Electronic supporting information (ESI)

Structural Diversity in New Coordination Polymers Modulated by Semirigid Ether-Linked Pyridine-Phthalate Building Block and Ancillary Ligands: Syntheses, Structures, and Luminescent Properties

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Geometry of the Free Ligand

Herein, we first discuss the nitrogen atom position effect on the benzene ring of the ligand by theoretical calculations. 4-(Pyridin-3-yloxy)benzene-1,2-dicarboxylic acid and 3-(pyridin-3-yloxy)benzene-1,2-dicarboxylic acid have been selected for model calculations. The optimized geometry and NBO charge distributions of the free ligands have been calculated at the B3LYP/6-31G (d, p) level.[1-2] Our calculation results (Scheme S1) suggest the following. 1) The negative NBO charge distribution values of the two ligands for the electron donors, N and O, agree with the corresponding atoms, and the potential outstanding coordination ability of two ligands exists in theory (−0.690, −0.625, −0.695, and −0.562; −0.690, −0.626, −0.695 and −0.563 for four carboxylate oxygen atoms, −0.463 and −0.437 for two pyridine nitrogen atoms, respectively). 2) The presence of nitrogen atoms in different positions has a slight effect on the NBO charge distributions of oxygen and nitrogen atoms. 3) As illustrated in Scheme 3, the HOMO-LUMO gaps were –4.62 and –4.36 eV for 4- and 3-pyridine functionalized ligands, respectively. Furthermore, location of nitrogen atom in different positions has no effect on value of LUMO, but would increase the value of HOMO which induces smaller HOMO-LUMO gaps obtained for H_2pbda. As we know, the smaller HOMO-LUMO gaps, the stronger coordination ability would be found for free ligands. Indeed, there are no coordination compounds of 4-(Pyridin-3-yloxy)benzene-1,2-dicarboxylic acid in the Cambridge Structural Database. Calculation results thus clearly indicate that the value of HOMO-LUMO gaps rather than NBO charges would play an important role in metal coordination processes.
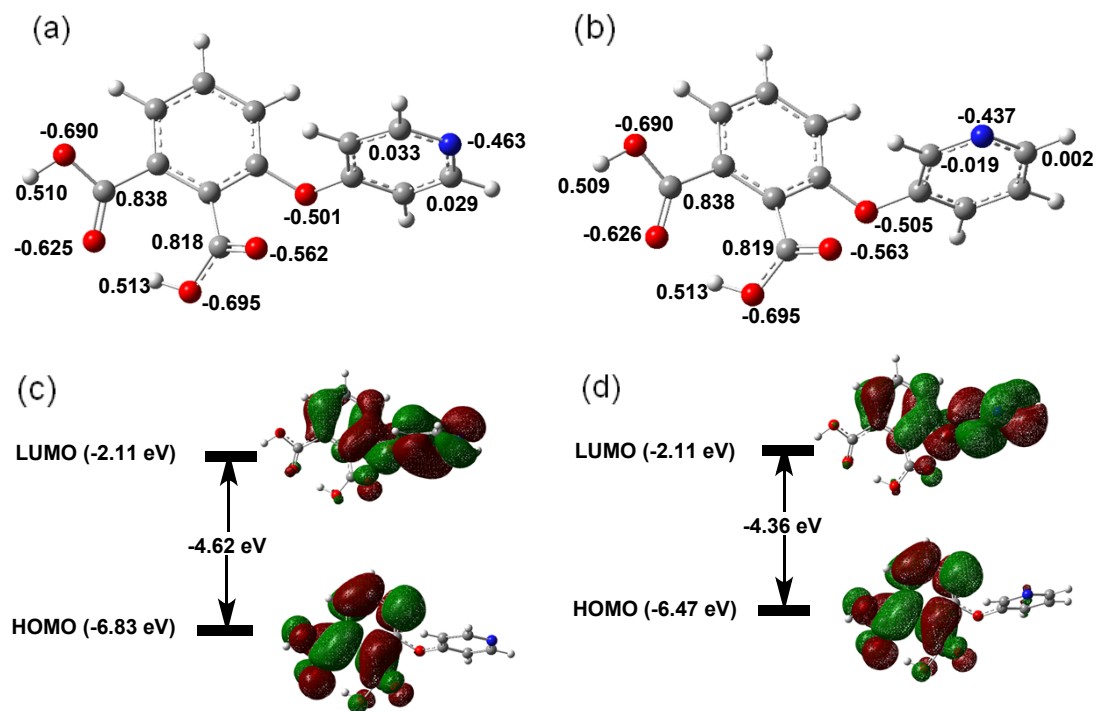
Scheme S1. The optimized geometries and NBO charge distributions and HOMO−LUMO energy gaps for respective compounds and interfacial plots of the orbitals: (a) and (c) for 4-(pyridin-3-yloxy)benzene-1,2-dicarboxylic acid, (b) and (d) for 3-(pyridin-3-yloxy)benzene-1,2-dicarboxylic acid. Gray, red, and blue atoms of the molecular drawings indicate the C, O, and N, respectively. Green and reddish brown parts on the interfacial plots refer to the different phases of the molecular wave functions, for which the isovalue is 0.02 ev.

