Fluorescent Metal-organic Polymers of Zinc and Cadmium from Hydrothermal in Situ Acylation Reaction

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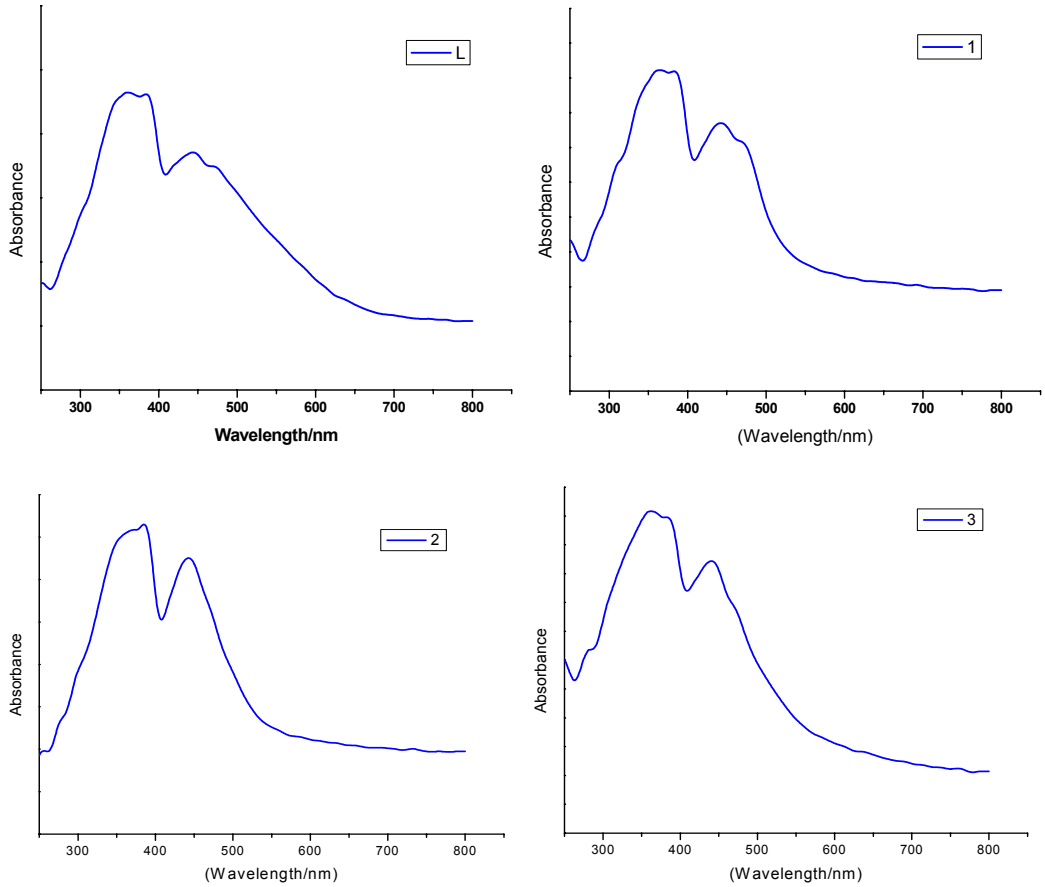
Figure S1 The UV-Vis solid state diffuse reflection spectra for H_4bbh (L) and compounds **1-4**.

Table S1 Selected bond lengths (Å) and angles (°) for compounds **1-4**

Table S2 Hydrogen-bonded parameters for compounds **1-4**

Table S3 Selected π-π interactions geometry for **1-4** (The plane-to-plane distance (*d*), the dihedral angles (*α*), the centroid-centroid distance (*c*) and the displacement angle between the planes (*θ*)).



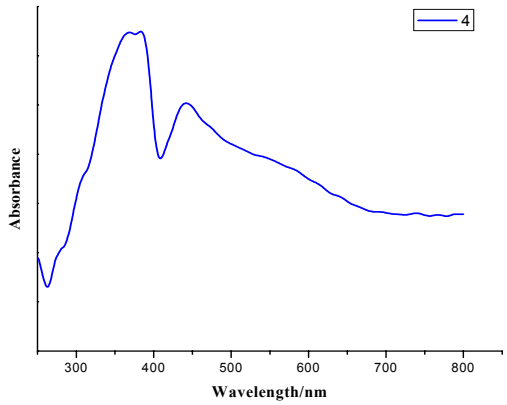


Fig. S1 The UV-Vis solid state diffuse reflection spectra for H_4bbh (L) and compounds **1**-**4**.

