Electronic Supplementary Information (ESI)

Exploring 4-(3-carboxyphenyl)picolinic acid as a semirigid building block for the hydrothermal self-assembly of diverse metal-organic and supramolecular networks

Jin-Zhong Gu [a,*], Xiao-Xiao Liang [a], Yan-Hui Cui [a], Jiang Wu [a], Alexander M. Kirillov [b]

[a]Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000 (P. R. China)

[b]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, The University of Lisbon, Av. Rovisco Pais, 1049-001, Lisbon (Portugal)

Fax: (+86) 931-891-5196

E-mail: gujzh@lzu.edu.cn

Synthesis and analytical data for 2–11

Synthesis of $[Zn(Hcppa)_2(H_2O)_2]\cdot 2H_2O$ (2). A mixture of $ZnCl_2$ (81.8 mg, 0.3 mmol), H_2cppa (73.0 mg, 0.3 mmol), NaOH (12.0 mg, 0.3 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Colorless crystals were isolated manually, washed with distilled water, and dried to furnish compound **2**. Yield: 55% (based on H_2cppa). Calcd for $C_{26}H_{24}ZnN_2O_{12}$: C 50.21, H 3.89, N 4.50%. Found: C 52.41, H 3.87, N 4.47%. IR (KBr, cm^{-1}): 3466 m, 3066 w, 1712 s, 1656 w, 1596 s, 1549 m, 1413 m, 1377 s, 1314 w, 1273 w, 1229 m, 1163 w, 1117 w, 1085 w, 1060 w, 1029 w, 998 w, 944 w, 906 w, 865 w, 834 w, 819 w, 808 w, 789 w, 758 m, 726 w, 710 m, 690 w, 657 w, 635 w, 593 w.

Synthesis of $[M(\mu_3\text{-cppa})(H_2O)_2]_n$ (M = Ni (3) and Co (4)). A mixture of $MCl_2\cdot 6H_2O$ (0.3 mmol), H_2cppa (73.0 mg, 0.3 mmol), NaOH (24.0 mg, 0.6 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Green or pink crystals were isolated manually, washed with distilled water, and dried to give compounds **3** and **4**, respectively. Yield: 60% for **3**, 55% for **4** (based on H_2cppa). Calcd for $C_{13}H_{11}NiNO_6$ (**3**): C 46.48, H 3.30, N 4.17%. Found: C 46.27, H 3.33, N 4.20%. IR (KBr, cm^{-1}): 3546 w, 3152 w, 1579 m, 1538 s, 1502 m, 1468 w, 1406 w, 1370 w, 1319 w, 1268 m, 1166 w, 1125 w, 1079 w, 1054 w, 1023 w, 977 m, 900 s, 819 m, 762 m, 670 m, 692 m, 634 m, 599 w, 578 w. Calcd for $C_{13}H_{11}CoNO_6$ (**4**): C 46.45, H 3.30, N 4.17%. Found: C 46.68, H 3.27, N 4.13%. IR (KBr, cm^{-1}): 3438 w, 1585 s, 1544 s, 1498 w, 1472 w, 1421 w, 1390 s, 1365 m, 1263 w, 1160 w, 1084 w, 1054 w, 1023 w, 962 w, 906 w, 859 w, 819 w, 767 m, 722 w, 681 w, 634 w, 599 w, 578 w.

Synthesis of $\{[Co(\mu\text{-cppa})(2,2'\text{-bipy})(H_2O)]\cdot H_2O\}_n$ (5). A mixture of $CoCl_2\cdot 6H_2O$ (71.0 mg, 0.30 mmol), H_2cppa (73.0 mg, 0.3 mmol), 2,2′-bipy (46.8 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Orange block-shaped crystals were isolated manually, washed with distilled water, and dried to produce compound **5**. Yield: 55% (based on H_2cppa). Calcd for $C_{23}H_{19}CoN_3O_6$: C 56.11, H

3.89, N 8.53%. Found: C 56.33, H 3.87, N 8.59%. IR (KBr, cm^{-1}): 3454 m, 1635 m, 1615 m, 1579 s, 1534 s, 1493 w, 1472 w, 1437 w, 1401 m, 1370 m, 1268 m, 1166 w, 1120 w, 1079 w, 1054 m, 1023 w, 962 w, 906 m, 859 w, 814 m, 767 s, 722 w, 676 s, 634 m, 578 w.

Synthesis of [Zn(μ-cppa)(2,2′-bipy)]$_n$ (6). The preparation of **6** was similar to that of **5** except $ZnCl_2$ (81.8 mg, 0.30 mmol) was used instead of $CoCl_2 \cdot 6H_2O$. After cooling the reaction mixture room temperature, colorless block-shaped crystals were isolated manually, washed with distilled water, and dried to give compound **6.** Yield: 60% (based on H_2cppa). Calcd for $C_{23}H_{15}ZnN_3O_4$: C 59.69, H 3.27, N 9.08%. Found: C 59.81, H 3.29, N 9.03%. IR (KBr, cm^{-1}): 1656 s, 1600 s, 1569 w, 1549 w, 1493 w, 1472 w, 1142 m, 1345 s, 1278 w, 1161 w, 1104 w, 1059 m, 1023 m, 977 w, 906 w, 850 m, 809 w, 762 m, 711 m, 676 m, 634 w, 568 w.