References

1. M. J. Frisch, *Gaussian 09*, revision A.01; Gaussian, Inc.: Wallingford, CT, U.S., 2009.

2. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; (d) W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; (e) P. J. Hay, W. R. Wadt, *J.Chem. Phys.*, 1985, **82**, 299.

Table S1. Selected Bond Lengths (Å) and Angles (°) for **1- 7**

1

Cd(1)-O(4)[#1]	2.2268(18)	Cd(1)-O(5)#2	2.3006(19)	Cd(1)-O(2)#3	2.3341(16)
Cd(1)-N(1)	2.363(2)	Cd(1)-O(3)#3	2.3765(16)	O(3)#3-Cd(1)-O(3)#2	68.34(7)
O(4)#1-Cd(1)-O(5)#2	87.02(6)	O(4)#1-Cd(1)-O(2)#3	156.43(6)	O(5)#2-Cd(1)-O(2)#3	112.54(6)
O(4)#1-Cd(1)-N(1)	109.42(7)	O(5)#2-Cd(1)-N(1)	82.79(7)	O(2)#3-Cd(1)-N(1)	86.87(7)
O(4)#1-Cd(1)-O(3)#3	101.14(6)	O(5)#2-Cd(1)-O(3)#3	138.34(6)	O(2)#3-Cd(1)-O(3)#3	55.58(6)
N(1)-Cd(1)-O(3)#3	130.09(7)	O(4)#1-Cd(1)-O(3)#2	91.96(6)	O(5)#2-Cd(1)-O(3)#2	70.63(6)
O(2)#3-Cd(1)-O(3)#2	82.92(6)	N(1)-Cd(1)-O(3)#2	144.98(6)		

2

Cd(1)-O(11)	2.189(4)	Cd(1)-N(1)#2	2.273(5)	Cd(1)-O(2)#1	2.214(4)
Cd(1)-O(9)	2.324(4)	Cd(1)-O(5)	2.339(4)	Cd(2)-O(12)	2.200(4)
Cd(2)-O(7)#3	2.292(5)	Cd(2)-O(10)#4	2.312(4)	Cd(2)-N(2)#5	2.328(5)
Cd(2)-O(4)	2.447(4)	Cd(2)-O(8)#3	2.507(4)	Cd(3)-O(11)	2.230(4)
Cd(3)-O(11)#6	2.288(4	Cd(3)-O(12)	2.302(4)	Cd(3)-O(4)#6	2.328(4)
Cd(3)-O(3)	2.384(5)	N(1)-Cd(1)#2	2.273(5)	N(2)-Cd(2)#8	2.328(5)
O(2)-Cd(1)#6	2.214(4)	O(4)-Cd(3)#1	2.328(4)	O(7)-Cd(2)#7	2.292(5)
O(8)-Cd(2)#7	2.507(4)	O(10)-Cd(2)#9	2.312(4)	O(11)-Cd(3)#1	2.288(4)
O(12)-Cd(3)#1	2.360(4)	O(11)-Cd(1)-O(2)#1	118.82(15)	O(11)-Cd(1)-N(1)#2	150.37(16)
O(2)#1-Cd(1)-N(1)#2	90.78(17)	O(11)-Cd(1)-O(9)	73.72(15)	O(2)#1-Cd(1)-O(9)	99.77(17)
N(1)#2-Cd(1)-O(9)	101.91(17)	O(11)-Cd(1)-O(5)	90.10(14)	O(2)#1-Cd(1)-O(5)	101.84(16)
N(1)#2-Cd(1)-O(5)	157.43(16)	O(12)-Cd(2)-O(7)#3	159.02(16)	O(12)-Cd(2)-O(10)#4	87.93(14)
O(12)-Cd(2)-O(4)	72.58(14)	O(12)-Cd(2)-N(2)#5	111.20(16)	O(7)#3-Cd(2)-N(2)#5	81.10(17)
O(7)#3-Cd(2)-O(4)	72.58(14)	O(10)#4-Cd(2)-O(4)	155.05(13)	N(2)#5-Cd(2)-O(4)	116.70(15)
O(4)-Cd(2)-O(8)#3	133.64(16)	O(4)-Cd(2)-O(8)#3	76.80(14)	O(11)#6-Cd(3)-O(12)	166.86(14)
O(11)-Cd(3)-O(4)#6	160.35(14)	O(12)-Cd(3)-O(4)#6	91.08(14)	O(11)-Cd(3)-O(12)#6	76.54(13)
O(12)-Cd(3)-O(12)#6	72.07(14)	O(12)-Cd(3)-O(3)	86.88(15)	O(12)#6-Cd(3)-O(3)	105.31(16)

