Structural Diversity for a series of Novel Zn-MOFs Based on Different Secondary Building Units

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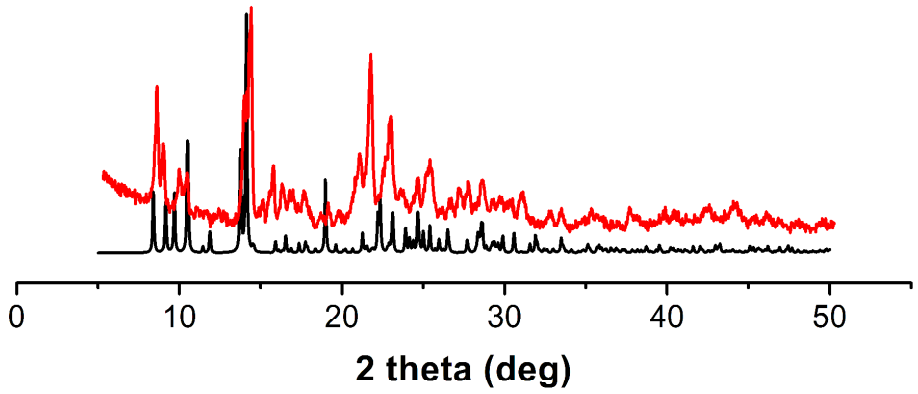
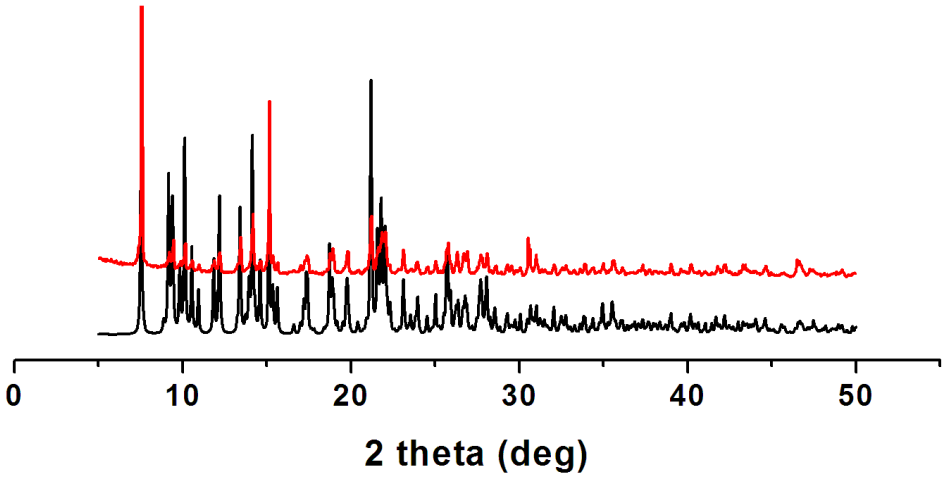
XRD Patterns and Thermal Analyses. In order to confirm the phase purity of these complexes, the PXRD patterns were recorded for complexes **1**-**6**, and they were comparable to the corresponding simulated ones calculated from the single-crystal diffraction data, indicating a pure phase of each bulky sample.