Synthesis of [Co(μ-cppa)(phen)(H_2O)]$_n$ [M = Co (7), Zn (8), Mn (9), and Cu (10)]. A mixture of $MCl_2 \cdot xH_2O$ (x = 6 for **7** and **9**, x = 2 for **10**, and x = 0 for **8**, 0.3 mmol), H_2cppa (73.0 mg, 0.3 mmol), phen (59.4, 0.3 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Orange, colorless, yellow, or blue crystals were isolated manually, washed with distilled water, and dried to furnish compounds **7**–**10**, respectively. Yield: 60% for **7**–**9**, 35% for **10** (based on H_2cppa). Calcd for $C_{25}H_{17}CoN_3O_5$ (**7**): C 60.25, H 3.44, N 8.43%. Found: C 60.37, H 3.46, N 8.38%. IR (KBr, cm^{-1}): 3193 w, 1635 m, 1600 s, 1554 m, 1518 w, 1493 w, 1472 w, 1421 m, 1380 s, 1340 m, 1268 w, 1222 w, 1145 w, 1104 w, 1079 w, 1054 w, 1018 w, 987 w, 926 w, 859 m, 829 w, 778 s, 731 m, 676 m, 625 w, 589 w. Calcd for $C_{25}H_{17}ZnN_3O_5$ (**8**): C 59.48, H 3.39, N 8.32%. Found: C 59.67, H 3.37, N 8.25%. IR (KBr, cm^{-1}): 3198 w, 3060 w, 1641 m, 1605 s, 1559 m, 1513 w, 1493 w, 1426 m, 1376 s, 1273 m, 1216 w, 1140 w, 1104 w, 1054 w, 1018 w, 982 w, 926 w, 906 w, 854 w, 818 w, 809 w, 773 m, 727 m, 676 m, 630 w, 589 w. Calcd for $C_{25}H_{17}MnN_3O_5$ (**9**): C 60.74, H 3.47, N 8.50%. Found: C 60.47, H 3.45, N 8.56%. IR (KBr, cm^{-1}): 3209 w, 3056 w, 1635 m, 1594 s, 1421 m, 1380 s, 1340 w, 1268 w, 1217 w, 1145 w, 1100 w, 1054 w, 1012 w, 987 w, 921 w, 900 w, 859 s, 809 w, 767 m, 727 m, 676 m, 625 w, 542 w. Calcd for $C_{25}H_{17}CuN_3O_5$ (**10**): C 59.70, H 3.41, N 8.35%. Found: C 59.84, H 3.38, N 8.40%. IR (KBr, cm^{-1}): 3472 m, 3066 w, 1710 m, 1598 s, 1548 m, 1412 m, 1378 s, 1316 w, 1226 w, 1164 w, 1084 w, 1056 w, 1028 w, 904 w, 864 w, 836 w, 802 w, 756 w, 712 m, 690 w, 660 w, 626 w, 594 w.

Synthesis of $\{[Cd_3(\mu_3\text{-cppa})_3(phen)_2]\cdot 4H_2O\}_n$ (11). The preparation of **11** was similar to that of **7** except using $CdCl_2\cdot H_2O$ (60.3 mg, 0.30 mmol) instead of $CoCl_2\cdot 6H_2O$. After cooling the reaction mixture to room temperature, colorless block-shaped crystals were isolated manually, washed with distilled water, and dried to give compound **11**. Yield: 55% (based on H_2cppa). Calcd for $C_{63}H_{45}Cd_3N_7O_{16}$: C 50.67, H 3.04, N 6.56%. Found: C 50.42, H 3.06, N 6.52%. IR (KBr, cm^{-1}): 3463 w, 3071 w, 1589 s, 1564 m, 1513 w, 1477 w, 1426 m, 1390 s, 1365 m, 1273 w, 1217 w, 1140 w, 1100 w, 1059 w, 1018 w, 911 w, 870 w, 843 767 m, 731 m, 686 w, 625 w, 553 w.

Description of TGA data

The stability of compounds **1**–**11** was investigated under N_2 atmosphere by thermogravimetric analysis (TGA, Fig. S2, ESI†) Compound **1** shows the loss of two crystallization and two coordinated H_2O molecules (exptl, 11.8%; calcd, 11.7%) in the 125–237 °C range, followed by the decomposition that begins at 270 °C. The TGA trace of **2** shows that the four H_2O molecules (two lattice and two coordinated H_2O) are released between 108–220 °C (exptl, 11.5%; calcd, 11.6%), while further heating of the sample up to 250 °C leads to its decomposition. For **3**, there is one distinct thermal effect in the 154–225 °C range that corresponds to the removal of two H_2O ligands (exptl, 11.0%; calcd, 10.7%); a dehydrated sample then remains stable up to ~348 °C. For **4**, the TGA curve exhibits a significant weight loss between 123–180 °C due to a loss of two H_2O ligands (exptl, 10.5%; calcd, 10.7%); further heating up to 350 °C results in the decomposition of a dehydrated sample. For **5**, there is a distinct thermal effect in the 133–174 °C range, which is associated with the removal of one crystallization and one coordinated H_2O molecule (exptl, 7.6%; calcd, 7.3%); a dehydrated sample then remains stable up to ~354 °C. TGA curve of **6** indicates that the compound is stable up to 351 °C without observing any loss of the weight. Compound **7** displays the removal of one H_2O ligand between 128 and 267 °C (exptl, 3.9%; calcd, 3.6%), while a dehydrated sample then remains stable up to ~335 °C. For **8**, the TGA trace exhibits a gradual weight loss between 40 and 230 °C, corresponding to the loss of one H_2O ligand (exptl, 3.8%; calcd, 3.6%); a decomposition is observed above 250 °C. For **9**, there is a thermal effect in the 113–216 °C range that is associated with a removal of one H_2O ligand (exptl, 3.7%; calcd, 3.6%); a dehydrated sample then decomposes above 271 °C. Compound **10** shows the loss of one coordinated water molecule between 128 and 222 °C (exptl, 3.9%; calcd, 3.6%), followed by the decomposition. For MOF **11**, there is one distinct thermal effect in the 30–184 °C range that is due to

the removal of four lattice H_2O molecules (exptl, 5.1%; calcd, 4.8%); a dehydrated sample is stable up to 320 °C.

