Electronic supplementary information

A series of coordination polymers based on reduced Schiff base multidentate anions and bis(imidazole) ligands: syntheses, structures and photoluminescence

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Table S1. Selected bond distances (Å) and angles (°) for compounds **1**-**11**.

1			
Zn(1)-O(4)$^{\#1}$	1.961(4)	Zn(1)-O(1)	1.988(4)
Zn(1)-N(4)$^{\#2}$	2.014(5)	Zn(1)-N(1)	2.031(5)
O(4)$^{\#1}$-Zn(1)-O(1)	93.61(17)	O(4)$^{\#1}$-Zn(1)-N(4)$^{\#2}$	117.3(2)
O(1)-Zn(1)-N(4)$^{\#2}$	124.0(2)	O(4)$^{\#1}$-Zn(1)-N(1)	114.5(2)
O(1)-Zn(1)-N(1)	102.1(2)	N(4)$^{\#2}$-Zn(1)-N(1)	104.8(2)
2			
Co(1)-O(3')$^{\#1}$	1.920(9)	Co(1)-N(1)	2.035(3)
Co(1)-O(2)	2.042(3)	Co(1)-N(4)$^{\#2}$	2.050(4)
Co(1)-O(1)	2.163(8)	Co(1)-O(3)$^{\#1}$	2.186(7)
Co(1)-O(4)$^{\#1}$	2.316(8)		

O(3')$^{\#1}$-Co(1)-N(1)	126.2(4)	O(3')$^{\#1}$-Co(1)-O(2)	86.0(3)
N(1)-Co(1)-O(2)	106.72(15)	O(3')$^{\#1}$-Co(1)-N(4)$^{\#2}$	102.5(4)
N(1)-Co(1)-N(4)$^{\#2}$	103.90(13)	O(2)-Co(1)-N(4)$^{\#2}$	134.03(18)
O(3')$^{\#1}$-Co(1)-O(1)	132.0(4)	N(1)-Co(1)-O(1)	95.8(2)
O(2)-Co(1)-O(1)	57.59(17)	N(4)$^{\#2}$-Co(1)-O(1)	86.11(18)
O(3')$^{\#1}$-Co(1)-O(3)$^{\#1}$	21.9(3)	N(1)-Co(1)-O(3)$^{\#1}$	147.8(2)
O(2)-Co(1)-O(3)$^{\#1}$	82.71(17)	N(4)$^{\#2}$-Co(1)-O(3)$^{\#1}$	89.2(2)
O(1)-Co(1)-O(3)$^{\#1}$	114.5(2)	O(3')$^{\#1}$-Co(1)-O(4)$^{\#1}$	42.2(4)
N(1)-Co(1)-O(4)$^{\#1}$	90.9(2)	O(2)-Co(1)-O(4)$^{\#1}$	120.6(3)
N(4)$^{\#2}$-Co(1)-O(4)$^{\#1}$	91.9(2)	O(1)-Co(1)-O(4)$^{\#1}$	173.2(3)
O(3)$^{\#1}$-Co(1)-O(4)$^{\#1}$	58.9(3)		

3

Cd(1)-N(4)$^{\#1}$	2.213(4)	Cd(1)-O(2)	2.244(3)
Cd(1)-N(1)	2.252(4)	Cd(1)-O(4)$^{\#2}$	2.255(4)
Cd(1)-O(1)	2.474(4)	Cd(1)-O(3)$^{\#2}$	2.648(3)
N(4)$^{\#1}$-Cd(1)-O(2)	110.68(14)	N(4)$^{\#1}$-Cd(1)-N(1)	102.83(14)
O(2)-Cd(1)-N(1)	134.69(13)	N(4)$^{\#1}$-Cd(1)-O(4)$^{\#2}$	135.10(14)
O(2)-Cd(1)-O(4)$^{\#2}$	83.56(14)	N(1)-Cd(1)-O(4)$^{\#2}$	93.81(16)
N(4)$^{\#1}$-Cd(1)-O(1)	104.44(14)	O(2)-Cd(1)-O(1)	53.98(14)
N(1)-Cd(1)-O(1)	89.15(14)	O(4)$^{\#2}$-Cd(1)-O(1)	117.37(14)
N(4)$^{\#1}$-Cd(1)-O(3)$^{\#2}$	85.58(13)	O(2)-Cd(1)-O(3)$^{\#2}$	120.77(13)
N(1)-Cd(1)-O(3)$^{\#2}$	90.73(13)	O(4)$^{\#2}$-Cd(1)-O(3)$^{\#2}$	52.41(12)
O(1)-Cd(1)-O(3)$^{\#2}$	169.74(13)		

4

N(1)-Zn(1)	2.007(2)	N(4)-Zn(1)$^{\#1}$	2.029(2)
O(1)-Zn(1)	1.938(2)	O(3)-Zn(1)$^{\#2}$	1.987(2)
O(1)-Zn(1)-O(3)$^{\#3}$	113.45(8)	O(1)-Zn(1)-N(1)	124.60(8)
O(3)$^{\#3}$-Zn(1)-N(1)	106.98(8)	O(1)-Zn(1)-N(4)$^{\#4}$	104.27(9)
O(3)$^{\#3}$-Zn(1)-N(4)$^{\#4}$	104.12(9)	N(1)-Zn(1)-N(4)$^{\#4}$	100.67(9)

5

Co(1)-O(4)$^{\#1}$	1.968(2)	Co(1)-N(1)	2.018(3)
Co(1)-O(1)	2.021(2)	Co(1)-N(4)$^{\#2}$	2.046(3)
O(4)$^{\#1}$-Co(1)-N(1)	130.33(12)	O(4)$^{\#1}$-Co(1)-O(1)	111.75(11)
N(1)-Co(1)-O(1)	105.25(11)	O(4)$^{\#1}$-Co(1)-N(4)$^{\#2}$	104.81(11)
N(1)-Co(1)-N(4)$^{\#2}$	99.18(12)	O(1)-Co(1)-N(4)$^{\#2}$	101.05(12)

6

Cd(1)-N(1)	2.208(2)	Cd(1)-O(1)	2.329(2)
Cd(1)-O(3)$^{\#1}$	2.3297(19)	Cd(1)-O(2)	2.345(2)
Cd(1)-O(3)$^{\#2}$	2.3881(19)	Cd(1)-O(4)$^{\#1}$	2.441(2)
Cd(1)-O(1W)	2.616(3)		
N(1)-Cd(1)-O(1)	102.91(7)	N(1)-Cd(1)-O(3)$^{\#1}$	103.70(7)
O(1)-Cd(1)-O(3)$^{\#1}$	152.85(7)	N(1)-Cd(1)-O(2)	154.72(8)
O(1)-Cd(1)-O(2)	55.34(6)	O(3)$^{\#1}$-Cd(1)-O(2)	97.53(7)
N(1)-Cd(1)-O(3)$^{\#2}$	87.20(7)	O(1)-Cd(1)-O(3)$^{\#2}$	99.45(8)
O(3)$^{\#1}$-Cd(1)-O(3)$^{\#2}$	76.59(7)	O(2)-Cd(1)-O(3)$^{\#2}$	84.49(7)
N(1)-Cd(1)-O(4)$^{\#1}$	113.88(8)	O(1)-Cd(1)-O(4)$^{\#1}$	118.32(7)
O(3)$^{\#1}$-Cd(1)-O(4)$^{\#1}$	53.80(6)	O(2)-Cd(1)-O(4)$^{\#1}$	89.71(8)
O(3)$^{\#2}$-Cd(1)-O(4)$^{\#1}$	128.78(6)	N(1)-Cd(1)-O(1W)	84.93(9)
O(1)-Cd(1)-O(1W)	75.44(10)	O(3)$^{\#1}$-Cd(1)-O(1W)	112.3(1)
O(2)-Cd(1)-O(1W)	99.69(9)	O(3)$^{\#2}$-Cd(1)-O(1W)	169.37(8)
O(4)$^{\#1}$-Cd(1)-O(1W)	61.34(9)		

