

## Supplementary Information

# Construction of Three-Dimensional Metal-Organic Frameworks in the Presence of a Tetrahedral Ligand and a Secondary Bidentate Linker

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1- Selected bond lengths and angles of compounds **1-3**.

2- Powder X-ray diffraction of compounds **1-3**.

3- Additional crystallographic figures.

### 1- Selected bond lengths and angles of compounds 1-3

**Table S1** Selected bond lengths (Å) and angles (°) for **1**.

Co1—N1 <sup>iii</sup>	2.030(4)	Co1—O11 <sup>iv</sup>	2.040(4)
Co1—O1	2.075(3)	Co1 <sup>vii</sup> —O9	2.021(4)
Co1 <sup>vi</sup> —O5	1.986(3)	Co2—O12 <sup>iv</sup>	2.001(4)
Co2—O2	1.998(4)	Co2—O6 <sup>i</sup>	2.117(3)
Co2—O8 <sup>ii</sup>	2.041(3)	Co2—N2	2.049(4)
O5 <sup>i</sup> —Co1—O9 <sup>ii</sup>	164.83(14)	O5 <sup>i</sup> —Co1—N1 <sup>iii</sup>	99.57(19)
O9 <sup>ii</sup> —Co1—N1 <sup>iii</sup>	95.38(19)	O5 <sup>i</sup> —Co1—O11 <sup>iv</sup>	93.00(15)
O9 <sup>ii</sup> —Co1—O11 <sup>iv</sup>	87.32(16)	N1 <sup>iii</sup> —Co1—O11 <sup>iv</sup>	98.3(2)
O5 <sup>i</sup> —Co1—O1	87.90(15)	O9 <sup>ii</sup> —Co1—O1	88.66(15)
N1 <sup>iii</sup> —Co1—O1	93.5(2)	O11 <sup>iv</sup> —Co1—O1	167.83(15)
O2—Co2—O12 <sup>iv</sup>	163.66(15)	O12 <sup>iv</sup> —Co2—O8 <sup>ii</sup>	87.78(16)
O2—Co2—O8 <sup>ii</sup>	93.06(16)	O12 <sup>iv</sup> —Co2—N2	95.99(15)
O2—Co2—N2	99.86(15)	O8 <sup>ii</sup> —Co2—N2	100.91(15)
O12 <sup>iv</sup> —Co2—O6 <sup>i</sup>	89.21(15)	O2—Co2—O6 <sup>i</sup>	86.31(15)
N2—Co2—O6 <sup>i</sup>	92.03(14)	O8 <sup>ii</sup> —Co2—O6 <sup>i</sup>	166.96(14)

Symmetry codes: (i) x, -y, 0.5+z; (ii) 0.5+x, 0.5+y, z; (iii) 0.5+x, -0.5+y, z; (iv) 0.5+x, 0.5-y, 0.5+z;

(v) -0.5+x, 0.5+y, z; (vi) x, -y, -0.5+z; (vii) -0.5+x, -0.5+y, z; (viii) -0.5+x, 0.5-y, -0.5+z.

**Table S2** Selected bond lengths (Å) and angles (°) for **2**.

Zn1—N1 <sup>v</sup>	1.985(4)	Zn1—O5 <sup>vi</sup>	2.004(4)
Zn1—O11 <sup>vii</sup>	2.028(4)	Zn1—O9 <sup>viii</sup>	2.037(4)
Zn1—O1	2.067(4)	Zn2—O12 <sup>vii</sup>	1.993(4)
Zn2—O6 <sup>vi</sup>	2.104(4)	Zn2—O8 <sup>viii</sup>	2.069(4)
Zn2—N2	2.008(4)	Zn2—O2	1.982(4)
N1 <sup>v</sup> —Zn1—O5 <sup>vi</sup>	102.33(18)	N1 <sup>v</sup> —Zn1—O11 <sup>vii</sup>	98.07(19)
O5 <sup>vi</sup> —Zn1—O11 <sup>vii</sup>	90.71(18)	N1 <sup>v</sup> —Zn1—O9 <sup>viii</sup>	97.76(18)
O5 <sup>vi</sup> —Zn1—O9 <sup>viii</sup>	159.79(16)	O11 <sup>vii</sup> —Zn1—O9 <sup>viii</sup>	88.56(19)
N1 <sup>v</sup> —Zn1—O1	97.66(18)	O5 <sup>vi</sup> —Zn1—O1	88.14(19)
O11 <sup>vii</sup> —Zn1—O1	164.10(18)	O9 <sup>viii</sup> —Zn1—O1	87.09(19)
O2—Zn2—O12 <sup>vii</sup>	158.31(17)	O2—Zn2—N2	102.81(18)
O12 <sup>vii</sup> —Zn2—N2	98.73(18)	O2—Zn2—O8 <sup>viii</sup>	90.01(18)
O12 <sup>vii</sup> —Zn2—O8 <sup>viii</sup>	87.79(18)	N2—Zn2—O8 <sup>viii</sup>	102.69(17)
O2—Zn2—O6 <sup>vi</sup>	87.10(18)	O12 <sup>vii</sup> —Zn2—O6 <sup>vi</sup>	88.77(18)
N2—Zn2—O6 <sup>vi</sup>	94.18(17)	O8 <sup>viii</sup> —Zn2—O6 <sup>vi</sup>	163.11(16)

Symmetry codes: (i) -0.5+x, 0.5+y, z; (ii) x, -y, -0.5+z; (iii) -0.5+x, -0.5+y, z; (iv) -0.5+x, 0.5-y, -0.5+z;

(v) 0.5+x, -0.5+y, z; (vi) x, -y, 0.5+z; (vii) 0.5+x, 0.5-y, 0.5+z; (viii) 0.5+x, 0.5+y, z.