Table S1 Selected bond lengths [Å] and angles [°] for the compounds **1**–**11**[a].

1					
Ni(1)-O(1)	2.023(2)	Ni(1)-O(1)#1	2.023(2)	Ni(1)-O(5)	2.119(2)
Ni(1)-O(5)#1	2.119(2)	Ni(1)-N(1)	2.014(3)	Ni(1)-N(1)#1	2.014(3)
N(1)-Ni(1)-O(1)#1	99.03(10)	N(1)-Ni(1)-O(1)	80.97(10)	N(1)-Ni(1)-O(5)	91.26(11)
N(1)#1-Ni(1)-O(5)	88.74(11)	O(1)#1-Ni(1)-O(5)	92.37(10)	O(1)-Ni(1)-O(5)	87.63(10)
2					
Zn(1)-O(1)	2.024(3)	Zn(1)-O(1)#1	2.025(3)	Zn(1)-O(5)	2.111(3)
Zn(1)-O(5)#1	2.111(3)	Zn(1)-N(1)	2.014(4)	Zn(1)-N(1)#1	2.014(4)
O(1)-Zn(1)-O(5)#1	92.61(15)	O(1)-Zn(1)-O(5)	87.38(15)	N(1)-Zn(1)-O(1)	80.84(14)
N(1)#1-Zn(1)-O(1)	99.16(14)	N(1)-Co(1)-O(5)	90.89(15)	N(1)-Co(1)-O(5)#1	89.11(15)
3					
Ni(1)-O(1)	2.089(2)	Ni(1)-O(2)#2	2.193(2)	Ni(1)-O(3)#1	1.997(2)
Ni(1)-O(5)	2.042(2)	Ni(1)-O(6)	2.096(2)	Ni(1)-N(1)	2.031(3)
O(3)#1-Ni(1)-N(1)	92.21(9)	O(3)#1-Ni(1)-O(5)	93.84(8)	N(1)-Ni(1)-O(5)	173.01(9)
O(3)#1-Ni(1)-O(1)	172.57(8)	N(1)-Ni(1)-O(1)	80.36(8)	O(5)-Ni(1)-O(1)	93.57(8)
O(3)#1-Ni(1)-O(6)	93.42(9)	N(1)-Ni(1)-O(6)	92.21(10)	O(5)-Ni(1)-O(6)	90.93(10)
O(1)-Ni(1)-O(6)	86.98(8)	O(3)#1-Ni(1)-O(2)#2	89.21(8)	N(1)-Ni(1)-O(2)#2	88.83(9)
O(5)-Ni(1)-O(2)#2	87.74(9)	O(1)-Ni(1)-O(2)#2	90.56(8)	O(6)-Ni(1)-O(2)#2	177.12(8)
4					
Co(1)-O(1)#2	2.241(2)	Co(1)-O(2)	2.106(2)	Co(1)-O(4)#1	2.013(2)
Co(1)-O(5)	2.142(2)	Co(1)-O(6)	2.093(2)	Co(1)-N(1)	2.071(3)
O(4)#1-Co(1)-N(1)	93.29(10)	O(4)#1-Co(1)-O(2)	172.03(9)	N(1)-Co(1)-O(2)	78.85(10)
O(4)#1-Co(1)-O(6)	93.10(9)	N(1)-Co(1)-O(6)	172.48(11)	O(2)-Co(1)-O(6)	94.66(9)
O(4)#1-Co(1)-O(5)	95.20(9)	N(1)-Co(1)-O(5)	92.19(10)	O(2)-Co(1)-O(5)	86.49(9)
O(6)-Co(1)-O(5)	91.19(10)	O(4)#1-Co(1)-O(1)#2	89.71(9)	N(1)-Co(1)-O(1)#2	88.63(10)
O(2)-Co(1)-O(1)#2	88.80(9)	O(6)-Co(1)-O(1)#2	87.43(10)	O(5)-Co(1)-O(1)#2	174.97(9)
5					
Co(1)-O(1)	2.087(2)	Co(1)-O(3)#1	2.106(2)	Co(1)-O(5)	2.133(3)
Co(1)-N(1)	2.124(3)	Co(1)-N(2)	2.109(3)	Co(1)-N(3)	2.148(3)
O(1)-Co(1)-O(3)#1	169.46(10)	O(1)-Co(1)-N(2)	86.75(10)	O(3)#1-Co(1)-N(2)	101.73(10)
O(1)-Co(1)-N(1)	77.74(10)	O(3)#1-Co(1)-N(1)	94.95(10)	N(2)-Co(1)-N(1)	161.23(11)
O(1)-Co(1)-O(5)	85.18(11)	O(3)#1-Co(1)-O(5)	88.28(11)	N(2)-Co(1)-O(5)	91.78(11)
N(1)-Co(1)-O(5)	97.30(11)	O(1)-Co(1)-N(3)	103.95(11)	O(3)#1-Co(1)-N(3)	84.29(10)
N(2)-Co(1)-N(3)	76.59(11)	N(1)-Co(1)-N(3)	96.79(11)	O(5)-Co(1)-N(3)	164.58(11)
6					
Zn(1)-O(1)	2.029(4)	Zn(1)-O(4)#1	1.972(4)	Zn(1)-N(1)	2.114(5)
Zn(1)-N(2)	2.135(5)	Zn(1)-N(3)	2.069(5)		
O(4)#1-Zn(1)-O(1)	122.87(19)	O(4)#1-Zn(1)-N(3)	127.5(2)	O(1)-Zn(1)-N(3)	108.13(19)
O(4)#1-Zn(1)-N(1)	97.57(19)	O(1)-Zn(1)-N(1)	78.4(2)	N(3)-Zn(1)-N(1)	104.2(2)
O(4)#1-Zn(1)-N(2)	90.57(19)	O(1)-Zn(1)-N(2)	90.49(19)	N(3)-Zn(1)-N(2)	76.7(2)
N(1)-Zn(1)-N(2)	168.6(2)				
7					
Co(1)-O(1)	2.054(3)	Co(1)-O(4)#1	2.107(3)	Co(1)-O(5)	2.084(3)
Co(1)-N(1)	2.147(4)	Co(1)-N(2)	2.176(4)	Co(1)-N(3)	2.125(4)