7

Zn(1)-O(1)	2.009(4)	Zn(1)-N(1)	2.046(5)
Zn(1)-N(4)$^{\#1}$	2.035(5)	Zn(1)-O(4)$^{\#2}$	2.113(5)
Zn(1)-O(3)$^{\#2}$	2.344(5)		
O(1)-Zn(1)-N(1)	103.53(18)	O(1)-Zn(1)-N(4)$^{\#1}$	107.26(18)
N(1)-Zn(1)-N(4)$^{\#1}$	95.79(17)	O(1)-Zn(1)-O(4)$^{\#2}$	129.89(18)
N(1)-Zn(1)-O(4)$^{\#2}$	103.70(18)	N(4)$^{\#1}$-Zn(1)-O(4)$^{\#2}$	110.85(19)
O(1)-Zn(1)-O(3)$^{\#2}$	94.24(18)	N(1)-Zn(1)-O(3)$^{\#2}$	160.51(17)
N(4)$^{\#1}$-Zn(1)-O(3)$^{\#2}$	86.37(17)	O(4)$^{\#2}$-Zn(1)-O(3)$^{\#2}$	57.84(17)

8

Co(1)-N(4)$^{\#1}$	2.058(2)	Co(1)-N(1)	2.059(2)
Co(1)-O(3)$^{\#2}$	2.0594(19)	Co(1)-O(1)	2.0993(19)
Co(1)-O(2)	2.2759(19)	Co(1)-O(4)$^{\#2}$	2.399(2)
N(4)$^{\#1}$-Co(1)-N(1)	93.63(8)	N(4)$^{\#1}$-Co(1)-O(3)$^{\#2}$	102.37(8)
N(1)-Co(1)-O(3)$^{\#2}$	102.37(9)	N(4)$^{\#1}$-Co(1)-O(1)	108.87(9)
N(1)-Co(1)-O(1)	104.90(8)	O(3)$^{\#2}$-Co(1)-O(1)	136.58(8)
N(4)$^{\#1}$-Co(1)-O(2)	87.23(8)	N(1)-Co(1)-O(2)	163.72(9)
O(3)$^{\#2}$-Co(1)-O(2)	93.29(8)	O(1)-Co(1)-O(2)	59.71(7)
N(4)$^{\#1}$-Co(1)-O(4)$^{\#2}$	160.28(8)	N(1)-Co(1)-O(4)$^{\#2}$	88.14(8)

O(3)$^{\#2}$-Co(1)-O(4)$^{\#2}$	58.18(7)	O(1)-Co(1)-O(4)$^{\#2}$	89.56(8)
O(2)-Co(1)-O(4)$^{\#2}$	96.52(7)		

9

Cd(1)-N(1)	2.239(2)	Cd(1)-O(1)	2.2583(17)
Cd(1)-O(3)$^{\#1}$	2.3197(17)	Cd(1)-O(2)$^{\#2}$	2.3452(16)
Cd(1)-O(1W)	2.358(2)	Cd(1)-O(4)$^{\#1}$	2.4786(19)
N(1)-Cd(1)-O(1)	107.93(7)	N(1)-Cd(1)-O(3)$^{\#1}$	109.80(7)
O(1)-Cd(1)-O(3)$^{\#1}$	95.00(7)	N(1)-Cd(1)-O(2)$^{\#2}$	88.76(6)
O(1)-Cd(1)-O(2)$^{\#2}$	155.13(6)	O(3)$^{\#1}$-Cd(1)-O(2)$^{\#2}$	96.47(6)
N(1)-Cd(1)-O(1W)	92.86(8)	O(1)-Cd(1)-O(1W)	81.25(7)
O(3)$^{\#1}$-Cd(1)-O(1W)	156.99(7)	O(2)$^{\#2}$-Cd(1)-O(1W)	79.57(7)
N(1)-Cd(1)-O(4)$^{\#1}$	163.10(7)	O(1)-Cd(1)-O(4)$^{\#1}$	81.57(7)
O(3)$^{\#1}$-Cd(1)-O(4)$^{\#1}$	54.47(6)	O(2)$^{\#2}$-Cd(1)-O(4)$^{\#1}$	87.28(6)
O(1W)-Cd(1)-O(4)$^{\#1}$	102.56(7)		

10

Zn(1)-O(1)	1.979(3)	Zn(1)-O(4)$^{\#1}$	2.016(2)
Zn(1)-N(1)	2.021(3)	Zn(1)-N(4)$^{\#2}$	2.024(3)
O(1)-Zn(1)-O(4)$^{\#1}$	106.62(11)	O(1)-Zn(1)-N(1)	113.24(14)
O(4)$^{\#1}$-Zn(1)-N(1)	122.13(11)	O(1)-Zn(1)-N(4)$^{\#2}$	115.37(11)
O(4)$^{\#1}$-Zn(1)-N(4)$^{\#2}$	95.76(13)	N(1)-Zn(1)-N(4)$^{\#2}$	102.75(15)

11

Cd(1)-N(1)	2.247(3)	Cd(1)-O(2)	2.261(2)
Cd(1)-O(1W)	2.314(3)	Cd(1)-O(4)$^{\#1}$	2.365(3)
Cd(1)-O(3)$^{\#1}$	2.488(3)	Cd(1)-N(3)$^{\#2}$	2.532(3)
N(1)-Cd(1)-O(2)	138.07(10)	N(1)-Cd(1)-O(1W)	90.44(12)
O(2)-Cd(1)-O(1W)	89.52(11)	N(1)-Cd(1)-O(4)$^{\#1}$	137.72(10)
O(2)-Cd(1)-O(4)$^{\#1}$	84.16(9)	O(1W)-Cd(1)-O(4)$^{\#1}$	87.66(11)
N(1)-Cd(1)-O(3)$^{\#1}$	85.30(10)	O(2)-Cd(1)-O(3)$^{\#1}$	136.27(9)
O(1W)-Cd(1)-O(3)$^{\#1}$	96.76(11)	O(4)$^{\#1}$-Cd(1)-O(3)$^{\#1}$	53.12(9)
N(1)-Cd(1)-N(3)$^{\#2}$	88.99(11)	O(2)-Cd(1)-N(3)$^{\#2}$	90.99(10)
O(1W)-Cd(1)-N(3)$^{\#2}$	179.41(11)	O(4)$^{\#1}$-Cd(1)-N(3)$^{\#2}$	92.68(10)
O(3)$^{\#1}$-Cd(1)-N(3)$^{\#2}$	83.06(10)		

