

## Supporting Information

### **Metal-Organic Frameworks Based on Transition-Metal Oxygen Clusters as Secondary Building Units: Synthesis, Structures and Properties**

Li-Min Zhao, Zhen-Jie Zhang, Shi-Yuan Zhang, Ping Cui, Wei Shi, Bin Zhao, Peng Cheng\*, Dai-Zheng Liao, Shi-Ping Yan

*Department of Chemistry, Nankai University, Tianjin 300071, China*

#### **Catalogue:**

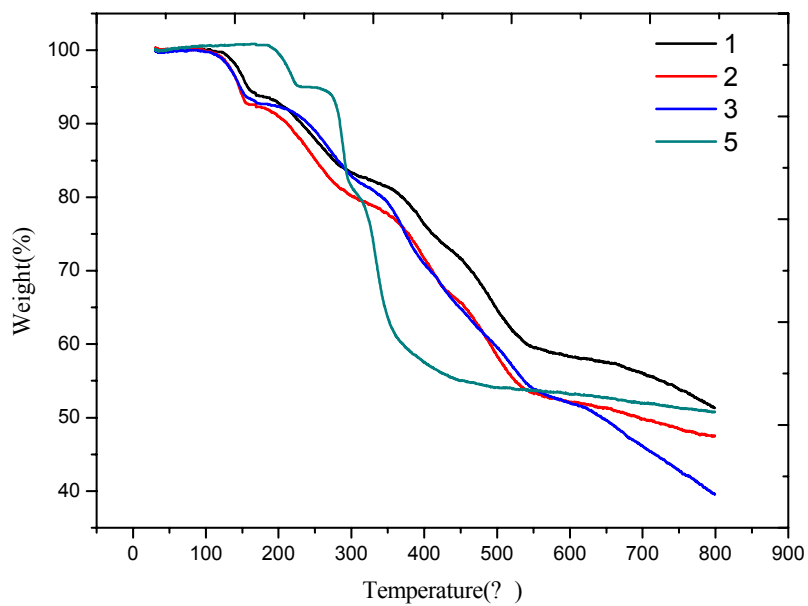
Fig. S1. The plot of TGA of compounds **1-3** and **5**.

Fig. S2. The absorption spectra of compounds **1-3** and **5**.

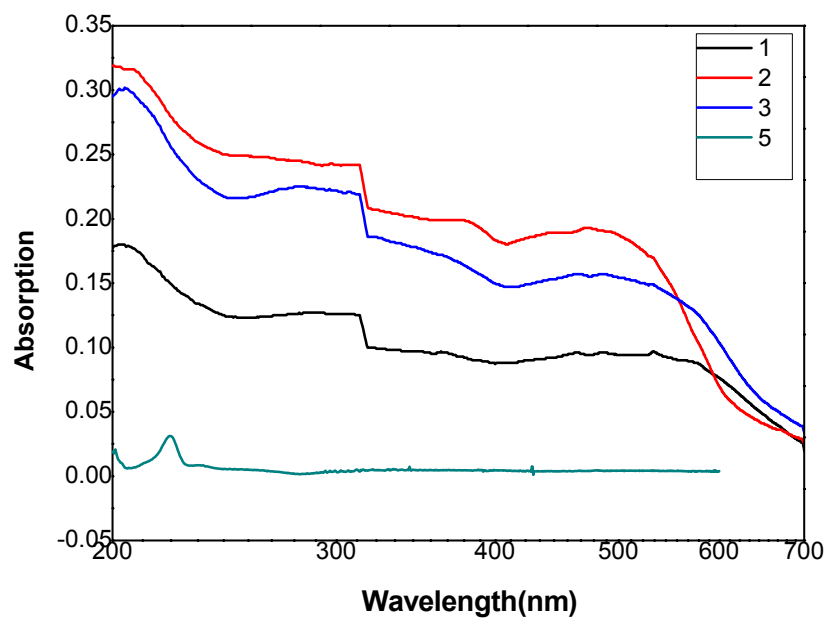
Table S1. Selected bonds length and angles for compounds **1-5**.

---

\* Corresponding author. E-mail: [pcheng@nankai.edu.cn](mailto:pcheng@nankai.edu.cn).