O(1)-Co(1)-O(5)	173.50(15)	O(1)-Co(1)-O(4)#1	92.54(14)	O(5)-Co(1)-O(4)#1	87.80(13)
O(1)-Co(1)-N(3)	93.69(15)	O(5)-Co(1)-N(3)	92.80(15)	O(4)#1-Co(1)-N(3)	89.36(15)
O(1)-Co(1)-N(1)	78.18(14)	O(5)-Co(1)-N(1)	95.34(15)	O(4)#1-Co(1)-N(1)	96.81(15)
N(3)-Co(1)-N(1)	169.96(15)	O(1)-Co(1)-N(2)	92.10(15)	O(5)-Co(1)-N(2)	89.00(14)
O(4)#1-Co(1)-N(2)	166.59(15)	N(3)-Co(1)-N(2)	77.79(15)	N(1)-Co(1)-N(2)	96.45(15)
8					
Zn(1)-O(1)	2.097(4)	Zn(1)-O(4)#1	2.069(4)	Zn(1)-O(5)	2.088(4)
Zn(1)-N(1)#1	2.157(4)	Zn(1)-N(2)	2.138(4)	Zn(1)-N(3)	2.234(5)
O(4)#1-Zn(1)-O(5)	172.94(16)	O(4)#1-Zn(1)-O(1)	92.43(17)	O(5)-Zn(1)-O(1)	88.09(16)
O(4)#1-Zn(1)-N(2)	93.52(17)	O(5)-Zn(1)-N(2)	93.53(17)	O(1)-Zn(1)-N(2)	89.68(19)
O(4)#1-Zn(1)-N(1)#1	78.00(17)	O(5)-Zn(1)-N(1)#1	94.97(17)	O(1)-Zn(1)-N(1)#1	100.21(17)
N(2)-Zn(1)-N(1)#1	167.15(18)	O(4)#1-Zn(1)-N(3)	92.52(18)	O(5)-Zn(1)-N(3)	88.67(17)
O(1)-Zn(1)-N(3)	165.43(16)	N(2)-Zn(1)-N(3)	76.35(19)	N(1)#1-Zn(1)-N(3)	94.22(18)
9					
Mn(1)-O(1)	2.125(3)	Mn(1)-O(4)#1	2.148(4)	Mn(1)-O(5)	2.149(3)
Mn(1)-N(1)	2.285(4)	Mn(1)-N(2)	2.248(4)	Mn(1)-N(3)	2.313(4)
O(1)-Mn(1)-O(4)#1	95.48(14)	O(1)-Mn(1)-O(5)	165.97(16)	O(4)#1-Mn(1)-O(5)	86.05(13)
O(1)-Mn(1)-N(2)	97.74(15)	O(4)#1-Mn(1)-N(2)	88.97(16)	O(5)-Mn(1)-N(2)	96.23(16)
O(1)-Mn(1)-N(1)	74.53(14)	O(4)#1-Mn(1)-N(1)	105.54(15)	O(5)-Mn(1)-N(1)	91.61(15)
N(2)-Mn(1)-N(1)	163.98(16)	O(1)-Mn(1)-N(3)	92.98(15)	O(4)#1-Mn(1)-N(3)	160.86(16)
O(5)-Mn(1)-N(3)	89.88(14)	N(2)-Mn(1)-N(3)	72.87(16)	N(1)-Mn(1)-N(3)	93.25(15)
10					
Cu(1)-O(1)	2.049(5)	Cu(1)-O(4)#1	2.104(5)	Cu(1)-O(5)	2.086(5)
Cu(1)-N(1)	2.149(5)	Cu(1)-N(2)	2.174(6)	Cu(1)-N(3)	2.123(5)
O(1)-Cu(1)-O(5)	173.13(19)	O(1)-Cu(1)-O(4)#1	92.7(2)	O(5)-Cu(1)-O(4)#1	88.09(18)
O(1)-Cu(1)-N(3)	93.9(2)	O(5)-Cu(1)-N(3)	92.9(2)	O(4)#1-Cu(1)-N(3)	89.3(2)
O(1)-Cu(1)-N(1)	78.08(18)	O(5)-Cu(1)-N(1)	95.06(19)	O(4)#1-Cu(1)-N(1)	97.2(2)
N(3)-Cu(1)-N(1)	169.83(18)	O(1)-Cu(1)-N(2)	92.0(2)	O(5)-Cu(1)-N(2)	88.7(2)
O(4)#1-Cu(1)-N(2)	166.62(19)	N(3)-Cu(1)-N(2)	77.9(2)	N(1)-Cu(1)-N(2)	96.0(2)
11					
Cd(1)-O(1)	2.513(8)	Cd(1)-O(2)	2.430(9)	Cd(1)-O(7)#2	2.588(10)
Cd(1)-O(8)#2	2.275(9)	Cd(1)-O(12)#1	2.284(9)	Cd(1)-N(4)	2.330(16)
Cd(1)-N(5)	2.366(10)	Cd(2)-O(1)	2.264(8)	Cd(2)-O(5)	2.250(9)
Cd(2)-N(1)	2.394(10)	Cd(2)-N(2)	2.359(9)	Cd(2)-N(6)	2.388(10)
Cd(2)-N(7)	2.363(10)	Cd(3)-O(3)#3	2.268(10)	Cd(3)-O(4)#3	2.601(10)
Cd(3)-O(5)	2.533(9)	Cd(3)-O(6)	2.472(11)	Cd(3)-O(9)	2.291(13)
Cd(3)-O(11)#4	2.264(13)	Cd(3)-N(3)	2.283(11)		
O(12)#1-Cd(1)-O(8)#2	94.8(4)	O(12)#1-Cd(1)-N(4)	175.6(5)	O(8)#2-Cd(1)-N(4)	88.8(5)
O(12)#1-Cd(1)-N(5)	106.7(4)	O(8)#2-Cd(1)-N(5)	143.8(4)	N(4)-Cd(1)-N(5)	71.4(5)
O(12)#1-Cd(1)-O(2)	91.1(4)	O(8)#2-Cd(1)-O(2)	78.2(4)	N(4)-Cd(1)-O(2)	87.2(6)
N(5)-Cd(1)-O(2)	128.8(3)	O(12)#1-Cd(1)-O(1)	88.3(3)	O(8)#2-Cd(1)-O(1)	130.5(4)
N(4)-Cd(1)-O(1)	87.5(4)	N(5)-Cd(1)-O(1)	80.0(3)	O(2)-Cd(1)-O(1)	52.3(3)
O(12)#1-Cd(1)-O(7)#2	98.6(4)	O(8)#2-Cd(1)-O(7)#2	52.1(4)	N(4)-Cd(1)-O(7)#2	85.6(5)
N(5)-Cd(1)-O(7)#2	95.3(3)	O(2)-Cd(1)-O(7)#2	129.8(3)	O(1)-Cd(1)-O(7)#2	172.6(3)
O(5)-Cd(2)-O(1)	146.7(4)	O(5)-Cd(2)-N(2)	72.4(3)	O(1)-Cd(2)-N(2)	87.9(3)
O(5)-Cd(2)-N(7)	119.5(3)	O(1)-Cd(2)-N(7)	88.9(3)	N(2)-Cd(2)-N(7)	157.0(4)
O(5)-Cd(2)-N(6)	88.5(4)	O(1)-Cd(2)-N(6)	119.3(3)	N(2)-Cd(2)-N(6)	91.7(3)
N(7)-Cd(2)-N(6)	70.2(4)	O(5)-Cd(2)-N(1)	87.1(3)	O(1)-Cd(2)-N(1)	71.8(3)
N(2)-Cd(2)-N(1)	104.5(3)	N(7)-Cd(2)-N(1)	96.1(4)	N(6)-Cd(2)-N(1)	161.1(3)