Symmetry codes for **1**: $^{\#1}$ -x+1, y-1, -z+1/2; $^{\#2}$ -x+3/2, -y+1/2, -z. For **2**: $^{\#1}$ -x+1, y-1, -z+3/2; $^{\#2}$ -x+1/2, -y+3/2, -z+2. For **3**: $^{\#1}$ -x-1/2, -y-1/2, -z+2; $^{\#2}$ -x, y+1, -z+3/2. For **4**: $^{\#1}$ x+1/2, -y+1/2, z-1/2; $^{\#2}$ x, y-1, z; $^{\#3}$ x, y+1, z; $^{\#4}$ x-1/2, -y+1/2, z+1/2. For **5**: $^{\#1}$ x, y-1,

z; [#2] x-1/2, -y+1/2, z+1/2. For **6**: [#1] -x+1, -y+1, -z; [#2] x-1, y-1, z. For **7**: [#1] x+1/2, -y-1/2, z; [#2] x, y, z+1. For **8**: [#1] x-1/2, -y-1/2, z; [#2] x, y, z+1. For **9**: [#1] -x+1, -y+1, -z+1; [#2] -x+1/2, y-1/2, -z+3/2. For **10**: [#1] x-1/2, -y+1/2, z-1/2; [#2] -x+1/2, y-1/2, -z+1/2. For **11**: [#1] x+1/2, y+1/2, z; [#2] -x+1, -y, -z+1.

Table S2. Hydrogen-Bonding Parameters for **1-5** and **7-11** (in Å and deg)

	D-H···A	d(D-H)	d(D···A)	∠(D-H···A)
1				
O(1W)-H(1WA)...O(1)[#3]	0.90(2)	2.49(16)	2.978(6)	115(13)
O(1W)-H(1WB)...O(1)[#4]	0.89(2)	2.10(5)	2.978(6)	166(16)
N(5)-H(5N)...O(4)	0.87(2)	2.05(5)	2.715(6)	132(6)
2				
N(5)-H(1N)...O(2)	0.78(5)	2.07(5)	2.660(5)	133(5)
O(1W)-H(1WB)...O(3')[#4]	1.08(16)	1.90(15)	2.919(10)	156(15)
3				
O(1W)-H(1WA)...O(4)[#4]	0.86(2)	2.27(10)	3.048(5)	152(18)
O(1W)-H(1WB)...O(4)	0.86(2)	2.25(9)	3.048(5)	154(17)
N(5)-H(5N)...O(2)	0.80(5)	2.01(5)	2.645(5)	137(5)
4				
N(5)-H(5N)...O(4)[#5]	0.815(16)	2.224(17)	3.034(4)	173(3)
O(1W)-H(1WA)...O(3)[#6]	0.894(18)	2.23(3)	3.047(3)	151(4)
O(1W)-H(1WB)...O(2)[#7]	0.891(18)	1.98(2)	2.872(4)	174(4)
5				
O(1W)-H(1B)...O(3)	0.92	2.06	2.922(5)	155.7
O(2W)-H(2B)...O(1W)	0.96	2.03	2.895(13)	148.9
N(5)-H(5N)...O(2)[#5]	0.76(4)	2.26(4)	3.014(4)	173(5)
7				
O(1W)-H(1WB)...O(4)[#5]	0.91(2)	2.15(4)	2.987(8)	153(8)
N(5)-H(5N)...O(2)[#6]	0.853(18)	2.27(3)	3.010(7)	146(3)
O(1W)-H(1WA)...O(1)	0.89(2)	2.07(3)	2.935(7)	163(8)
8				
N(5)-H(5N)...O(4)[#5]	0.78(3)	2.35(3)	3.099(3)	160(3)
O(1W)-H(1WB)...O(3)[#6]	0.851(18)	2.15(3)	2.886(3)	144(4)
O(1W)-H(1WA)...O(1)	0.861(18)	2.17(2)	2.984(3)	158(4)

9				
O(1W)-H(1WA)...O(3)$^{\#5}$	0.827(18)	1.884(19)	2.711(2)	177(4)
O(3W)-H(3WA)...O(4)$^{\#1}$	0.85(2)	2.03(3)	2.867(4)	165(6)
O(1W)-H(1WB)...O(2W)	0.796(18)	2.28(3)	2.984(5)	148(4)
O(2W)-H(2WB)...O(1)	0.85(6)	2.05(3)	2.856(4)	159(7)
10				
O(6)-H(6)...O(3)$^{\#5}$	0.82	1.77	2.573(4)	165.8
N(5)-H(5N)...O(2)$^{\#6}$	0.84(3)	2.21(3)	3.046(4)	174(4)
11				
O(1W)-H(1WA)...O(5)$^{\#5}$	0.84(4)	2.30(3)	3.037(5)	145(4)
O(1W)-H(1WB)...O(1)$^{\#6}$	0.842(19)	1.93(2)	2.765(4)	173(5)

Symmetry code for **1**: $^{\#3}$ -x+1, y+1, -z+1/2; $^{\#4}$ x, y+1, z. For **2**: $^{\#4}$ x, y-1, z. For **3**: $^{\#4}$ -x, y, -z+3/2. For **4**: $^{\#5}$ -x, -y-1, -z; $^{\#6}$ x+1/2, -y-1/2, z-1/2; $^{\#7}$ -x+1, -y, -z. For **5**: $^{\#5}$ -x+1, -y+1, -z+1. For **7**: $^{\#5}$ -x+1, -y, z+1/2; $^{\#6}$ -x+1/2, y+1/2, z-1/2. For **8**: $^{\#5}$ -x+1/2, y+1/2, z+1/2; $^{\#6}$ -x, -y, z+1/2. For **9**: $^{\#1}$ -x+1, -y+1, -z+1; $^{\#5}$ x-1/2, -y+1/2, z+1/2. For **10**: $^{\#5}$ x+1/2, -y+1/2, z-1/2; $^{\#6}$ -x+3/2, y+1/2, -z+1/2. For **11**: $^{\#5}$ -x+1/2, y+1/2, -z+1/2; $^{\#6}$ -x+1/2, -y+1/2, -z+1.

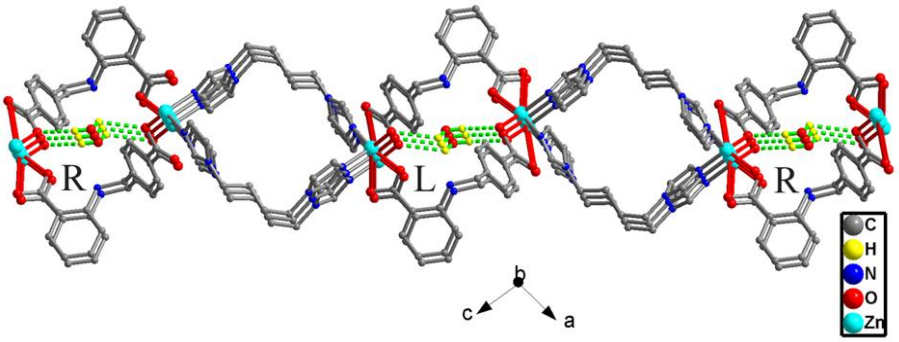


Fig. S1 The helical channels and the hydrogen bonds in the layer of **1**.

