn(2)-O(1)	106.08(10)
O(4)#2-Zn(1)-O(1)	84.32(9)	O(8)#1-Zn(2)-N(2)	109.87(11)
O(5)-Zn(1)-O(1)	90.21(9)	O(3)#2-Zn(2)-N(2)	103.29(11)
N(1)#3-Zn(1)-O(1)	172.11(10)	O(1)-Zn(2)-N(2)	107.71(11)
O(7)#1-Zn(1)-O(6)	154.73(9)		
N(1)-Cd(1)-O(1)	135.59(11)	N(1)-Cd(1)-O(2)	81.99(12)
O(1)#1-Cd(1)-O(1)	96.9(2)	O(1)#1-Cd(1)-O(2)	115.10(14)
N(1)#1-Cd(1)-O(2)#1	81.99(12)	O(1)-Cd(1)-O(2)	53.62(11)
8			
O(5)-Cd(1)-N(2)	102.1(3)	N(3)#3-Cd(2)-N(4)#2	171.4(4)
O(5)-Cd(1)-N(1)	94.4(3)	O(4)#1-Cd(2)-O(8)#6	87.2(4)
N(2)-Cd(1)-N(1)	163.3(3)	N(3)#3-Cd(2)-O(8)#6	88.9(3)
O(5)-Cd(1)-O(3)#1	112.7(3)	N(4)#2-Cd(2)-O(8)#6	92.9(3)
N(2)-Cd(1)-O(3)#1	86.5(3)	O(4)#1-Cd(2)-O(5)	77.2(4)
N(1)-Cd(1)-O(3)#1	84.6(3)	N(3)#3-Cd(2)-O(5)	86.8(3)
O(5)-Cd(1)-O(1)	93.6(3)	N(4)#2-Cd(2)-O(5)	93.8(3)
N(2)-Cd(1)-O(1)	85.0(3)	O(8)#6-Cd(2)-O(5)	163.4(3)
N(1)-Cd(1)-O(1)	96.8(3)	O(4)#1-Cd(2)-O(7)#6	141.6(4)
O(3)#1-Cd(1)-O(1)	153.5(3)	N(3)#3-Cd(2)-O(7)#6	87.6(3)
O(5)-Cd(1)-O(2)	146.8(3)	N(4)#2-Cd(2)-O(7)#6	86.7(3)
N(2)-Cd(1)-O(2)	84.5(3)	O(8)#6-Cd(2)-O(7)#6	54.5(3)
N(1)-Cd(1)-O(2)	83.2(3)	O(5)-Cd(2)-O(7)#6	141.2(3)
O(3)#1-Cd(1)-O(2)	100.0(3)	O(4)#1-Cd(2)-O(6)	130.1(4)
O(1)-Cd(1)-O(2)	54.2(3)	N(3)#3-Cd(2)-O(6)	85.9(3)
N(3)#3-Cd(2)-O(4)#1	95.3(4)	N(4)#2-Cd(2)-O(6)	87.6(3)

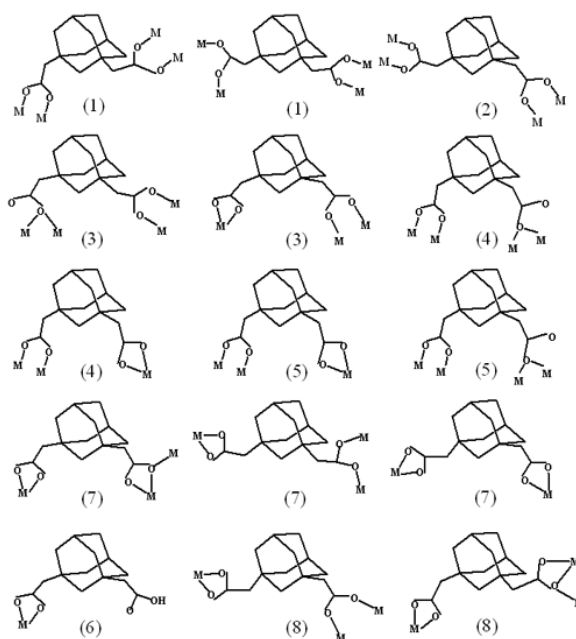
O(6)-Cd(2)-O(3) 101.75(11) O(12)-Cd(3)-O(9) 90.49(15) O(4)#1-Cd(2)-N(4)#2 93.2(3) O(5)-Cd(2)-O(6) 53.0(2)

