Supporting Information

Spontaneous resolution of two chiral metal–organic frameworks through local geometric and lattice frustration effects

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S1 – Synthesis

1.1 General

Unless otherwise specified, all reagents and starting materials were purchased from standard commercial sources and used without further purification. *Caution!* Cadmium nitrate tetrahydrate, $Cd(NO_3)_2 \cdot 4H_2O$, is highly toxic and should be manipulated with utmost care and due diligence.

1.2 Synthesis of [Cd(pdc)(DMF)] (3DL-MOF-3)

Bicyclo[1.1.1]pentane-1,3-dicarboxylic acid (5.70 mg, 0.0365 mmol) and cadmium nitrate tetrahydrate (11.26 mg, 0.0365 mmol) were added to separate 21 mL glass scintillation vials and then *N*,*N*-dimethylformamide (3 mL) was added to each vial. Each vial was heated to 120 °C to dissolve the reagents. After complete dissolution, the vial containing the cadmium salt solution was transferred by syringe to the vial containing the dicarboxylic acid solution. The resulting mixture was capped and heated at 120 °C for 18 h to afford colourless rectangular prismatic crystals. Yield: 9.5 mg (77%). Raman (cm^{-1}) ν 2943 (w), 2886 (w), 2820 (w), 1651 (w), 1519 (w), 1437 (m), 1421 (m), 1250 (w), 1134 (w), 1117 (w), 1040 (w), 1010 (w), 921 (s), 866 (m), 821 (m), 718 (w), 682 (w), 550 (w), 521 (w), 410 (w), 375 (w), 292 (w). Elemental analysis calculated for $C_{10}H_{13}NO_5Cd$ (%): C 35.36, H 3.86, N 4.12; found (%) C 35.29, H 3.92, N 4.00.

1.3 Synthesis of $[Cd_3(cdc)_3(DMF)_3]$ (3DL-MOF-4)

Cubane-1,4-dicarboxylic acid (7.02 mg, 0.0365 mmol) and cadmium nitrate tetrahydrate (11.26 mg, 0.0365 mmol) were added to separate 21 mL glass scintillation vials and then *N*,*N*-dimethylformamide (3 mL) was added to each vial. Each vial was heated to 120 °C to dissolve the reagents. After complete dissolution, the vial containing the cadmium salt solution was transferred by syringe to the vial containing the dicarboxylic acid solution. The resulting mixture was capped and heated at 120 °C for 18 h to afford colourless rectangular prismatic crystals. Yield: 10.1 mg (73%). Raman (cm^{-1}) ν 2994 (w), 2935 (w), 1659 (w), 1530 (w), 1444 (m), 1415 (s), 1236 (m), 1175 (w), 1103 (m), 1031 (w), 993 (s), 887 (s), 877 (s), 685 (m), 663 (m), 412 (m), 381 (m), 225 (m). Elemental analysis calculated for $C_{39}H_{39}N_3O_{15}Cd_3$ (%): C 41.56, H 3.49, N 3.73; found (%) C 41.66, H 3.52, N 3.86.

S2 – Single Crystal X-Ray Diffraction

Table S2.1 Crystal data and structure refinement for **3DL-MOF-3α**.

Empirical formula	$C_{10}H_{13}NO_5Cd$
Formula weight	339.61
Temperature / K	100(2)
Crystal system	hexagonal
Space group	$P6_1$
a / Å	9.3792(4)
c / Å	22.4879(9)
V / Å^3	1713.21(16)
Z	6
ρ_{calc} / g cm^{-3}	1.975
μ / mm^{-1}	1.921
F(000)	1008
Crystal size / mm^3	0.25 × 0.10 × 0.03
Radiation	MoKα (λ = 0.71073 Å)
2Θ range for data collection / °	5.014 to 61.988
Index ranges	-12 ≤ h ≤ 13, -13 ≤ k ≤ 12, -32 ≤ l ≤ 32
Reflections collected	15958
Independent reflections	3644 [R_{int} = 0.0557, R_{sigma} = 0.0610]
Data/restraints/parameters	3644/67/166
Goodness-of-fit on F^2	1.004
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0284, wR_2 = 0.0453
Final R indexes [all data]	R_1 = 0.0327, wR_2 = 0.0463
Largest diff. peak/hole / e Å^{-3}	0.59/-0.54
Flack parameter	-0.06(3)
CCDC number	2167454

Table S2.2 Crystal data and structure refinement for **3DL-MOF-3β**.