Table S1 Selected bond lengths (Å) and angles (°) for compounds **1**-**4**

1					
Zn(1)-O(2)	1.966(3)	Zn(1)-O(3) A	1.986(3)	Zn(1)-N(2)	2.120(4)
Zn(1)-O(1)	2.143(3)	Zn(1)-N(1)	2.154(3)		
O(2)-Zn(1)-O(3) A	109.66(12)	O(2)-Zn(1)-O(1)	98.99(14)	O(3) A-Zn(1)-O(1)	91.06(13)
O(2)-Zn(1)-N(2)	102.30(14)	N(2)-Zn(1)-O(1)	88.69(14)	O(2)-Zn(1)-N(1)	111.25(13)
O(3) A-Zn(1)-N(2)	147.66(14)	O(3) A-Zn(1)-N(1)	86.42(13)	N(2)-Zn(1)-N(1)	77.42(14)
O(1)-Zn(1)-N(1)	148.69(16)				
2					
Zn(1)-O(1) A	1.950(2)	Zn(1)-N(2)	2.035(3)	Zn(1)-N(3)	2.045(3)
Zn(1)-N(1)	2.087(3)	Zn(1)-O(2)	2.444(2)		
O(1) A-Zn(1)-N(2)	111.90(11)	O(1) A-Zn(1)-N(3)	100.27(10)	N(2)-Zn(1)-N(3)	136.32(11)
O(1) A-Zn(1)-N(1)	113.10(10)	N(2)-Zn(1)-N(1)	80.33(11)	N(3)-Zn(1)-N(1)	113.82(11)
O(1) A-Zn(1)-O(2)	97.72(9)	N(2)-Zn(1)-O(2)	87.94(9)	N(3)-Zn(1)-O(2)	58.26(9)
N(1)-Zn(1)-O(2)	149.17(10)				
3					
Zn(1)-O(3) A	1.923(2)	Zn(1)-O(1)	1.925(2)	Zn(1)-O(1W)	1.976(3)
Zn(1)-N(3)	2.033(3)				
O(3) A-Zn(1)-O(1)	124.17(10)	O(3) A-Zn(1)-O(1W)	102.53(12)	O(1)-Zn(1)-O(1W)	112.08(12)
O(3) A-Zn(1)-N(3)	115.59(11)	O(1)-Zn(1)-N(3)	95.39(10)	O(1W)-Zn(1)-N(3)	106.28(12)
4					
Cd(1)-O(2) B	2.270(2)	Cd(1)-O(2) C	2.285(2)	Cd(1)-N(6)	2.330(3)
Cd(1)-N(5)	2.331(3)	Cd(1)-O(1)	2.367(2)	Cd(1)-N(1)	2.373(3)
O(2) B-Cd(1)-O(2) C	72.85(8)	O(2) B-Cd(1)-N(6)	108.20(9)	O(2) C-Cd(1)-N(6)	102.81(9)
O(2) B-Cd(1)-N(5)	157.16(8)	O(2) C-Cd(1)-N(5)	84.66(8)	N(6)-Cd(1)-N(5)	72.39(10)
O(2) B-Cd(1)-O(1)	95.00(8)	O(2) C-Cd(1)-O(1)	106.31(8)	N(6)-Cd(1)-O(1)	147.03(9)
N(5)-Cd(1)-O(1)	95.12(9)	O(2) B-Cd(1)-N(1)	84.72(8)	O(2) C-Cd(1)-N(1)	150.56(9)
N(6)-Cd(1)-N(1)	102.18(9)	N(5)-Cd(1)-N(1)	117.82(9)	O(1)-Cd(1)-N(1)	56.02(8)

Symmetry codes for compound **1**: A -x+2,-y+1,-z+2

Symmetry codes for compound **2**: A -x,-y+1,-z+1

Symmetry codes for compound **3**: A -x+1, -y+1, -z+2.

Symmetry codes for compound **4**: B -x+1, -y+2, -z; C x, y-1, z.