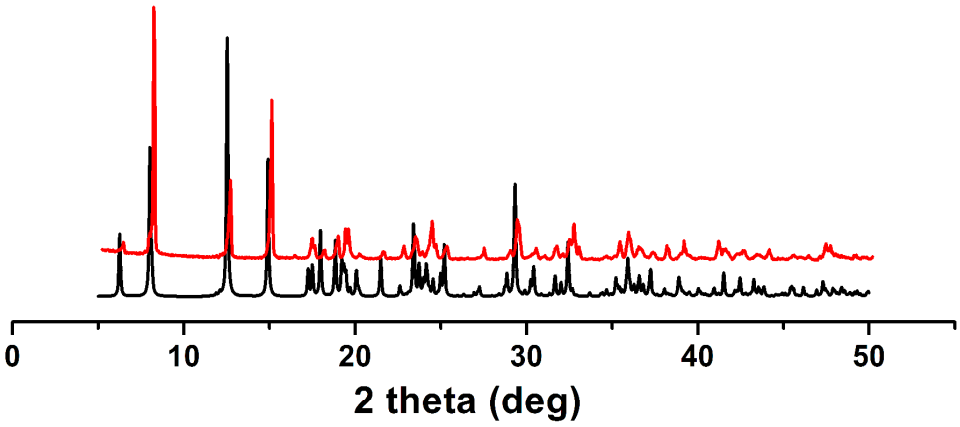
Thermal stability of the six complexes was also estimated. For complex **1**, the CH_3OH molecules released easily at room temperature, so complex **1** shows a weight loss of 11% from 49.8 to 190.1 °C corresponding to the release of lattice DMF molecules (calcd, 12%). And after that, the coordinated DMF molecules and tci ligand begin to decompose. The overall framework of **2** begins to collapse at 90.3 °C and the water molecules (obsd, 6%, calcd, 7%) are lost during the storage. The TGA curve of **3** shows a preliminary weight loss of two lattice water molecules (obsd, 6%, calcd, 7%) from 45.2 to 116.8 °C. The further weight losses represented the release of coordinated water molecule and the decomposition of the compounds. For complex **4**, the first step weight loss, attributed to the gradual release of four water molecules, is observed in the range 39.6 – 245.1 °C (obsd, 7%; calcd, 6%). The second step weight from 245.1 to 437 °C corresponds to the decomposition of tci ligand. For complex **5**, a weight loss of 7% occurs before 317.6 °C corresponding to the loss of water molecules (calcd, 8%), and then, the framework begins to collapse. For complex **6**, a weight loss of 10% appears in the range of 60.3 – 272.1 °C, which is probably due to the six water molecules (9%). And then the framework begins to decompose.