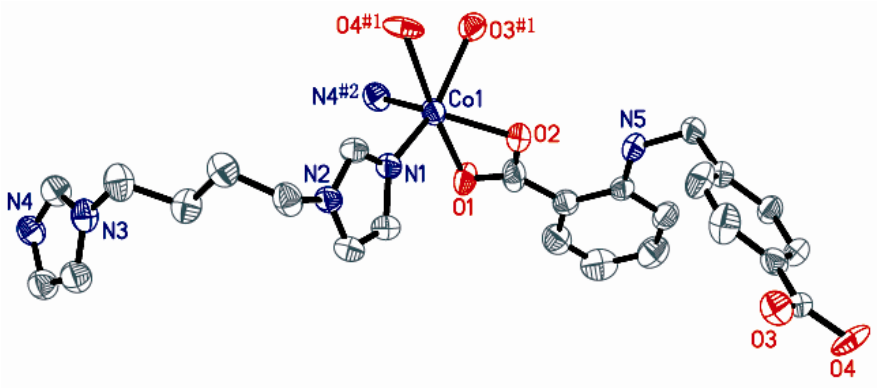
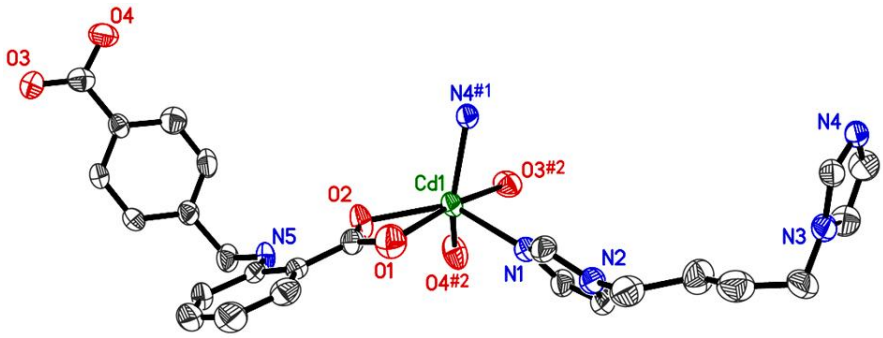
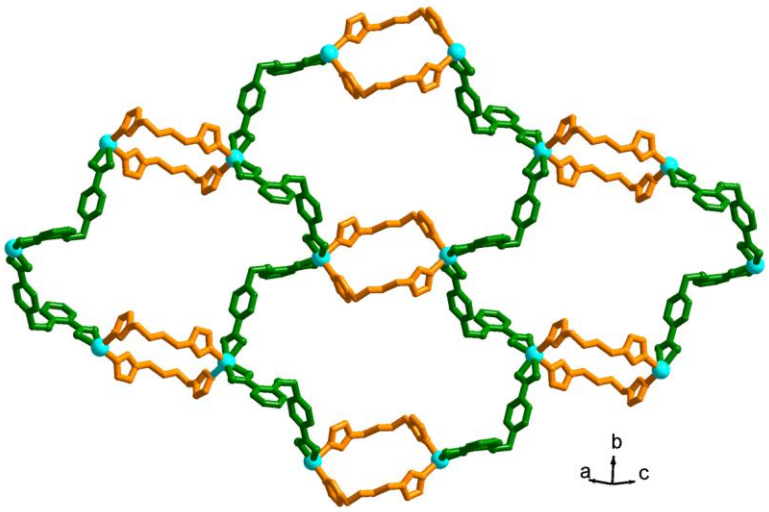


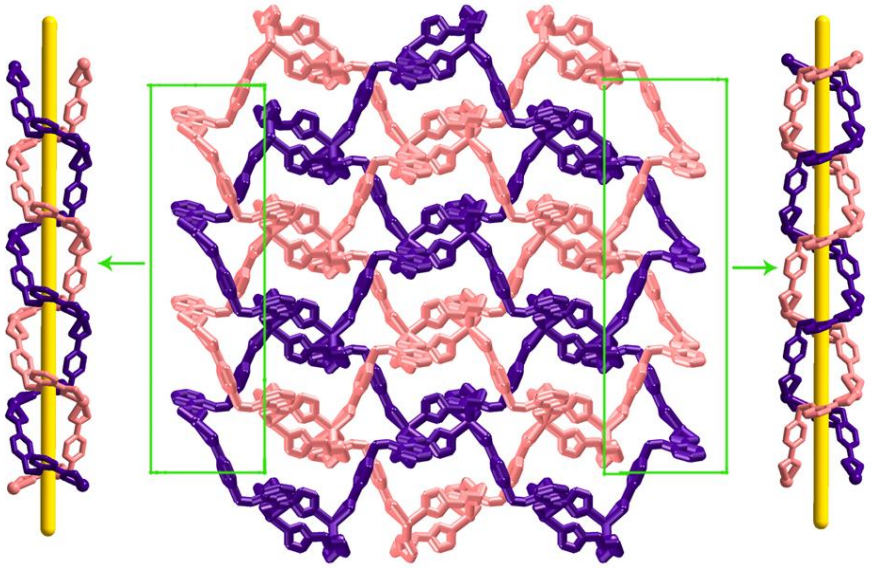
Fig. S2 ORTEP diagram showing the coordination environment for Co(II) atom in **2**. Symmetry codes: #1 -x+1, y-1, -z+3/2; #2 -x+1/2, -y+3/2, -z+2.



(a)



(b)



(c)

Fig. S3 (a) ORTEP diagram showing the coordination environment for Cd atom in **3**. Symmetry codes: $^{\#1}$ -x-1/2, -y-1/2, -z+2; $^{\#2}$ -x, y+1, -z+3/2. (b) View of the layer connected by $[Co(bbi)_2Co]$ or $[Cd(bbi)_2Cd]$ dimers and L^1 anions of **2** and **3**. (c) Two-fold interpenetrating layer and the double-stranded helix of **2** and **3** along the *b*-axis.

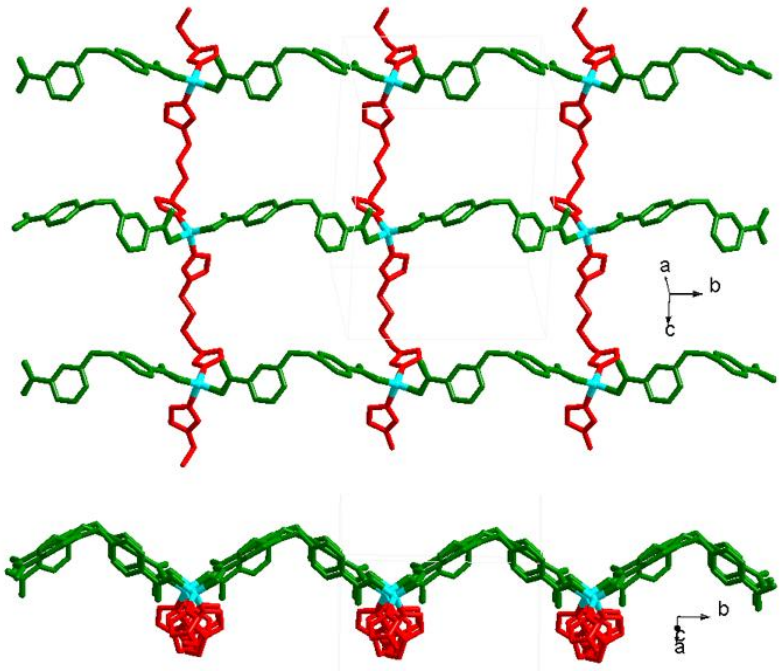


Fig. S4 View of the 2D undulated layer from different directions in **4** (L^2 and bbi ligands were shown in distinct color).