[a] Symmetry codes: **1**: #1 $-x+1/2, -y+1/2, -z+1$; #2 $x, -y, z+1/2$; #3 $-x+1/2, y+1/2, -z+1/2$; #4 $-x+1, y, -z+3/2$. **3**: #1 $x, -y+1, z-1/2$; #2 $x+1, y, z+1$. **4**: #2 $-x+1, -y+2, -z+1$; #3 $-x, -y+1, -z$; #4 $x, y-1, z-1$. **5**: #1 $-x+1, -y+1, -z$; #2 $-x+2, -y+2, -z+1$; #3 $x, y-1, z-1$. **6**: #1 $-x, y, -z+1/2$. **7**: #1 $x+1, y+1, z$; #2 $-x+1, -y+1, -z+1$; #3 $-x+1, -y+1, -z+2$; #4 $x-1, y, z$. **8**: #1 $-x, y-1/2, -z+3/2$; #2 $x+1, y, z$; #3 $-x+1, y+1/2, -z+3/2$; #6 $-x+1, y-1/2, -z+3/2$.

Table S3. Possible hydrogen bond geometries for complexes 6 ^[a]

Complex	D—H···A (Å)	D—H (Å)	H···A (Å)	D···A (Å)	<DHA (°)
6	O(4)-H(4)···O(2)#3	0.82	1.86	2.661(6)	164.5

[a] Symmetry codes: **6**: #3 $x, -y+1, z+1/2$.



Scheme S1 Coordination modes and configurations of ADA ligands observed in 1–8.

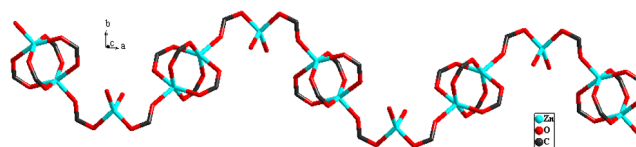


Figure S1 View of a 1D infinite Zn–O–C–O–Zn chains running along the *a* direction.

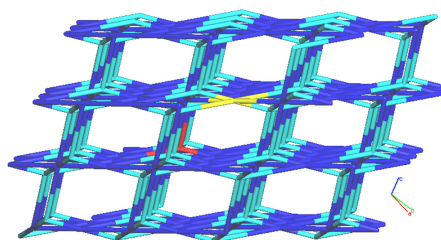


Figure S2 The 3-D net with 4,6-connected vertices of **1**.

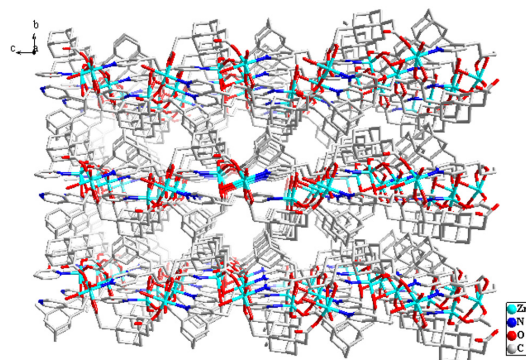


Figure S3 View of the parallel offset 2D layers in **3** by weak van der Waals interactions.

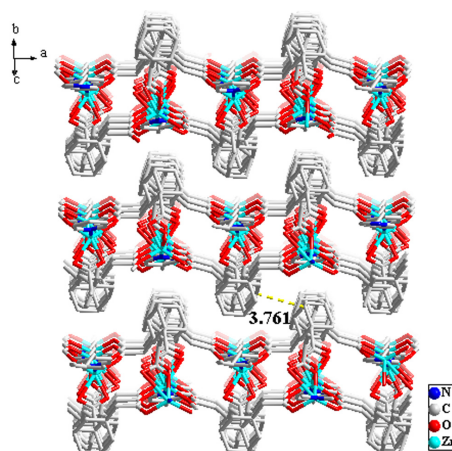


Figure S4 View of the parallel offset 2D layers in **4** by weak van der Waals interactions.