Symmetry codes:

#1 -x+1/2,y+1/2,-z+3/2；#2 -x+1/2,-y+1/2,-z+2 ；#3 x+1/2,-y+1/2, z-1/2 for **1**.

#1 y-1/4,-x+3/4,z-1/4；#2 -x,-y+1,-z；#3 -y+3/4,x+1/4,z-3/4；#4 -x+1/2,-y+1,z-1/2；#5 x, y-1/2,-z；#6 -y+3/4,x+1/4,z+1/4 for **2**.

3

Cd1—N1#1	2.324 (7)	Cd1—N2	2.253 (6)	Cd1—O1#1	2.360 (6)
Cd1—O2#1	2.332 (5)	Cd1—O3	2.291 (5)	Cd1—O4	2.498 (6)
N1—Cd1#5	2.324 (7)	O1—Cd1#3	2.360 (6)	O2—Cd1#3	2.332 (5)
N1#1—Cd1—C1#1	98.5 (2)	N1#2—Cd1—O2#1	87.5 (2)	N1#2—Cd1—O4	143.9 (2)
N1#2—Cd1—O1#1	106.1 (3)	N2—Cd1—N1#2	111.9 (2)	N2—Cd1—O1#1	88.8 (2)
N2—Cd1—O2#1	143.5 (2)	N2—Cd1—O4	88.6 (2)	O1^i—Cd1—O4	103.6 (2)
O2#1—Cd1—O1#1	55.44 (19)	O2#1^i—Cd1—O4	92.79 (19)	O3—Cd1—N1#2	91.3 (2)
O3—Cd1—O1C	155.4 (2)	O3—Cd1—O4	54.70 (18)	C1—O1—Cd1#3	90.3 (5)
O3—Cd1—O2C	109.52(18)				

Symmetry codes: #1 *x*, −*y*+1/2, *z*−1/2; #2 *x*+1, *y*, *z*; #3 *x*, −*y*+1/2, *z*+1/2; #4 −*x*+1, −*y*+1, −*z*+2; (#5) *x*−1, *y*, *z*.

4

N1—Co1#1	2.042 (3)	O9—Co1#2	1.924 (2)	Co1—N1#3	2.042 (3)
Co1—O9#2	1.924 (2)	Co1—N2	2.044 (3)	Co1—O2	1.930 (2)
C20—N1—Co1#1	120.5 (2)	C16—N1—Co1#1	119.9 (2)	N1#3—Co1—N2	118.01 (11)
O9#2—Co1—N1#3	108.38 (11)	O9#2—Co1—N2	110.11 (11)	O9#2—Co1—O2	117.19 (10)
O2—Co1—N1#3	110.57 (10)	O2—Co1—N2	92.27 (10)	C27—N2—Co1	123.2 (2)
C28—N2—Co1	120.0 (2)	C8—O2—Co1	121.3 (2)		