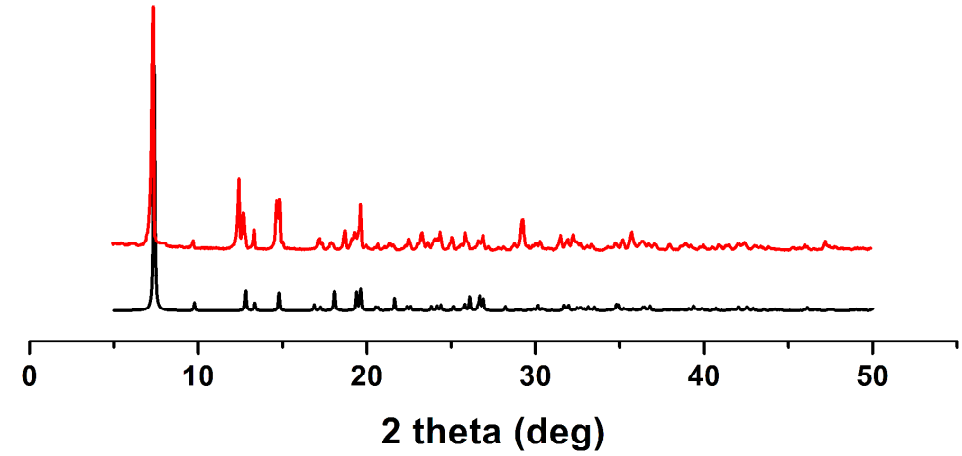
Complex 1



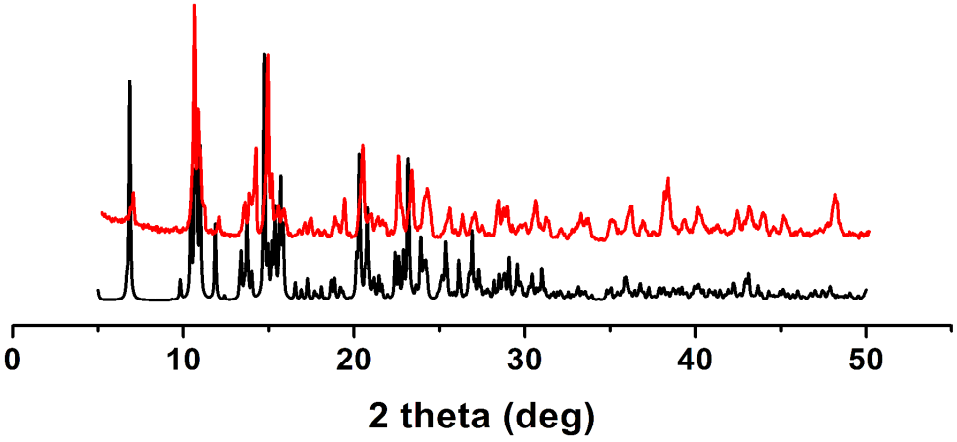
Complex 2



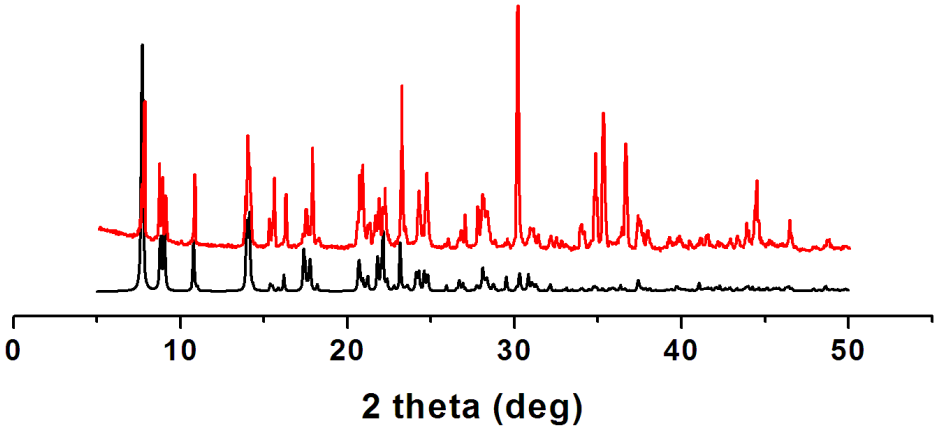
Complex 3



Complex 4



Complex 5



Complex 6

Figure S1: PXRD patterns of **1-6**

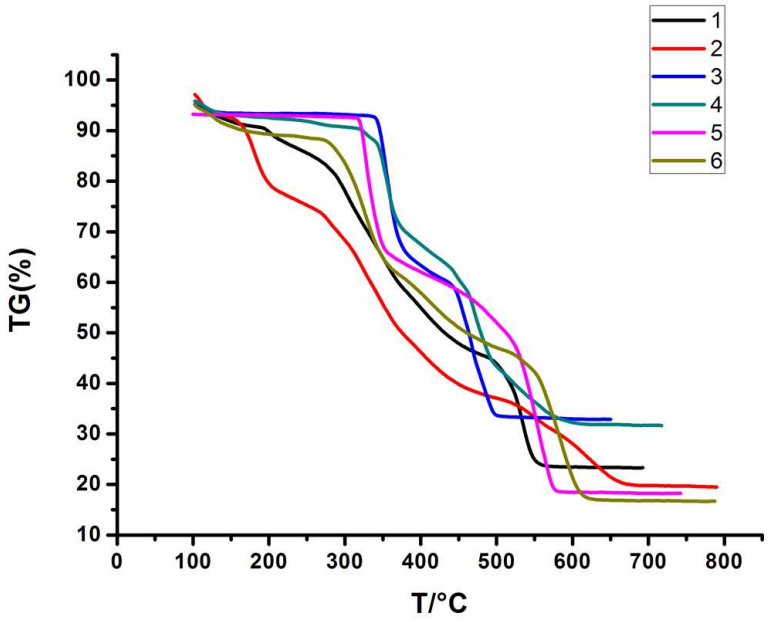


Figure S2. TG plots of complexes **1**-**6**.