Table S2 Hydrogen-bonded parameters for compounds **1**-**4**

D-H···A	*d* (D-H)(Å)	*d* (H..A)(Å)	*d* (D..A)(Å)	∠(D-H···A)(°)
1				
N4-H4···O5 D	0.86	1.98	2.838(4)	177
N6-H6···O4 C	0.86	1.96	2.823(4)	176
O1-H1WA···O4 B	0.80(5)	1.96(5)	2.738(5)	164(5)
O1-H1WB···N5 A	0.87(10)	2.01(10)	2.761(5)	146(8)
2				
N5-H5···O3 B	0.86	1.92	2.778(3)	175
N6-H6···O4 D	0.86	1.95	2.809(3)	175
C8-H8···O4 E	0.93	2.33	3.198(4)	156
C1-H1···O3 B	0.93	2.42	3.260(4)	150
3				
O1W-H1WA···O2 B	0.79(7)	1.87(7)	2.611(4)	156(7)
O1W-H1WB···O4 C	0.83(7)	1.99(7)	2.786(4)	161(6)
N1-H1···O4 D	0.86	2.02	2.859(4)	165
4				
N2-H2···O4 G	0.86	1.94	2.802(3)	175
N3-H3···O3 F	0.86	1.95	2.810(3)	175
C13-H13···O4 E	0.93	2.50	3.358(5)	153

Symmetry codes for compound **1**: A, 2-x, 1-y, 2-z; B, -1+x, y, z; C, x, -1+y, z; D, x, 1+y, z.

Symmetry codes for compound **2**: B, x, 1+y, z; D, x, -1+y, z; E, 1+x, y, -1+z.

Symmetry codes for compound **3**: B x, y, z+1; C 1-x, 2-y, 2-z; D -1+x, -1+y, -1+z.

Symmetry codes for compound **4**: E 1-x, 1-y, 1-z; F 1+x, y, z; G -1+x, y, z.

Table S3 Selected π-π interactions geometry for **1-4** (The plane-to-plane distance (*d*), the dihedral angles (*α*), the centroid-centroid distance (*c*) and the displacement angle between the planes (*θ*)).

π-π interactions	*d* (Å)	*α* (º)	*c* (Å)	*θ* (º)	Symmetry codes
1					
Cg1→Cg1 #1 (intra-molecular)	3.356	0.00	3.6984	24.86	#1 (2-x,1-y,2-z)
Cg1→Cg2 #2 (inter-moleculars)	3.434	2.94	3.6135	18.15	#2 (1+x,y,z)
Cg2→Cg2 #3 (inter-moleculars)	3.435	0.00	3.7207	22.58	#3 (1-x, 1-y, 1-z)
Ring 1: $C_{14}C_{15}C_{16}C_{19}C_{20}C_{21}$; Ring 2: $C_4C_5C_6C_7C_8C_9$					
Centroid coordinates: Cg1, (1.09793, 0.56820, 0.85922); Cg2, (0.29822, 0.55372, 0.57092).					
2					
Cg1→Cg1 #1 (intra-molecular)	3.345	0.00	3.9227	31.50	#1 (-x,1-y,1-z)
Cg1→Cg1 #2 (inter-molecular)	3.340	0.00	3.7109	25.84	#2 (-1-x, 1-y, 1-z)
Cg2→Cg3 #3 (inter-molecular)	3.391	3.25	3.7846	26.35	#3 (-x, 2-y, -z)
Cg2→Cg3 #4 (inter-molecular)	3.469	3.25	3.8296	25.08	#4 (1-x, 2-y, -z)
Ring 1: $C_{11}C_{13}C_{14}C_{17}C_{18}C_{20}$; Ring 2: $C_1C_2C_3C_4C_5\ N_1$; Ring 3: $C_6C_7C_8C_9C_{10}N_2$					
Coordinates: Cg1, (-0.22922, 0.42980, 0.47035); Cg2, (0.20342, 1.11457, 0.04390); Cg3, (0.34955, 0.74333, -0.09783).					
3					
Cg1→Cg2 #1 (inter-layers)	3.356	6.17	3.6516	23.22	#1 (x, y, -1+z)
Ring 1: $C_6C_9C_{10}C_{6a}C_{9a}C_{10a}$; Ring 2: $C_4C_1C_3C_{4b}C_{1b}C_{3b}$, (a: 1-x, 2-y, 1-z, b: x, y, -1+z)					
Coordinates: Cg1, (0.5, 1, 0.5); Cg2, (1, 1, 1.5).					
4					
Cg1→Cg1 #1 (intra-chain)	3.329	0.02	3.8542	30.26	#1 (1-x, 2-y, -z)
Cg2→Cg3 #2 (inter-chains)	3.483	3.02	3.6307	16.38	#2 (-x,1-y, 1-z)
Ring 1: $C_3C_4C_6C_8C_7C_5$; Ring 2: $C_{11}C_{12}C_{13}C_{14}C_{15}N_5$; Ring 3: $C_{17}C_{18}C_{19}C_{20}C_{16}N_6$					
Coordinates: Cg1, (0.50618, 1.04165, 0.16502); Cg2, (0.29615, 0.33728, 0.44047); Cg3, (-0.00635, 0.48269, 0.24633).					