Symmetry codes: #1 x, −y, z−1/2; #2 −x+1/2, −y+1/2, −z+1; #3 x, −y, z+1/2;

5

Zn1—O5	1.997 (2)	Zn1—N2	2.028 (2)	Zn1—O3#1	2.428 (2)
Zn1—N5#2	2.063 (2)	Zn1—O2#1	2.040 (2)	O3—Zn1#3	2.428 (2)
N5—Zn1#4	2.063 (2)	O2—Zn1#3	2.040 (2)		
O5—Zn1—N2	107.95 (9)	O5—Zn1—O3#1	166.93 (8)	O5—Zn1—N5#2	96.60 (9)
O5—Zn1—O2#1	109.30 (9)	N2—Zn1—O2#1	127.96 (9)	O2#1—Zn1—O3#1	58.14 (8)
N2—Zn1—O3#1	84.24 (9)	O3#1^i—Zn1—C12#1	28.58 (9)	O2#1—Zn1—N5#2	110.75 (10)
N2—Zn1—N5#2	99.54 (10)	N5#2—Zn1—O3#1	85.70 (9)		

Symmetry codes: #1 −*x*+1, *y*−1/2, −*z*+1/2; #2 *x*, −*y*−1/2, *z*+1/2; #3 −*x*+1, *y*+1/2, −*z*+1/2; #4 *x*, −*y*−1/2, *z*−1/2.

6

O3—Cd1#1	2.404 (3)	O2—Cd1#1	2.313 (3)	N2—Cd1#2	2.286 (3)
Cd1—O3#3	2.404 (3)	Cd1—O2#3	2.313 (3)	Cd1—N2#4	2.286 (3)
Cd1—N1	2.245 (3)	Cd1—O7	2.463 (3)	Cd1—O8	2.300 (3)
O8—Cd1—C11#3	136.60 (11)	O3#3—Cd1—C11#3	27.81 (10)	O2#3—Cd1—O3#3	55.63 (9)
O8—Cd1—C2	27.59 (10)	O3#3—Cd1—C2	157.18 (11)	O2#3—Cd1—C11#3	27.91 (11)
O8—Cd1—O7	55.06 (9)	O3#3—Cd1—O7	133.35 (9)	O2#3—Cd1—C2	105.60 (10)
N2#4—Cd1—O3#3	85.33 (10)	N2#4—Cd1—C2	115.01 (12)	N1—Cd1—O3#3	89.75 (10)
N2#4—Cd1—O2#3	108.25 (11)	N2#4—Cd1—O7	141.31 (10)	N1—Cd1—O2#3	134.66 (11)
N2#4—Cd1—C11#3	96.04 (11)	N2#4—Cd1—O8	88.22 (10)	N1—Cd1—C11#3	114.13 (11)
N1—Cd1—N2#4	95.36 (11)	N1—Cd1—O8	108.38 (10)	O8—Cd1—O3#3	161.27 (9)
N1—Cd1—C2	98.03 (10)	O7—Cd1—C11#3	118.41 (10)	O8—Cd1—O2#3	110.44 (9)
N1—Cd1—O7	86.52 (9)				

Symmetry codes: #1 −*x*+1, *y*+1/2, −*z*+1/2; #2 *x*, −*y*−1/2, *z*−1/2; #3 −*x*+1, *y*−1/2, −*z*+1/2;
#4 *x*, −*y*−1/2, *z*+1/2.

7

Co1—N1#1	2.055 (3)	Co1—O2	1.940 (3)	Co1—O2	1.940 (3)
Co1—N2	2.011 (4)	N1—Co1#4	2.055 (3)	N1—Co1#4	2.055 (3)
N2—Co1—N1#1	104.60 (14)	C1—N1—Co1#4	121.7 (3)	O4#2—Co1—N2	103.68 (14)
O2—Co1—N1#1	111.56 (13)	C1—N1—C5	117.3 (4)	C16—N2—Co1	125.6 (3)
O2—Co1—N2	104.52 (14)	C5—N1—Co1#4	120.7 (3)	O4#2—Co1—N1#1	102.71 (13)
O2—Co1—O4#2	127.57 (13)	C14—N2—Co1	129.6 (3)		