Table S1: selected bond lengths and angles of complexes **1-6**

Complex 1			
Zn(1)-O(2)#1	2.039(4)	Zn(1)-O(6)	2.083(4)
Zn(1)-O(3)	2.201(4)	Zn(2)-O(5)	1.909(4)
Zn(2)-O(4)#1	1.919(4)	Zn(2)-O(11)	1.990(4)
Zn(2)-O(1)	2.015(5)	Zn(2)-O(2)	2.443(4)
O(2)#1-Zn(1)-O(6)	87.58(15)	O(2) -Zn(1)-O(6)	92.42(16)
O(2)-Zn(1)-O(3)#1	94.54(14)	O(2)#1-Zn(1)-O(3)#1	85.46(14)
O(6)#1-Zn(1)-O(3)#1	84.61(14)	O(6)-Zn(1)-O(3)#1	95.39(14)
O(5)-Zn(2)-O(4)#1	117.49(17)	O(5)-Zn(2)-O(11)	95.59(15)
O(4)#1-Zn(2)-O(11)	96.18(16)	O(5)-Zn(2)-O(1)	127.67(18)
O(4)#1-Zn(2)-O(1)	107.92(18)	O(11)-Zn(2)-O(1)	104.31(18)
O(5)-Zn(2)-O(2)	93.83(15)	O(4)#1-Zn(2)-O(2)	95.20(14)
O(1) -Zn(2)-O(2)	56.19(16)	O(11)-Zn(2)-O(2)	159.85(15)
Complex 2			
Zn(1)-O(4)#1	1.978(3)	Zn(1)-O(1)#2	1.985(3)
Zn(1)-O(18)	1.986(4)	Zn(1)-O(22)	2.049(3)
Zn(2)-O(17)#3	1.973(4)	Zn(2)-O(9)	1.990(3)
Zn(2)-O(11)	1.999(3)	Zn(2)-O(10)	2.041(3)
Zn(3)-O(20)	2.066(4)	Zn(3)-O(21)	2.085(4)
Zn(3)-O(16)#4	2.093(4)	Zn(3)-O(11)#5	2.144(3)
O(4)#1-Zn(1)-O(1)#2	137.09(14)	O(18)-Zn(1)-O(22)	94.67(15)
O(9)-Zn(2)-O(11)	143.21(14)	O(9)-Zn(2)-O(10)	95.89(14)
O(11)-Zn(2)-O(10)	106.67(13)	O(21)-Zn(3)-O(16)#4	174.16(13)
O(16)#4-Zn(3)-O(11)#5	88.80(13)	O(11)#5-Zn(3)-O(1)#2	90.46(11)
Complex 3			
Zn(1)-O(5)#1	1.977(4)	Zn(1)-O(4)#2	1.979(4)
Zn(1)-O(6)#3	2.008(4)	Zn(1)-O(1)	2.025(4)
Zn(1)-O(10)	2.466(5)	O(1)-Na(1)#3	2.464(5)
O(2)#5-Na(1)	2.208(5)	O(3)#6-Na(1)	2.307(5)
O(4)#2-Na(1)	2.462(5)	O(5)-Na(1)	2.517(4)
O(8)#2-Na(1)	2.396(4)	O(5)#1-Zn(1)-O(4)#2	118.66(16)
O(5)#1-Zn(1)-O(6)#3	119.78(15)	O(4)#2-Zn(1)-O(6)#3	115.12(16)
O(5)#1-Zn(1)-O(1)	104.75(16)	O(4)#2-Zn(1)-O(1)	99.09(18)
O(6)#3-Zn(1)-O(1)	91.30(18)	O(5)#1-Zn(1)-O(10)	80.78(17)
O(4)#2-Zn(1)-O(10)	82.23(19)	O(6)#3-Zn(1)-O(10)	81.54(17)
O(2)#5-Na(1)-O(3)#6	97.5(2)	O(2)#5-Na(1)-O(8)#2	108.27(18)
O(3)#6-Na(1)-O(8)#2	100.33(18)	O(3)#6-Na(1)-O(4)#2	86.33(19)
O(8)#2-Na(1)-O(4)#2	87.17(15)	O(4)#2-Na(1)-O(1)	76.39(16)
Complex 4			
Zn(1)-O(6)	1.954(4)	Zn(1)-O(7)#1	1.960(3)