**Fig. S1.** The TGA digram for compounds 1-3 and 5.



**Fig. S2.** The absorption spectra of compounds 1-3 and 5.

**Table S1. Selected bonds length and angles for compounds 1-5.**

1		2		3	
Zn(1)-O(9)	1.897(3)	O(7)-Zn(2)#1	2.225(5)	Cd(1)-O(2)	2.182(5)
Zn(1)-O(10)	1.919(3)	Zn(1)-O(1)	1.957(5)	Cd(1)-O(3)#1	2.229(6)
Zn(1)-O(8)	2.015(5)	Zn(1)-O(3)#2	1.984(5)	Cd(1)-N(3)	2.292(6)
Zn(1)-N(1)	2.031(6)	Zn(1)-N(1)	2.070(6)	Cd(1)-O(9)	2.322(6)
Zn(3)-O(10)# 1	1.917(3)	Zn(1)-O(8)	2.174(5)	Cd(1)-N(1)	2.397(7)
Zn(3)-O(2)	1.951(6)	Zn(1)-N(5)	2.235(6)	Cd(1)-O(1)	2.706(6)
Zn(3)-N(5)	2.024(7)	Zn(2)-N(4)#3	2.080(5)	Cd(2)-N(6)#3	2.256(6)
Zn(3)-O(1)	2.089(3)	Zn(2)-N(4)	2.080(5)	Cd(2)-O(7)	2.331(6)
Zn(3)-O(3)	2.445(9)	Zn(2)-O(9)#3	2.146(5)	Cd(2)-O(8)	2.359(6)
Zn(2)-O(9)#2	1.944(3)	Zn(2)-O(9)	2.146(5)	Cd(2)-O(7)	2.331(6)
Zn(2)-O(9)	1.944(3)	Zn(2)-O(7)#4	2.225(5)		
Zn(2)-N(4)#3	2.211(6)	Zn(2)-O(7)#5	2.225(5)		
Zn(2)-N(4)#4	2.211(6)				
Zn(2)-O(7)	2.217(3)				
Zn(2)-O(7)#2	2.217(3)				
O(9)-Zn(1)-O(10)	109.15(14)	S(1)-O(7)-Zn(2)#1	156.2(3)	O(2)-Cd(1)-O(3)#1	118.3(2)
O(9)-Zn(1)-O(8)	114.00(17)	O(1)-Zn(1)-O(3)#2	113.8(2)	O(2)-Cd(1)-N(3)	149.2(2)
O(10)-Zn(1)-O(8)	105.10(18)	O(1)-Zn(1)-N(1)	146.9(2)	O(3)#1-Cd(1)-N(3)	92.3(3)
O(9)-Zn(1)-N(1)	112.5(2)	O(3)#2-Zn(1)-N(1)	99.0(2)	O(2)-Cd(1)-O(9)	91.0(2)
O(10)-Zn(1)-N(1)	108.9(2)	O(1)-Zn(1)-O(8)	87.21(19)	N(3)-Cd(1)-O(9)	83.1(2)
O(8)-Zn(1)-N(1)	106.8(2)	O(3)#2-Zn(1)-O(8)	95.6(2)	O(3)#1-Cd(1)-N(1)	100.3(3)
O(10)#1-Zn(3)-O(2)	129.5(2)	N(1)-Zn(1)-O(8)	85.5(2)	N(3)-Cd(1)-N(1)	85.6(2)
O(10)#1-Zn(3)-N(5)	104.0(2)	O(1)-Zn(1)-N(5)	91.3(2)	O(2)-Cd(1)-O(1)	51.80(18)
O(2)-Zn(3)-N(5)	115.7(3)	O(3)#2-Zn(1)-N(5)	97.7(2)	O(9)-Cd(1)-O(1)	83.5(2)
O(10)#1-Zn(3)-O(1)	103.56(14)	N(1)-Zn(1)-N(5)	88.3(2)	N(1)-Cd(1)-O(1)	84.7(2)
O(10)#1-Zn(3)-O(3)	93.8(2)	N(4)#3-Zn(2)-O(9)#3	88.4(2)	O(3)#1-Cd(1)-O(4)#1	49.5(2)
O(2)-Zn(3)-O(3)	58.4(3)	N(4)-Zn(2)-O(9)#3	91.6(2)	N(3)-Cd(1)-O(4)#1	135.4(2)
N(5)-Zn(3)-O(3)	89.6(3)	N(4)#3-Zn(2)-O(9)	91.6(2)	O(9)-Cd(1)-O(4)#1	116.4(2)
O(1)-Zn(3)-O(3)	154.00(18)	N(4)-Zn(2)-O(9)	88.4(2)	N(1)-Cd(1)-O(4)#1	81.0(2)
O(9)#2-Zn(2)-N(4)#3	92.38(18)			O(2)-Cd(1)-C(8)#1	96.5(2)
4					
Cd(1)-O(9)#1	2.264(4)	O(9)#1-Cd(1)-O(9)#2	180.00(7)	O(11)-Cd(3)-O(10)#10	81.30(13)
Cd(1)-O(11)	2.281(3)	O(9)#1-Cd(1)-O(11)#3	82.03(10)	O(11)#10-Cd(3)-O(3)	79.38(9)
Cd(2)-O(2)	2.222(4)	O(9)#2-Cd(1)-O(11)#3	97.97(10)	O(8)#11-Cd(3)-O(3)	174.84(14)
Cd(2)-O(7)#9	2.252(3)	O(11)#3-Cd(1)-O(11)#4	90.91(17)	O(9)-Cd(4)-O(7)	94.34(13)
Cd(2)-O(7)	2.293(3)	O(11)-Cd(1)-O(11)#4	89.09(17)	O(9)-Cd(4)-O(11)#2	83.61(13)
Cd(3)-O(11)	2.224(3)	O(2)-Cd(2)-O(7)#8	101.76(10)	O(7)-Cd(4)-O(11)#2	171.99(11)
Cd(3)-O(11)#10	2.224(3)	O(7)#8-Cd(2)-O(7)#9	103.20(15)	O(9)-Cd(4)-O(8)	100.27(11)
Cd(3)-O(10)	2.375(3)	O(2)-Cd(2)-O(7)#10	102.28(10)	O(7)-Cd(4)-O(8)	95.54(12)
Cd(3)-O(3)	2.462(4)	O(7)#8-Cd(2)-O(7)#10	155.50(3)	O(9)-Cd(4)-O(1)	81.44(11)