Symmetry codes: #1 *x*+1, −*y*+1/2, *z*−1/2; #2 *x*, −*y*+1/2, *z*−1/2; #3 −*x*+1, −*y*, −*z*−1;
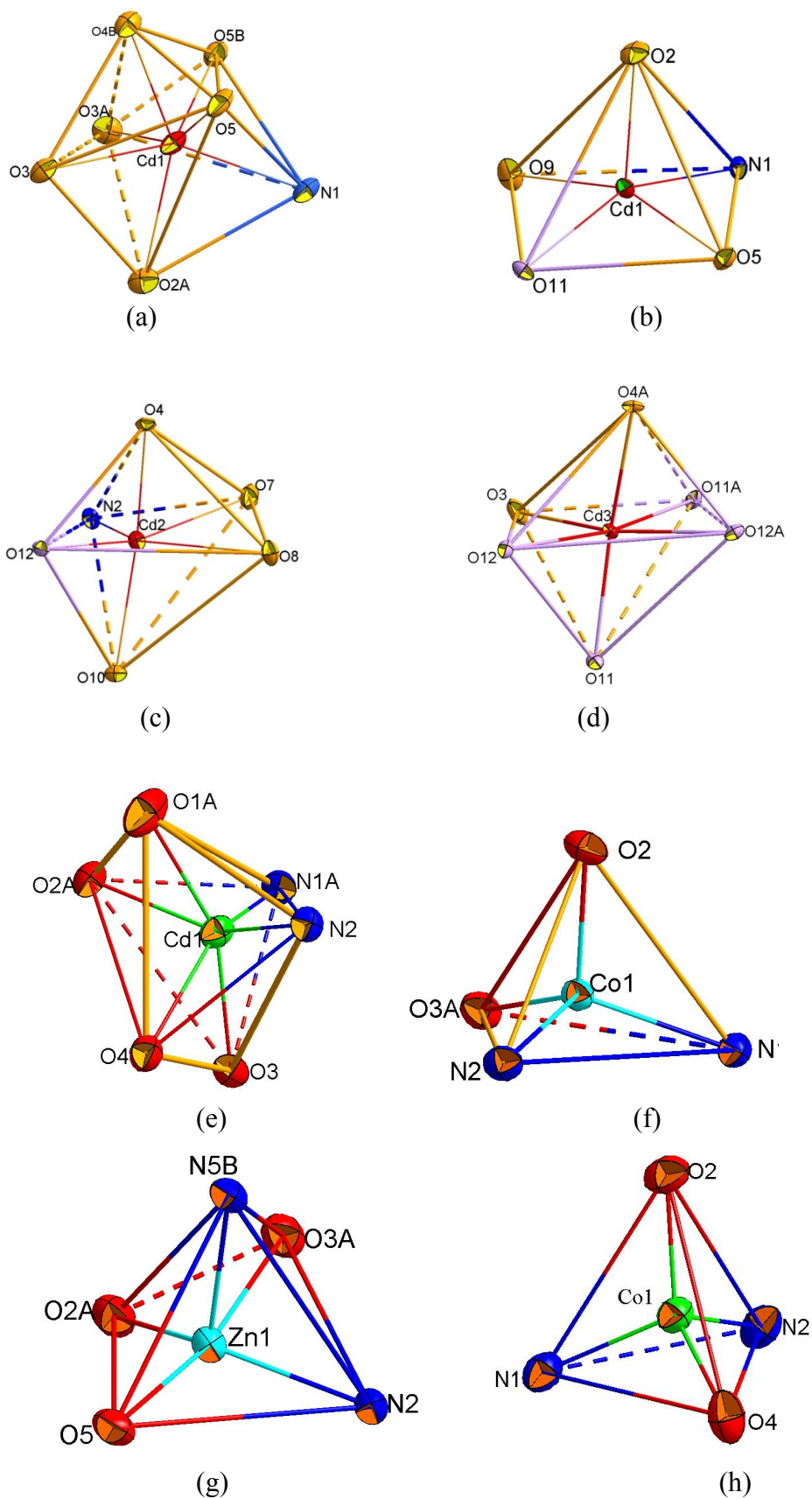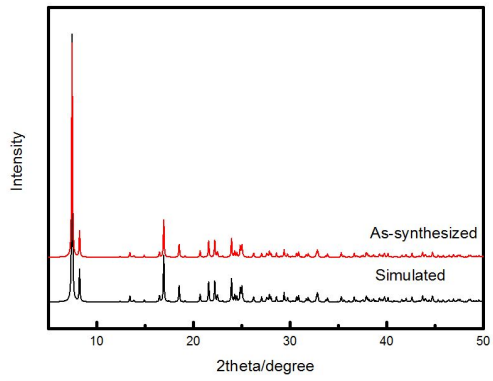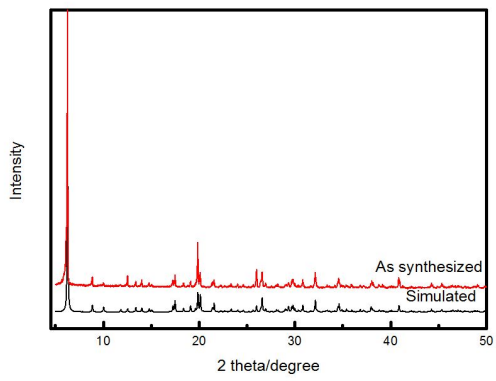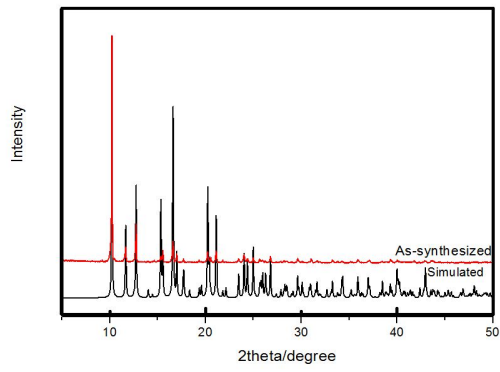#4 *x*−1, −*y*+1/2, *z*+1/2;