O(3)#3-Cd(3)-O(11)#4	98.5(4)	O(3)#3-Cd(3)-N(3)	151.4(4)	O(11)#4-Cd(3)-N(3)	83.3(4)
O(3)#3-Cd(3)-O(9)	94.9(4)	O(11)#4-Cd(3)-O(9)	150.8(4)	N(3)-Cd(3)-O(9)	72.8(4)
O(3)#3-Cd(3)-O(6)	78.6(4)	O(11)#4-Cd(3)-O(6)	104.5(4)	N(3)-Cd(3)-O(6)	128.9(3)
O(9)-Cd(3)-O(6)	103.6(4)	O(3)#3-Cd(3)-O(5)	129.0(4)	O(11)#4-Cd(3)-O(5)	91.1(4)
N(3)-Cd(3)-O(5)	79.3(3)	O(9)-Cd(3)-O(5)	100.4(4)	O(6)-Cd(3)-O(5)	50.7(3)
O(3)#3-Cd(3)-O(4)#3	53.7(3)	O(11)#4-Cd(3)-O(4)#3	83.5(4)	N(3)-Cd(3)-O(4)#3	98.5(3)
O(9)-Cd(3)-O(4)#3	83.7(4)	O(6)-Cd(3)-O(4)#3	132.2(3)	O(5)-Cd(3)-O(4)#3	174.4(3)
Cd(2)-O(1)-Cd(1)	149.2(4)	Cd(2)-O(5)-Cd(3)	145.0(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x*+1, –*y*+1, –*z*+1 for **1**; #1 –*x*+1, –*y*, –*z* for **2**; #1 –*x*+2, *y*–1/2, –*z*+3/2; #2 *x*, –*y*+3/2, *z*–1/2 for **3**; #1 –*x*+1, *y*–1/2, –*z*+3/2; #2 *x*, –*y*+3/2, *z*–1/2 for **4**; #1 *x*–1/2, –*y*+3/2, *z*–1/2 for **5**; #1 –*x*+1/2, *y*+1/2, –*z*+3/2 for **6**; #1 –*x*+3/2, –*y*, *z*+1/2 for **7**; #1 –*x*+5/2, –*y*+1, *z*+1/2 for **8**; #1 –*x*–1/2, –*y*, *z*–1/2 for **9**; #1 –*x*+5/2, –*y*, *z*–1/2 for **10**; #1 –*x*+1/2, *y*–1/2, –*z*+3/2; #2 *x*–1/2, –*y*+1/2, *z*+1/2; #3 *x*+1/2, –*y*+1/2, *z*–1/2; #4 –*x*+3/2, *y*–1/2, –*z*+3/2 for **11**.

Table S2 Conventional hydrogen bonds in crystal packing [Å, °] of **1**–**5** and **7**–**10**.