Cd(4)-O(9)	2.228(3)	O(7)#9-Cd(2)-O(7)#10	76.32(12)
Cd(4)-O(7)	2.243(3)	O(11)-Cd(3)-O(8)#11	103.46(10)
Cd(4)-O(8)	2.266(3)	O(11)-Cd(3)-O(8)#11	103.46(10)
Cd(4)-O(4)#2	2.354(3)	O(11)-Cd(3)-O(10)	159.09(13)

5

Cu(1)-O(2)	1.9307(18)	O(2)-Cu(1)-O(10)	96.61(7)	O(12)#3-Cu(2)-Cu(1)#3	39.56(5)
Cu(1)-O(2)	1.9307(18)	O(2)-Cu(1)-O(12)	169.54(9)	O(1)-Cu(3)-O(9)#5	84.43(8)
Cu(1)-O(13)	1.9707(19)	O(2)-Cu(1)-O(13)	86.51(8)	O(1)-Cu(3)-O(9)#1	99.75(9)
Cu(1)-Cu(2)#1	3.0410(5)	O(12)-Cu(1)-O(13)	89.91(8)		
Cu(2)-O(8)	1.946(2)	O(10)-Cu(1)-O(11)	86.48(7)		
Cu(2)-O(12)#3	1.9887(17)	O(8)-Cu(2)-O(12)#2	159.21(8)		
Cu(2)-O(10)#3	2.2841(18)	O(8)-Cu(2)-O(10)#3	101.78(8)		
Cu(3)-O(10)	1.9015(18)	O(8)-Cu(2)-Cu(1)#3	86.68(6)		
Cu(3)-O(1)	1.9463(19)	O(10)-Cu(3)-O(1)	93.59(8)		

**Symmetry transformations used to generate equivalent atoms:**

- #1  $x, y-1, z$  #2  $-x+1, -y+1, -z$  #3  $x, y, z-1$  #4  $-x+1, -y+1, -z+1$  #5  $x, y+1, z$   
 #6  $x, y, z+1$  #7  $-x+2, -y-1, -z-1$
- #1  $x-1, y+1, z-1$  #2  $x, y-1, z$  #3  $-x+2, -y, -z+2$  #4  $-x+1, -y+1, -z+1$  #5  $x+1, y-1, z+1$   
 #6  $-x, y, -z+1/2$  #7  $x, y+1, z$
- #1  $x, y+1, z$  #2  $-x+1, -y, -z+1$  #3  $x-1, y-1, z-1$  #4  $-x, -y-1, -z$  #5  $x, y-1, z$   
 #6  $-x, y, -z+1/2$  #7  $x+1, y+1, z+1$
- #1  $x-1/2, y-1/2, z-1$  #2  $-x+3/2, -y+3/2, -z+1$  #3  $-x+1, -y+1, -z$  #4  $-x+1, y, -z$  #5  $x, -y+1, z$   
 #6  $x-1/2, -y+3/2, z-1$  #7  $-x+3/2, y-1/2, -z+1$  #8  $-x+3/2, -y+3/2, -z+2$  #9  $-x+3/2, y+1/2, -z+2$   
 #10  $x, -y+2, z$  #11  $x-1/2, y+1/2, z-1$
- #1  $x+1, y-1, z$  #2  $-x+1, -y+1, -z$  #3  $x-1, y+1, z$  #4  $-x, -y+2, -z$  #5  $-x+1, -y+1, -z+1$