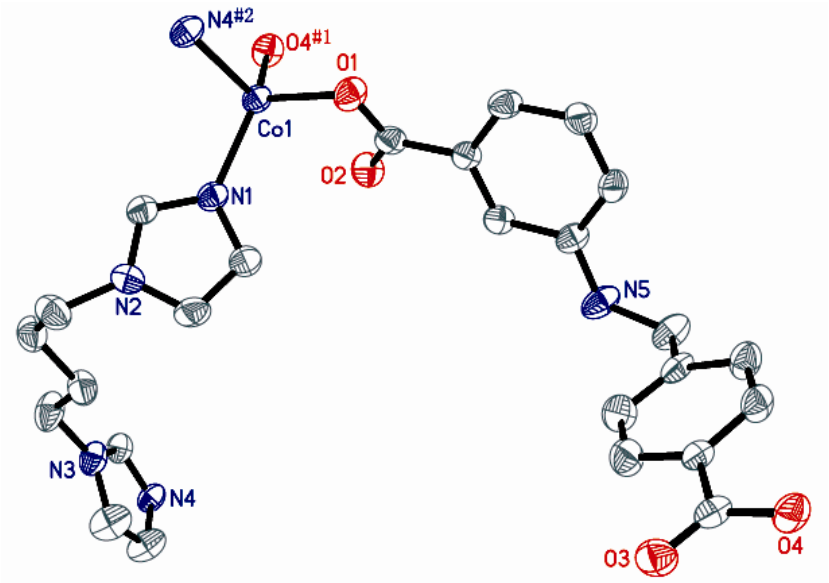


Fig. S5 (a) ORTEP diagram showing the coordination environment for Co atom in **5**. Symmetry codes: #1 x, y-1, z; #2 x-1/2, -y+1/2, z+1/2.

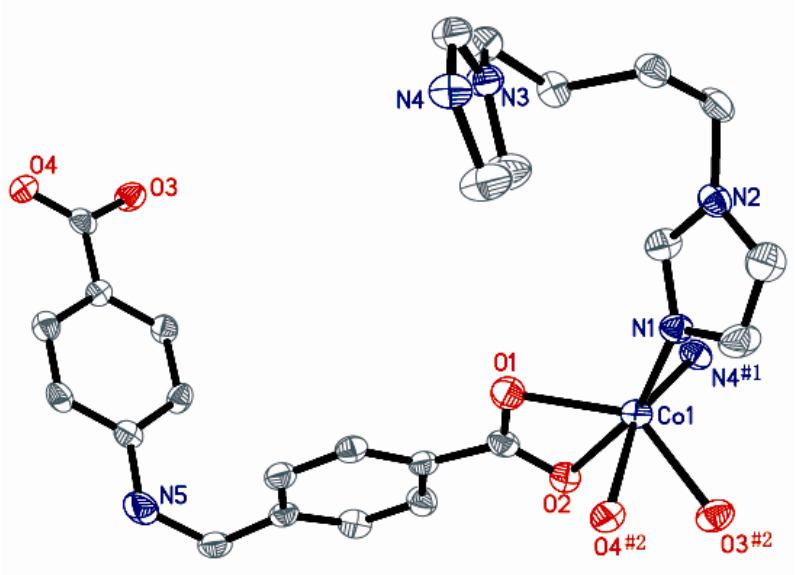
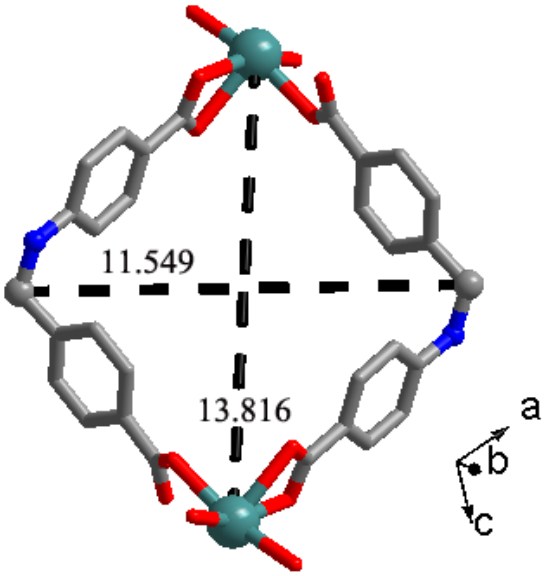
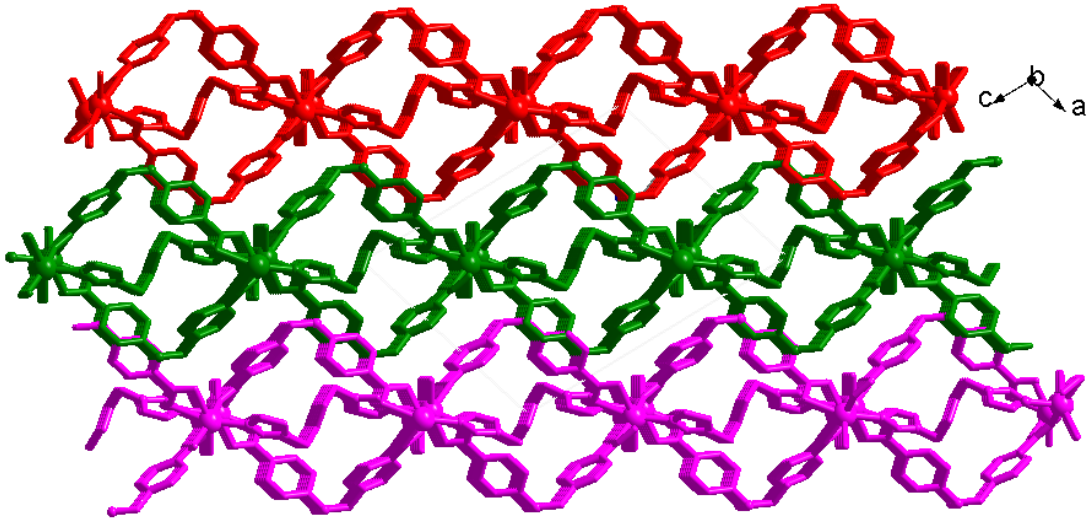


Fig. S6 (a) ORTEP diagram showing the coordination environment for Co atom in **8**. Symmetry codes: #1 x-1/2, -y-1/2, z; #2 x, y, z+1.