Complexes	D-H···A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(3)-H(3)···O(2)	0.82	1.92	2.689(3)	156	*x*-1, *y*, *z*
	O(5)-H(1W)···O(2)	0.84	1.85	2.697(4)	180	-*x*+1, *y*-1/2, -*z*+1/2
	O(5)-H(2W)···O(6)	0.68	2.13	2.807(4)	173	*x*, *y*, *z*-1
	O(6)-H(3W)···O(4)	0.87	1.98	2.846(4)	177	-*x*, -*y*+1, -*z*+1
	O(6)-H(4W)···O(5)	0.85	1.97	2.808(4)	173	-*x*+1, -*y*+1, -*z*+1
2	O(4)-H(4)···O(2)	0.82	1.90	2.678(5)	157	*x*+1, *y*, *z*
	O(5)-H(5A)···O(6)	0.87	1.93	2.793	174	-*x*+2, -*y*, -*z*+1
	O(5)-H(5B)···O(2)	0.87(2)	1.84(4)	2.708(5)	173.5(2)	-*x*+1, *y*+1/2, -*z*+3/2
	O(6)-H(6A)···O(3)	0.83	2.05	2.844	162	*x*-1, *y*, *z*
	O(6)-H(6B)···O(5)	0.86	1.93	2.788	175	*x*+1, -*y*+1, -*z*+1
3	O(5)-H(1W)···O(4)	0.92	1.76	2.643(3)	156	-*x*, *y*-1/2, -*z*+3/2
	O(6)-H(3W)···O(4)	0.85	1.86	2.706(3)	180	*x*-1, -*y*+3/2, *z*-1/2
	O(6)-H(4W)···O(1)	0.80	2.20	3.003(3)	174	*x*, -*y*+3/2, *z*+1/2
4	O(5)-H(1W)···O(2)	0.86	2.16	2.996(3)	164	*x*, -*y*+3/2, *z*+1/2
	O(5)-H(2W)···O(3)	0.85	1.86	2.709(3)	179	*x*-1, -*y*+3/2, *z*-1/2
	O(6)-H(3W)···O(3)	0.92	1.88	2.671(4)	143	-*x*+1, *y*-1/2, -*z*+3/2
	O(6)-H(4W)···O(1)	0.81	2.59	2.997(4)	113	*x*, –*y*+3/2, *z*–1/2
5	O(5)-H(1W)···O(4)	0.93(5)	1.68(5)	2.583(4)	162(4)	*x*-1/2, -*y*+3/2, *z*-1/2
	O(5)-H(2W)···O(2)	0.87(5)	1.87(5)	2.733(4)	177(4)	-*x*+1, -*y*+1, -*z*+1
	O(6)-H(3W)···O(4)	0.86	2.50	3.057(5)	124	*x*-1/2, -*y*+3/2, *z*-1/2
	O(6)-H(4W)···O(2)	0.84	1.96	2.787(4)	165	-*x*+1, -*y*+1, -*z*+1
7	O(5)-H(1W)···O(2)	0.88	1.85	2.672(5)	156	-*x*+1, *y*+1/2, -*z*+3/2
	O(5)-H(2W)···O(3)	0.88	1.84	2.636(5)	150	-*x*+3/2, -*y*, *z*+1/2
8	O(5)-H(1W)···O(2)	0.77	1.88	2.642(6)	172	

	O(5)-H(2W)···O(3)	0.85	1.82	2.673(6)	179	*x*-1/2, -*y*+1/2, -*z*
9	O(5)-H(1W)···O(3)	0.77	1.89	2.649(5)	172	-*x*-1/2, -*y*, *z*-1/2
	O(5)-H(2W)···O(2)	0.85	1.80	2.649(5)	180	-*x*, *y*+1/2, -*z*+1/2
10	O(5)-H(1W)···O(2)	0.85	1.81	2.659(7)	180	-*x*+2, *y*+1/2, -*z*+1/2
	O(5)-H(2W)···O(3)	0.94	1.73	2.645(7)	164	-*x*+5/2, -*y*, *z*-1/2

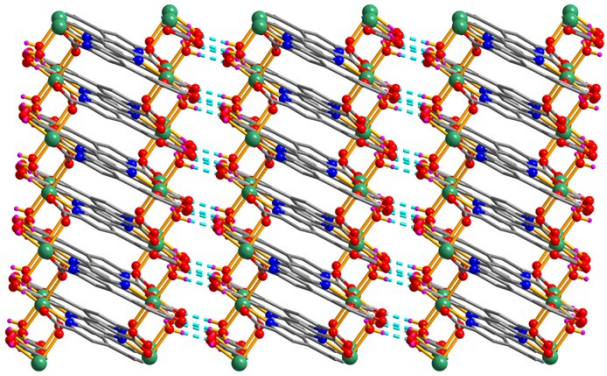
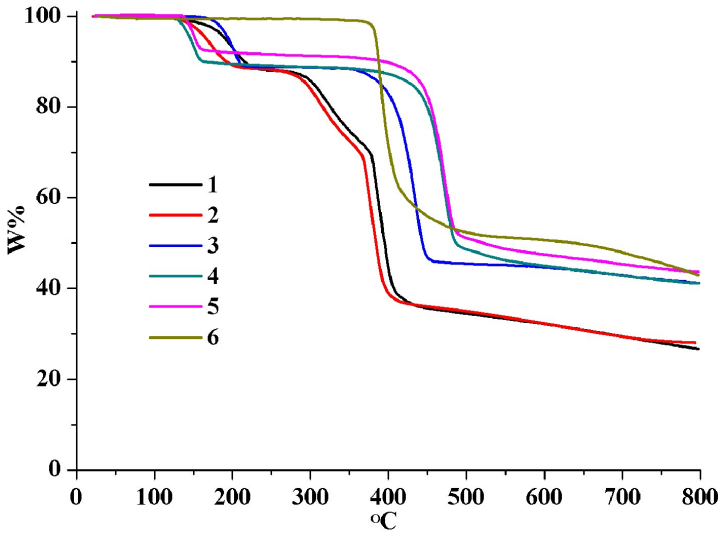


Fig. S1 3D supramolecular framework in **3** viewed along the *ac* plane (H bonds are represented by blue lines).