Zn(1)-O(8)	2.014(3)	Zn(1)-O(4)	2.181(3)
Zn(1)-O(7)	2.214(3)	Zn(2)-O(7)#3	2.020(3)
Zn(2)-O(8) #1	2.117(3)	Zn(2)-O(11)	2.161(3)
Zn(3)-O(10)#5	1.959(4)	Zn(3)-O(8)	1.976(3)
Zn(3)-O(5)	1.985(4)	Zn(2)-Zn(1)#1	3.099 (9)
O(6)-Zn(1)-O(7)#1	119.42(14)	O(6)-Zn(1)-O(8)	125.33(14)
O(7)#1-Zn(1)-O(8)	114.05(15)	O(6)-Zn(1)-O(4)	92.19(15)
O(7)#1-Zn(1)-O(4)	98.30(13)	O(8)-Zn(1)-O(4)	90.76(13)
O(6)-Zn(1)-O(7)	95.20(14)	O(7)#2-Zn(1)-O(7)	79.93(13)
O(7)#1-Zn(2)-O(8)#3	94.39(12)	O(7)#3-Zn(2)-O(8)#3	85.61(12)
O(8)#3-Zn(2)-O(8)#1	180.00(16)	O(8)#3-Zn(2)-O(11)	92.67(13)
O(7)#1-Zn(2)-O(11)#4	93.90(13)	O(8)#3-Zn(2)-O(11)#4	87.33(13)
O(10)#5-Zn(3)-O(9)	127.69(16)	O(10)#5-Zn(3)-O(8)	110.56(14)
O(10)#5-Zn(3)-O(5)	100.88(16)	O(9)-Zn(3)-O(5)	98.74(16)
O(8)-Zn(3)-O(5)	101.52(14)		
Complex 5			
Zn(1)-O(13)	2.001(7)	Zn(1)-O(9)	2.013(6)
Zn(1)-O(17)#1	2.037(8)	Zn(1)-N(5)	2.115(8)
Zn(1)-N(4)	2.165(8)	Zn(2)-O(10)	2.013(6)
Zn(2)-O(11)	2.062(6)	Zn(2)-O(16)#2	2.067(7)
Zn(2)-O(12)	2.104(7)	Zn(2)-O(14)	2.192(7)
Zn(2)-O(13)	2.242(7)	Zn(3)-O(19)#3	1.969(8)
Zn(3)-O(4)	2.019(8)	Zn(3)-N(10)	2.090(9)
Zn(3)-N(9)	2.086(9)	Zn(3)-O(5)	2.396(10)
O(13)-Zn(1)-O(9)	106.6(3)	O(13)-Zn(1)-N(5)	107.8(3)
O(17)#1-Zn(1)-N(5)	88.6(3)	O(9)-Zn(1)-N(4)	90.2(3)
N(5)-Zn(1)-N(4)	77.3(3)	O(10)-Zn(2)-O(11)	91.5(3)
O(11)-Zn(2)-O(16)#2	101.6(3)	O(10)-Zn(2)-O(14)	97.3(3)
O(19)#3-Zn(3)-O(4)	133.0(4)	O(4)-Zn(3)-O(5)	58.9(3)
N(10)-Zn(3)-O(5)	153.1(3)	N(9)-Zn(3)-O(5)	88.1(3)
Complex 6			
Zn(1)-O(3)#1	1.941(3)	Zn(1)-O(6)#2	1.965(3)
Zn(1)-O(1)	2.020(5)	Zn(1)-N(7)	2.082(3)
Zn(2)-N(10)	2.104(4)	Zn(2)-N(10)#3	2.104(4)
Zn(2)-O(5)	2.122(3)	Zn(2)-O(5)#3	2.122(3)
Zn(2)-O(10)	2.135(3)	O(3)#1-Zn(1)-O(6)#2	116.04(14)
O(3)#1-Zn(1)-O(1)	107.34(3)	O(6)#2-Zn(1)-O(1)	135.81(3)
O(3)#1-Zn(1)-N(7)	97.59(14)	O(6)#2-Zn(1)-N(7)	91.70(12)
O(1)-Zn(1)-N(7)	90.65(15)	N(10)-Zn(2)-O(5)	91.45(12)
N(10)#3-Zn(2)-O(5)	88.55(12)	O(5)-Zn(2)-O(5)#3	180.0
N(10)-Zn(2)-O(10)	89.43(15)	N(10)#3-Zn(2)-O(10)	90.57(15)
O(5)-Zn(2)-O(10)	94.52(12)	O(5) -Zn(2)-O(10)#3	85.48(12)

Symmetry transformations used to generate equivalent atoms in complex **1**: (#1)

-x,-y+1,-z+1. Complex **2**: (#1) x-1,y+1,z+1; (#2) x-1,y,z+1; (#3) x,y-1,z; (#4) -x,-y+1,-z+2 (#5) -x,-y,-z+2. Complex **3**: (#1) -x,y,-z+3/2; (#2) -x+1,y,-z+3/2; (#3) -x,y+1,-z+3/2; (#5) x,y+1,z; (#6) -x+1,y+1,-z+3/2. Complex **4**: (#1) -x+2,-y+1,-z+1; (#2) x+1,y,z; (#3) x-1,y,z; (#4) -x+1,-y+1,-z+1; (#5) x,-y+1/2,z+1/2. Complex **5**: (#1) -x+1/2,y+1/2,-z+3/2; (#2) -x,y-1/2,-z+3/2; (#3) x+1,-y+5/2,z+1/2. Complex **6**: (#1) x+1,y,z; (#2) x,y+1,z; (#3) -x,-y,-z+2.