(a)



(b)

Fig. S7. (a) View of the $[Cd_2(L^3)_2]$ ring in **9**. (b) The 3D supramolecular structure of **9.**

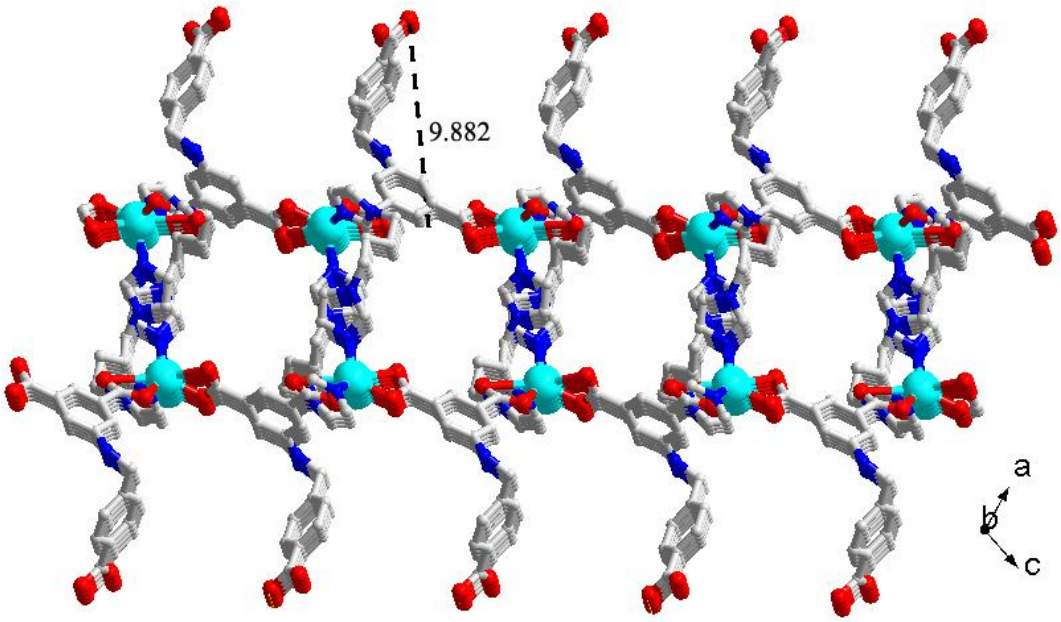
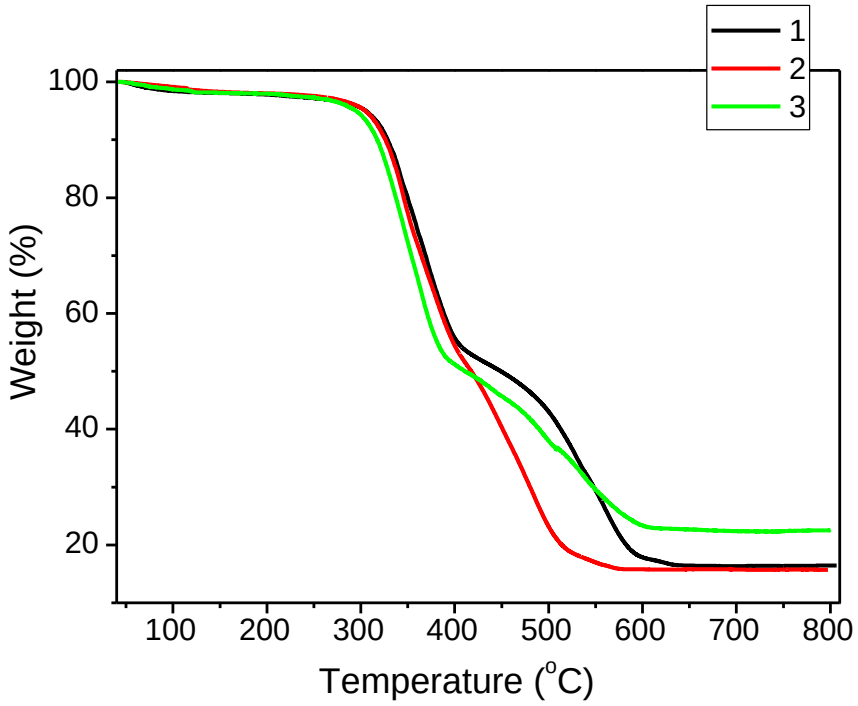


Fig. S8. View of the undulated layer of **10** with dangling arms.



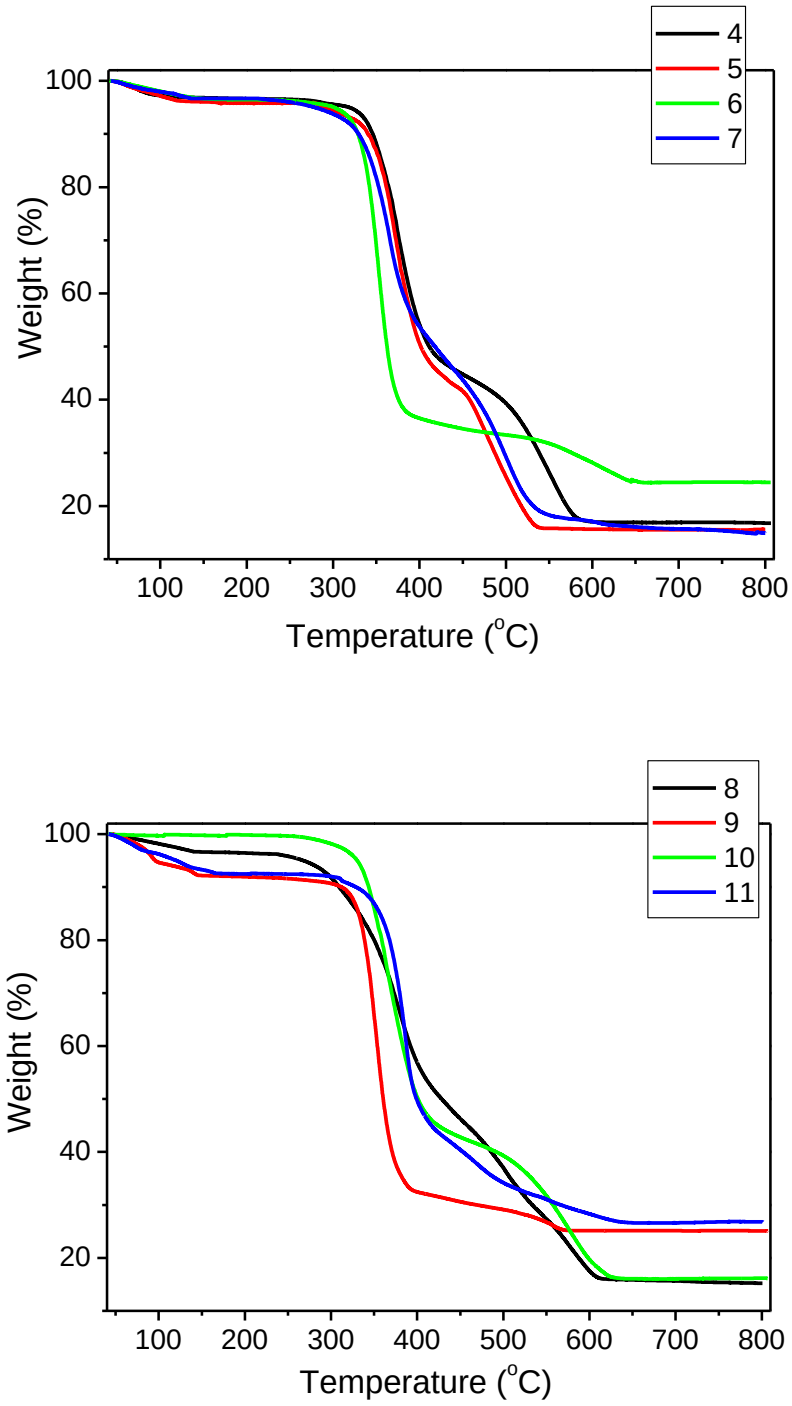


Fig. S9. TGA curves of compounds **1-11**.