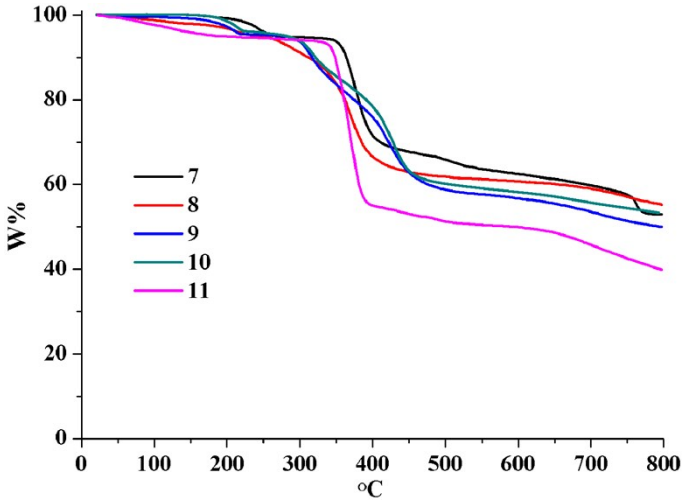
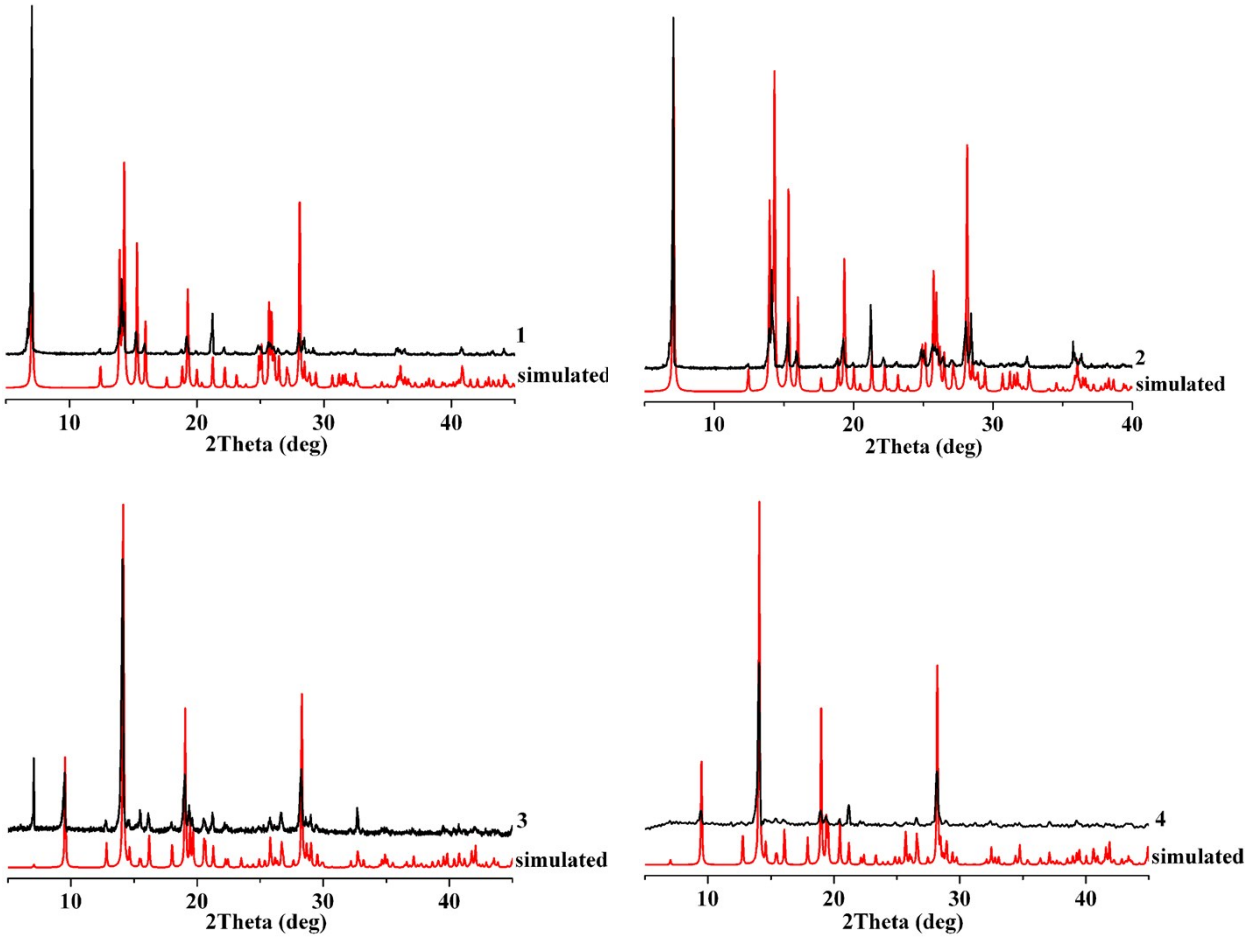
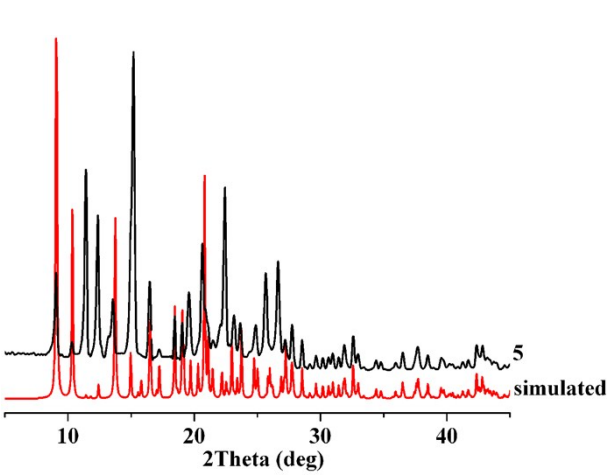
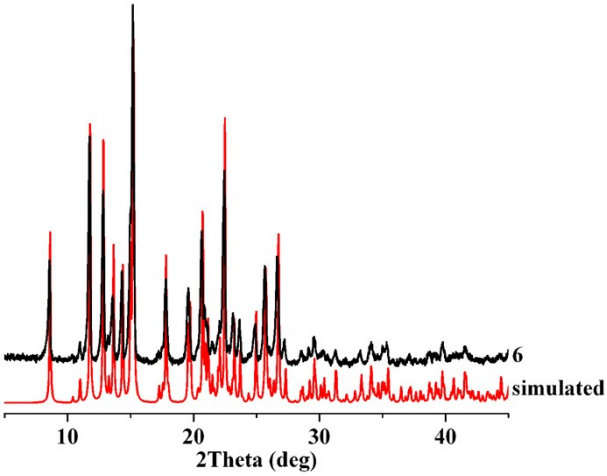
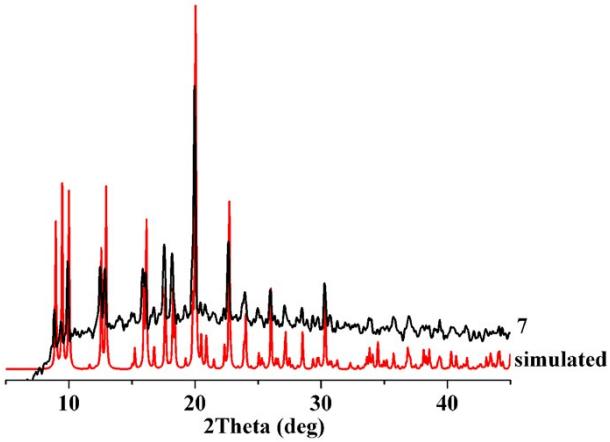