Fig. S1. The coordination polyhedra of metal(II) ions in **1** (a), **2** (b-d), **3** (e), **4** (f), **5** (g) and **7** (h).
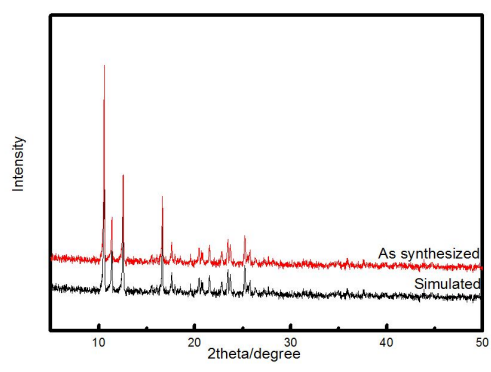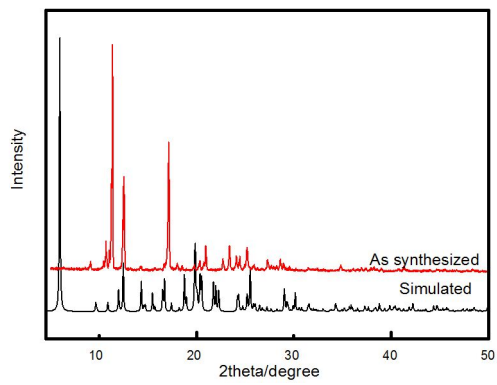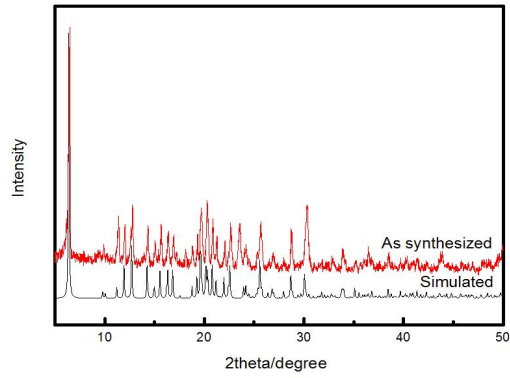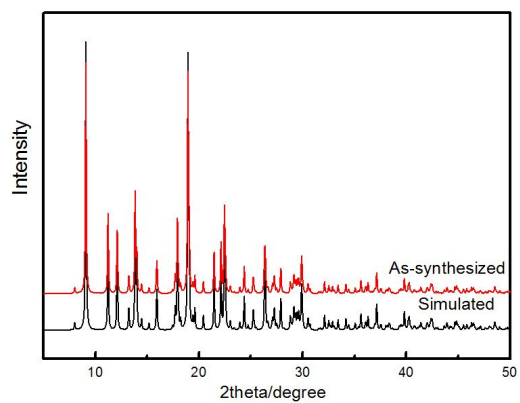
1