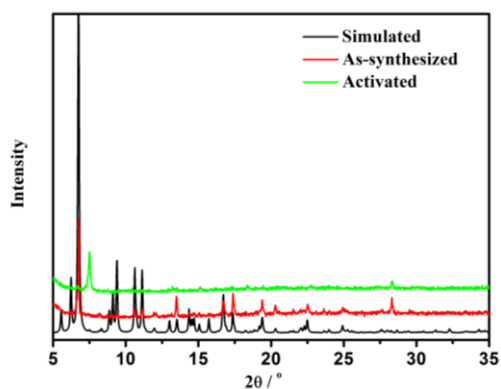
**Table S3** Selected bond lengths (Å) and angles (°) for **3**.

Cd1—O8 <sup>iii</sup>	2.341(4)	Cd1—O5 <sup>iv</sup>	2.386(3)
Cd1—O1	2.362(4)	Cd1—O6 <sup>iv</sup>	2.420(4)
Cd1—O11 <sup>v</sup>	2.412(4)	Cd1—O2	2.543(3)
Cd1—O12 <sup>v</sup>	2.441(4)	Cd1—O9 <sup>iii</sup>	2.580(5)
O8 <sup>iii</sup> —Cd1—O1	84.52(14)	O8 <sup>iii</sup> —Cd1—O5 <sup>iv</sup>	134.59(16)
O1—Cd1—O5 <sup>iv</sup>	124.20(13)	O8 <sup>iii</sup> —Cd1—O11 <sup>v</sup>	91.14(14)
O1—Cd1—O11 <sup>v</sup>	137.92(18)	O5 <sup>iv</sup> —Cd1—O11 <sup>v</sup>	87.52(15)
O8 <sup>iii</sup> —Cd1—O6 <sup>iv</sup>	169.37(15)	O1—Cd1—O6 <sup>iv</sup>	85.15(14)
O5 <sup>iv</sup> —Cd1—O6 <sup>iv</sup>	54.63(14)	O11 <sup>v</sup> —Cd1—O6 <sup>iv</sup>	94.87(14)
O8 <sup>iii</sup> —Cd1—O12 <sup>v</sup>	88.94(15)	O1—Cd1—O12 <sup>v</sup>	84.39(16)
O5 <sup>iv</sup> —Cd1—O12 <sup>v</sup>	124.62(15)	O11 <sup>v</sup> —Cd1—O12 <sup>v</sup>	53.64(16)
O6 <sup>iv</sup> —Cd1—O12 <sup>v</sup>	87.59(14)	O8 <sup>iii</sup> —Cd1—O2	89.90(12)
O1—Cd1—O2	53.34(13)	O5 <sup>iv</sup> —Cd1—O2	83.77(13)
O11 <sup>v</sup> —Cd1—O2	168.73(17)	O6 <sup>iv</sup> —Cd1—O2	85.91(12)
O12 <sup>v</sup> —Cd1—O2	137.61(17)	O8 <sup>iii</sup> —Cd1—O9 <sup>iii</sup>	51.57(14)
O1—Cd1—O9 <sup>iii</sup>	117.98(13)	O5 <sup>iv</sup> —Cd1—O9 <sup>iii</sup>	83.03(15)
O11 <sup>v</sup> —Cd1—O9 <sup>iii</sup>	90.13(15)	O6 <sup>iv</sup> —Cd1—O9 <sup>iii</sup>	136.96(16)
O12 <sup>v</sup> —Cd1—O9 <sup>iii</sup>	127.80(14)	O2—Cd1—O9 <sup>iii</sup>	81.74(13)
O8 <sup>iii</sup> —Cd1—C17 <sup>iv</sup>	161.0(2)	O1—Cd1—C17 <sup>iv</sup>	105.55(17)
O5 <sup>iv</sup> —Cd1—C17 <sup>iv</sup>	26.99(15)	O11 <sup>v</sup> —Cd1—C17 <sup>iv</sup>	91.71(15)
O6 <sup>iv</sup> —Cd1—C17 <sup>iv</sup>	27.65(14)	O12 <sup>v</sup> —Cd1—C17 <sup>iv</sup>	107.75(17)
O2—Cd1—C17 <sup>iv</sup>	83.76(13)	O9 <sup>iii</sup> —Cd1—C17 <sup>iv</sup>	109.7(2)
O8 <sup>iii</sup> —Cd1—C33 <sup>v</sup>	90.16(16)	O1—Cd1—C33 <sup>v</sup>	111.4(2)
O5 <sup>iv</sup> —Cd1—C33 <sup>v</sup>	106.88(19)	O11 <sup>v</sup> —Cd1—C33 <sup>v</sup>	26.60(17)
O6 <sup>iv</sup> —Cd1—C33 <sup>v</sup>	91.30(16)	O12 <sup>v</sup> —Cd1—C33 <sup>v</sup>	27.03(18)
O2—Cd1—C33 <sup>v</sup>	164.6(2)	O9 <sup>iii</sup> —Cd1—C33 <sup>v</sup>	110.1(2)
C17 <sup>iv</sup> —Cd1—C33 <sup>v</sup>	100.65(17)		