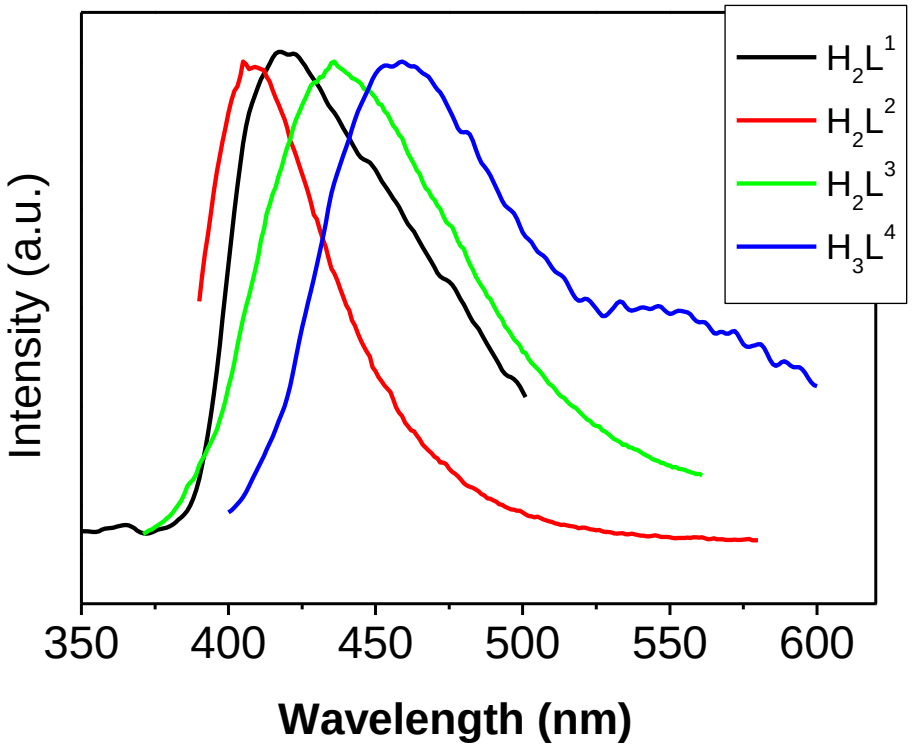
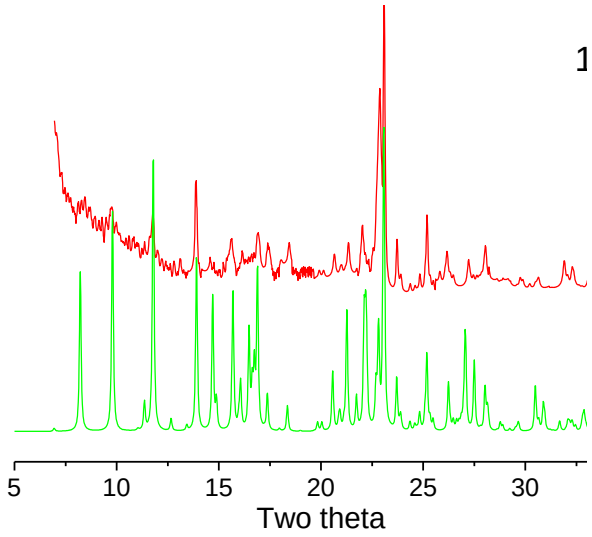
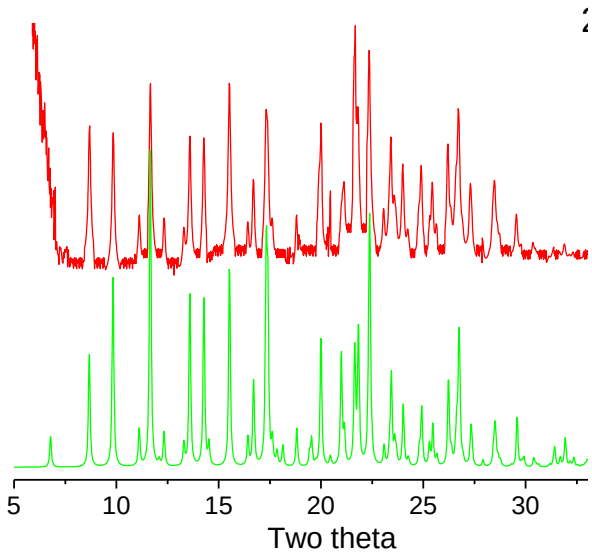
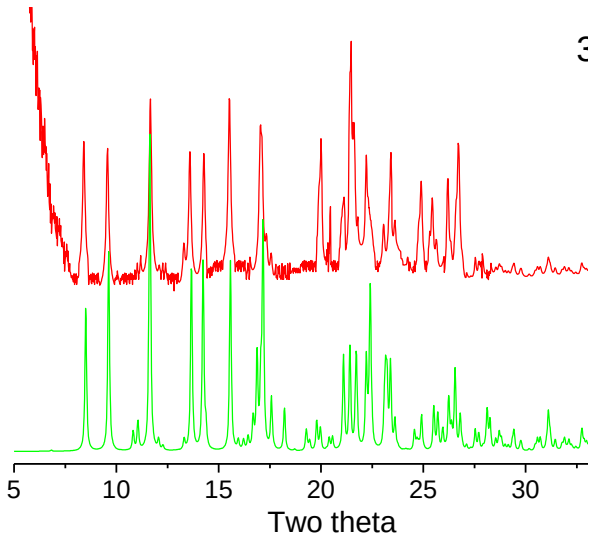
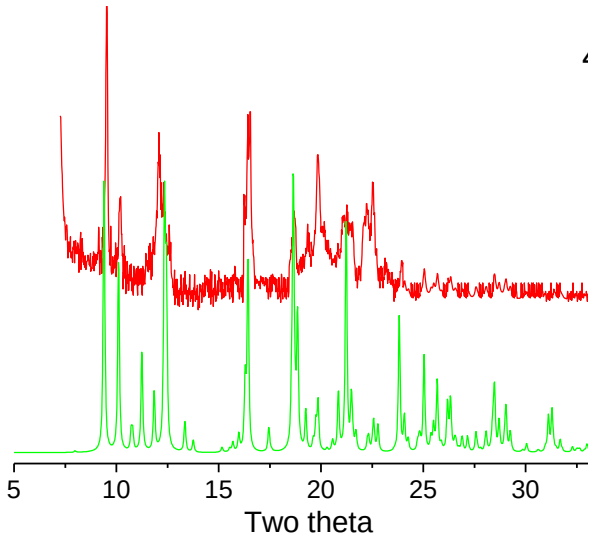


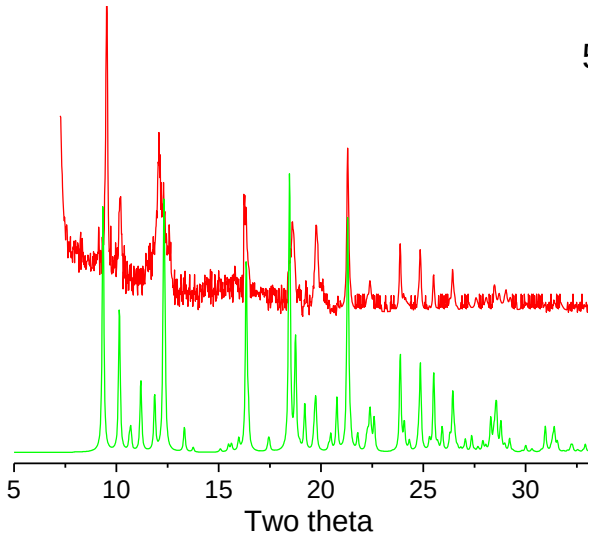
Fig. S10. Solid-state emission spectra of H_2L^1, H_2L^2, H_2L^3 and H_3L^4 at room temperature.