Empirical formula	$C_{10}H_{13}NO_5Cd$
Formula weight	339.61
Temperature / K	100(2)
Crystal system	hexagonal
Space group	$P6_5$
a / Å	9.3938(3)
c / Å	22.5064(8)
V / Å^3	1719.96(13)
Z	6
ρ_{calc} / g cm^{-3}	1.967
μ / mm^{-1}	1.913
F(000)	1008
Crystal size / mm^3	0.25 × 0.09 × 0.03
Radiation	MoKα (λ = 0.71073 Å)
2Θ range for data collection / °	5.008 to 66.288
Index ranges	-14 ≤ h ≤ 13, -9 ≤ k ≤ 13, -34 ≤ l ≤ 34
Reflections collected	14182
Independent reflections	4334 [R_{int} = 0.0447, R_{sigma} = 0.0606]
Data/restraints/parameters	4334/67/166
Goodness-of-fit on F^2	1.027
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0277, wR_2 = 0.0465
Final R indexes [all data]	R_1 = 0.0312, wR_2 = 0.0474
Largest diff. peak/hole / e Å^{-3}	0.60/-0.53
Flack parameter	-0.06(2)
CCDC number	2167455

Table S2.3 Selected bond lengths for **3DL-MOF-3α**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Cd1	O1	2.184(3)	C1	C2	1.499(5)
Cd1	O4^1	2.259(3)	C7	C6	1.503(5)
Cd1	O3^1	2.568(2)	C2	C3A	1.563(7)
Cd1	O3^2	2.381(3)	C2	C5A	1.561(5)
Cd1	O5	2.234(3)	C2	C4A	1.530(8)
Cd1	O2^3	2.307(3)	C2	C3B	1.546(18)
Cd1	C7^1	2.753(3)	C2	C5B	1.540(15)
O1	C1	1.266(4)	C2	C4B	1.55(2)
O4	C7	1.265(4)	C3A	C6	1.562(7)
O3	C7	1.252(5)	C6	C5A	1.531(7)
O5	C8	1.247(4)	C6	C4A	1.540(7)

Table S2.3 Selected bond lengths for **3DL-MOF-3α**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
N1	C9	1.457(5)	C6	C3B	1.520(18)
N1	C8	1.302(5)	C6	C5B	1.545(16)
N1	C10	1.464(5)	C6	C4B	1.543(18)
O2	C1	1.253(5)			

Symmetry codes: [1]1+Y-X, 1-X, -1/3+Z; [2]1+Y, 1-X+Y, -1/6+Z; [3]+Y, 1-X+Y, -1/6+Z

Table S2.4 Selected bond angles for **3DL-MOF-3α**.