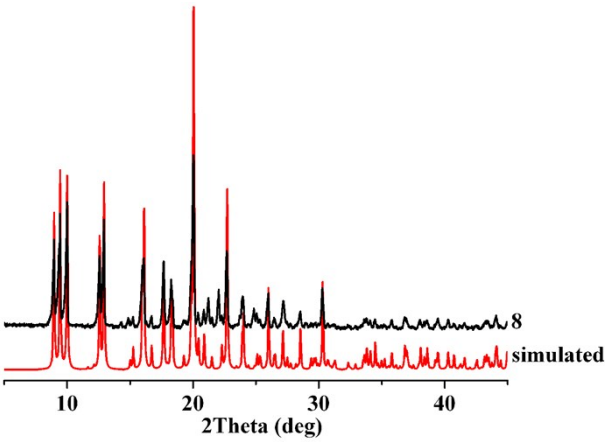
Fig. S2 Thermogravimetric analysis (TGA) curves of compounds **1**–**11**.

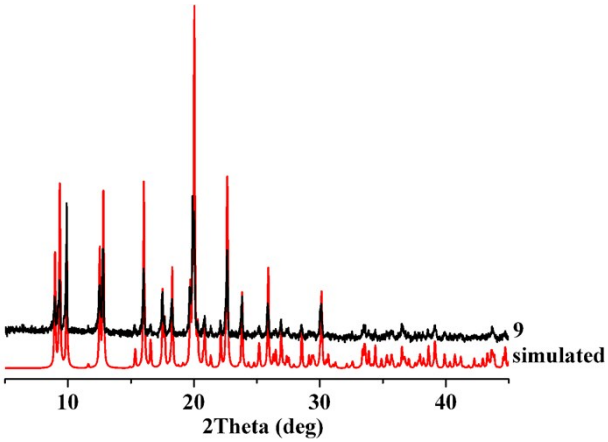


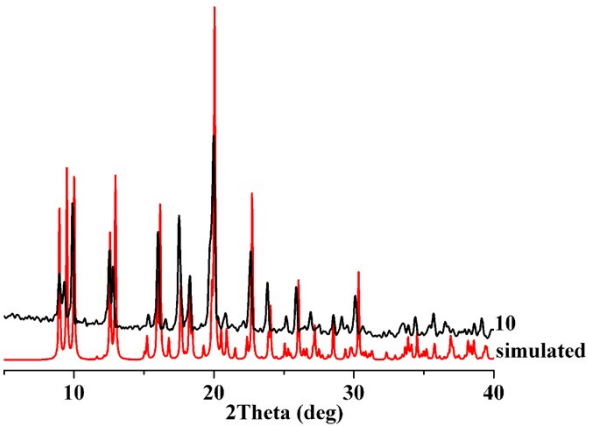

5
simulated
10
20
30
40
2Theta (deg)


6
simulated
10
20
30
40
2Theta (deg)


7
simulated
10
20
30
40
2Theta (deg)


8
simulated
10
20
30
40
2Theta (deg)


9
simulated
10
20
30
40
2Theta (deg)


10
simulated
10
20
30
40
2Theta (deg)

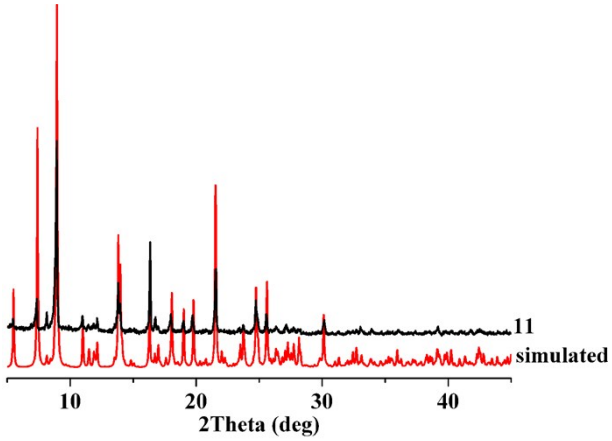


Fig. S3 PXRD patterns of compounds **1–11** at room temperature. Black paterns correspnond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.