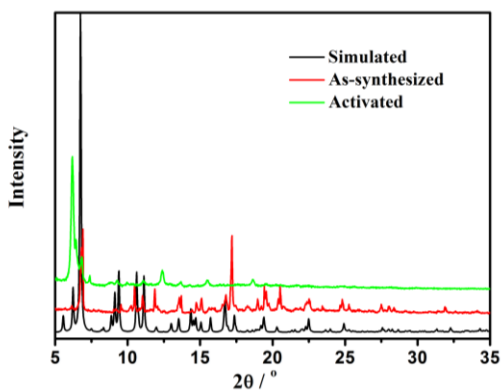
Symmetry codes: (i) x, 2-y, -0.5+z; (ii) 0.5+x, 1.5-y, -0.5+z; (iii) 1-x, 1-y, 2-z; (iv) x, 2-y, 0.5+z;

(v) -0.5+x, 1.5-y, 0.5+z; (vi) 1-x, y, 1.5-z.

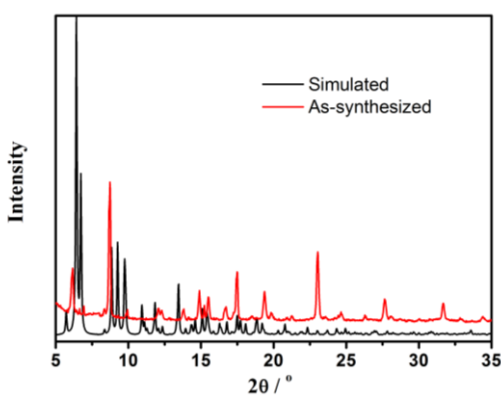
## 2- Powder X-ray diffraction of compounds 1-3



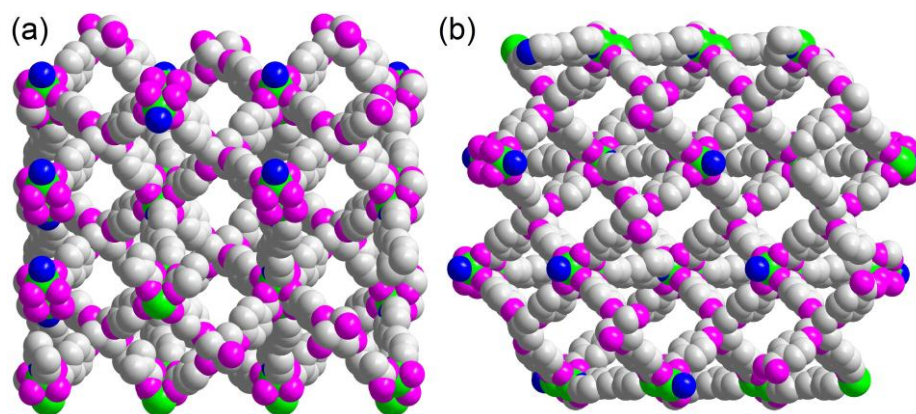
**Fig. S1.** X-ray powder diffraction patterns of compound 1.



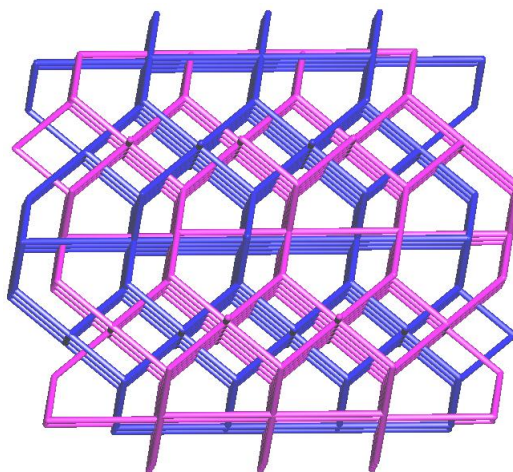
**Fig. S2.** X-ray powder diffraction patterns of compound 2.



**Fig. S3.** X-ray powder diffraction patterns of compound 3.



**Fig. S4** The space-filling views of **2** along the [100] and [010] directions (C, grey; N, blue; O, purple; Zn, green). Hydrogen atoms are omitted for clarity.



**Fig. S5.** The simplified doubly-interpenetrating (4,6)-sqc422 network of **2**.