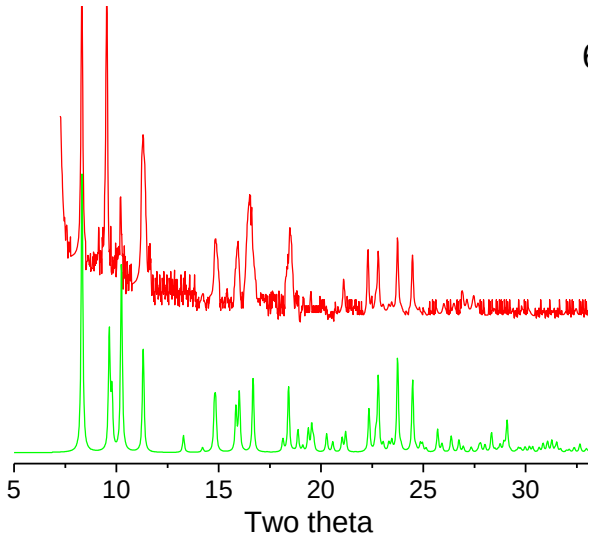


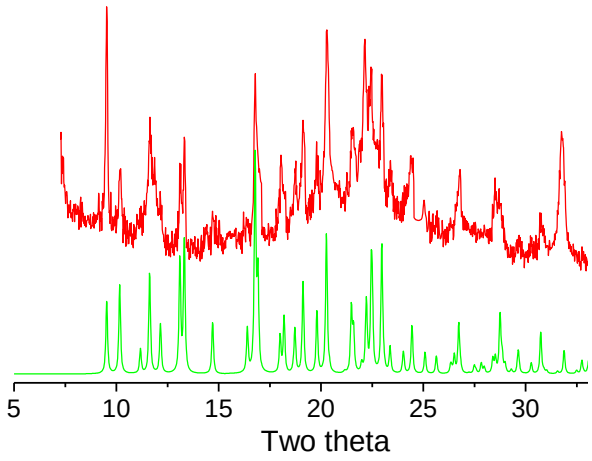


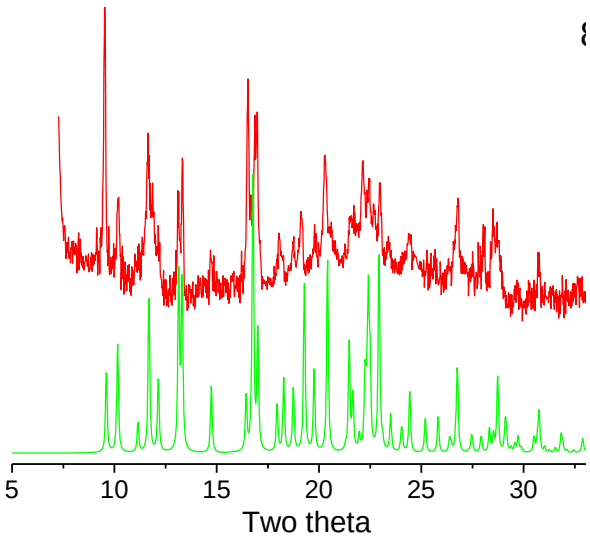


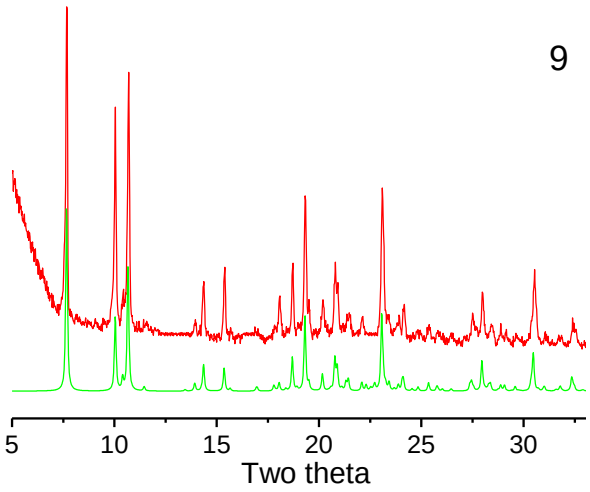


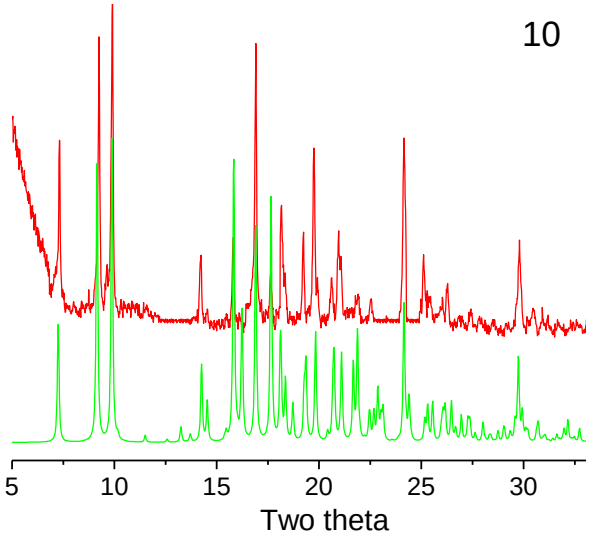












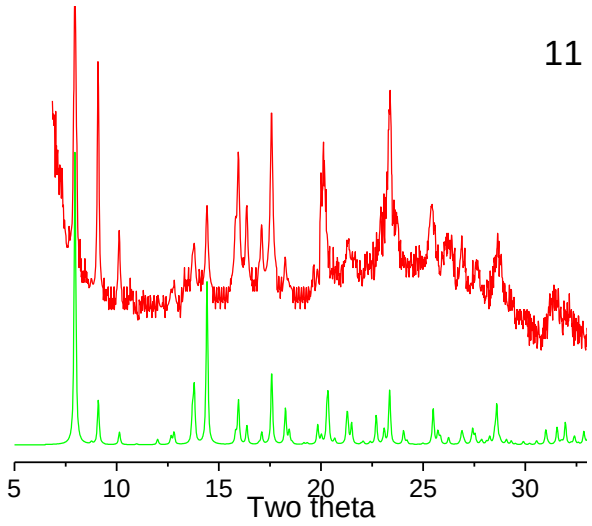


Fig. S11. The simulated (green) and experimental (red) XRPD patterns for the compounds **1-11** (the diffraction peaks of both simulated and experimental patterns match well in relevant positions, indicating that the phase purities of compounds **1-11** are good).