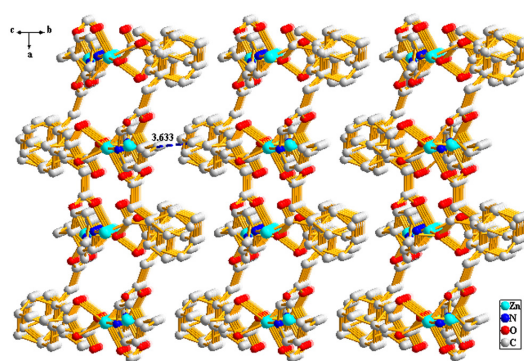


Figure S5 View of the parallel offset 2D layers in **5** by weak van der Waals interactions.

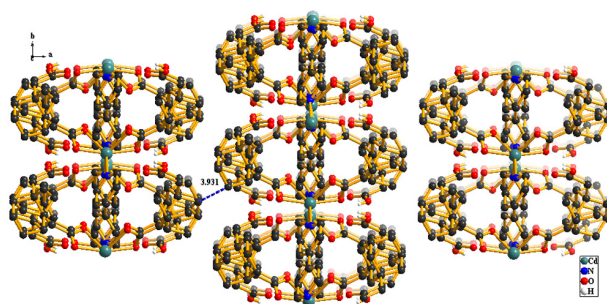


Figure S6 View of the parallel offset 2D layers in **6** by weak van der Waals interactions.

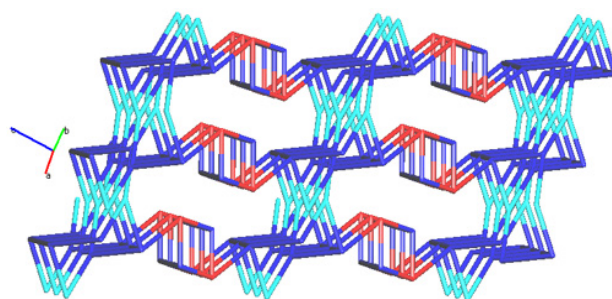


Figure S7 View of the topology of **7**.

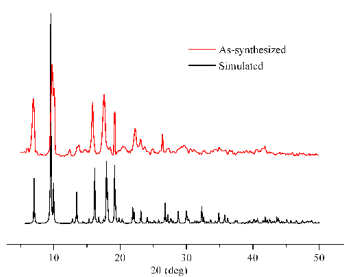


Figure S8

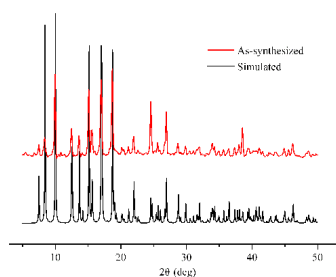


Figure S9

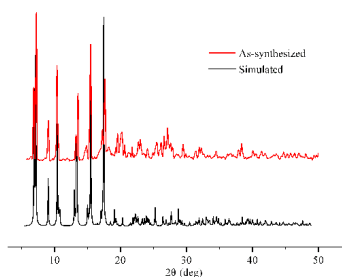


Figure S10

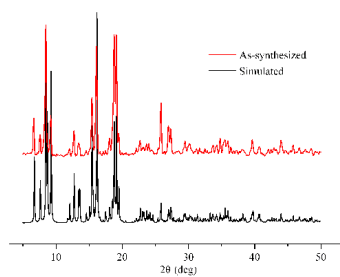


Figure S11

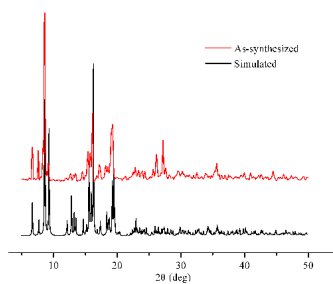


Figure S12

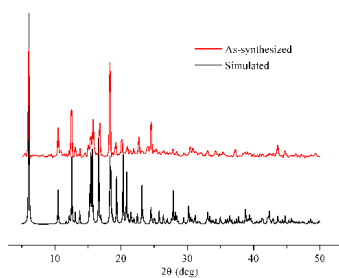


Figure S13

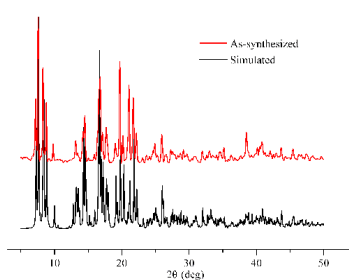


Figure S14

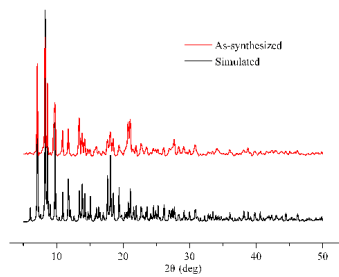


Figure S15

Figure S8-S15 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and as-synthesized product of 1–8.