2

3

4

5

6

7

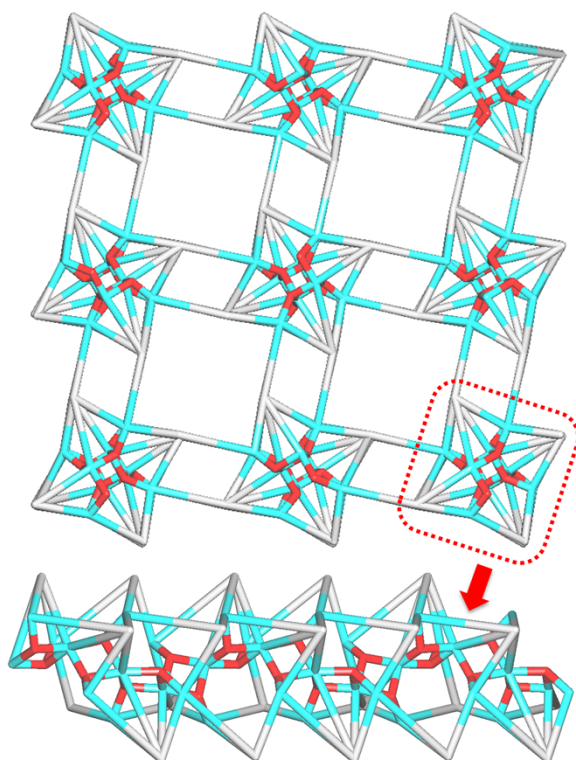**Fig. S2.** Powder X-ray diffraction of 1-7.

Fig. S3. Topological representation of the underlying 3D metal-organic framework in **2** showing a very complex heptanodal 3,3,4,5,5,6,6-connected net with unique topology (Schläfli symbol of $(4 \cdot 6^5)(4^2 \cdot 6^7 \cdot 8)(4^3)_2(4^4 \cdot 6^5 \cdot 8)(4^7 \cdot 6^8)(4^8 \cdot 6^6 \cdot 8)$; view along the *c* axis) and its chain motif fragment seen along the *a* axis; color codes: 5- and 6-connected Cd1/Cd2/Cd3 nodes (cyan), centroids of 4- and 6-connected $\mu_{4(6)}$-pbda nodes (gray), centroids of 3-connected μ_3-OH nodes (red).
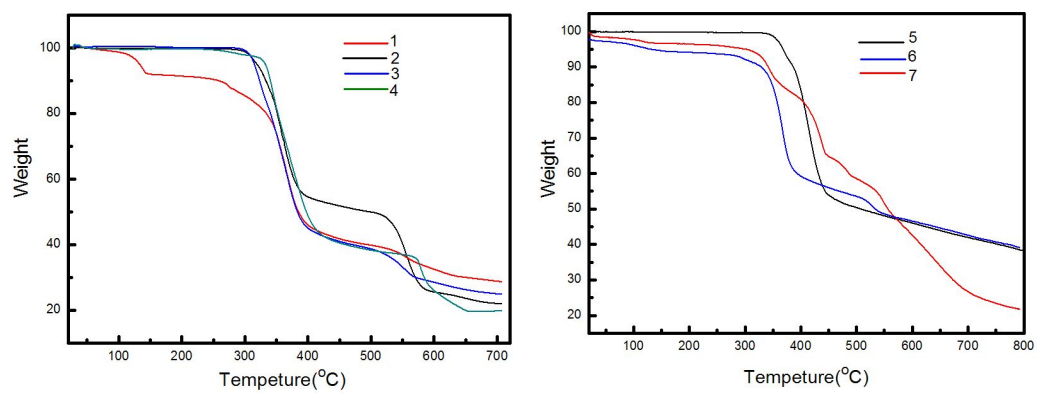
Fig. S4. TGA curves for compounds **1–7**