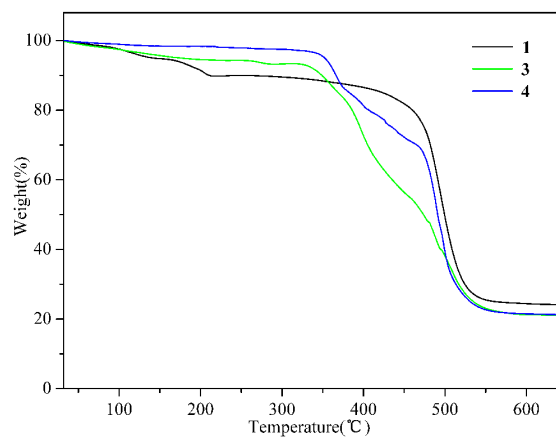


Figure S16 TG graphs of complexes 1, 3 and 4

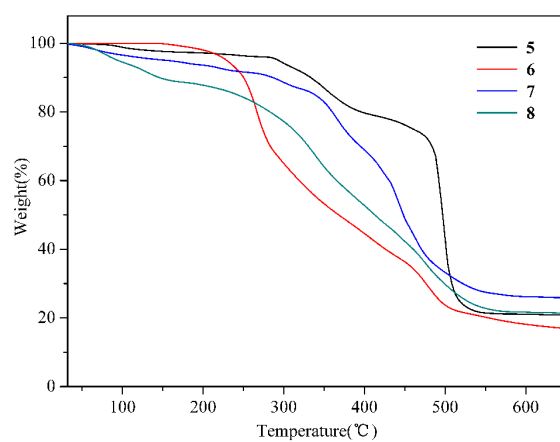


Figure S17 TG graphs of complexes 5–8

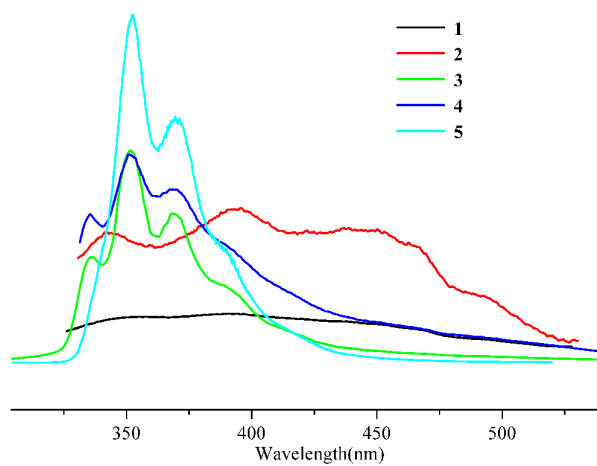


Figure S18 Fluorescence spectra of complexes 1–5 in the solid state at room temperature.

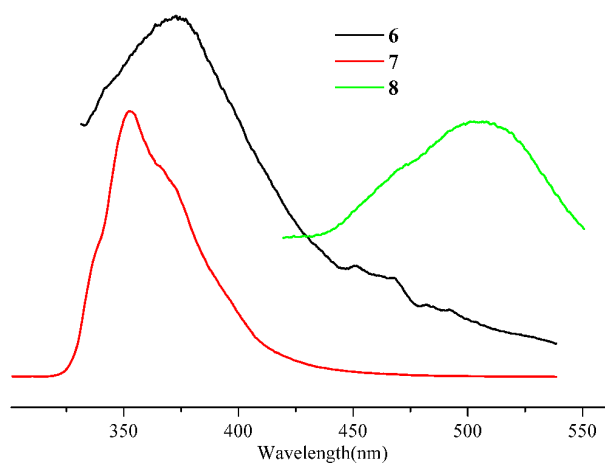


Figure S19 Fluorescence spectra of complexes 6–8 in the solid state at room temperature.