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
O1	Cd1	O4[1]	105.60(11)	O3	C7	Cd1[4]	68.27(18)
O1	Cd1	O3[2]	86.17(9)	O3	C7	O4	122.2(3)
O1	Cd1	O3[1]	91.76(9)	O3	C7	C6	120.8(3)
O1	Cd1	O5	144.99(9)	C6	C7	Cd1[4]	168.9(2)
O1	Cd1	O2[3]	98.42(11)	O5	C8	N1	124.3(3)
O1	Cd1	C7[1]	98.26(11)	C1	C2	C3A	126.5(4)
O4[1]	Cd1	O3[2]	87.17(9)	C1	C2	C5A	128.6(4)
O4[1]	Cd1	O3[1]	53.88(9)	C1	C2	C4A	126.6(3)
O4[1]	Cd1	O2[3]	124.15(9)	C1	C2	C3B	128.2(8)
O4[1]	Cd1	C7[1]	27.01(11)	C1	C2	C5B	127.6(7)
O3[2]	Cd1	O3[1]	138.84(9)	C1	C2	C4B	126.5(7)
O3[1]	Cd1	C7[1]	26.94(10)	C5A	C2	C3A	86.4(4)
O3[2]	Cd1	C7[1]	112.87(10)	C4A	C2	C3A	87.5(4)
O5	Cd1	O4[1]	104.76(11)	C4A	C2	C5A	87.8(4)
O5	Cd1	O3[2]	78.32(9)	C3B	C2	C4B	84.5(14)
O5	Cd1	O3[1]	120.40(8)	C5B	C2	C3B	90.8(11)
O5	Cd1	O2[3]	78.31(10)	C5B	C2	C4B	84.9(13)
O5	Cd1	C7[1]	116.65(10)	C6	C3A	C2	73.3(3)
O2[3]	Cd1	O3[2]	144.85(10)	C7	C6	C3A	127.4(4)
O2[3]	Cd1	O3[1]	76.13(9)	C7	C6	C5A	127.1(3)
O2[3]	Cd1	C7[1]	100.99(10)	C7	C6	C4A	126.2(4)
C1	O1	Cd1	114.8(3)	C7	C6	C3B	128.0(7)
C7	O4	Cd1[4]	98.8(2)	C7	C6	C5B	127.3(6)
Cd1[5]	O3	Cd1[4]	109.47(11)	C7	C6	C4B	125.5(8)
C7	O3	Cd1[5]	124.6(2)	C5A	C6	C3A	87.5(4)
C7	O3	Cd1[4]	84.79(19)	C5A	C6	C4A	88.5(4)
C8	O5	Cd1	124.4(2)	C4A	C6	C3A	87.1(4)
C9	N1	C10	116.1(4)	C3B	C6	C5B	91.6(12)
C8	N1	C9	121.9(3)	C3B	C6	C4B	85.7(13)
C8	N1	C10	121.9(4)	C4B	C6	C5B	85.0(13)
C1	O2	Cd1[6]	132.9(3)	C6	C5A	C2	74.2(3)
O1	C1	C2	115.0(3)	C2	C4A	C6	74.8(3)
O2	C1	O1	125.5(3)	C6	C3B	C2	74.9(8)
O2	C1	C2	119.4(3)	C2	C5B	C6	74.4(7)
O4	C7	Cd1[4]	54.20(19)	C6	C4B	C2	74.1(8)

Table S2.4 Selected bond angles for **3DL-MOF-3α**.

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
O4	C7	C6	117.0(4)				

Symmetry codes: [1]1+Y-X, 1-X, -1/3+Z; [2]1+Y, 1-X+Y, -1/6+Z; [3]+Y, 1-X+Y, -1/6+Z; [4]1-Y, +X-Y, 1/3+Z; [5]-Y+X, -1+X, 1/6+Z; [6]1-Y+X, +X, 1/6+Z

Table S2.5 Selected bond lengths for **3DL-MOF-3β**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Cd1	O4[1]	2.262(2)	C7	C6	1.507(4)
Cd1	O1	2.184(2)	C2	C1	1.501(4)
Cd1	O3[2]	2.379(2)	C2	C5A	1.568(6)
Cd1	O3[1]	2.572(2)	C2	C4A	1.540(7)
Cd1	O5	2.239(2)	C2	C3A	1.559(5)
Cd1	O2[3]	2.309(3)	C2	C5B	1.526(16)
Cd1	C7[1]	2.750(3)	C2	C4B	1.542(18)
O4	C7	1.259(4)	C2	C3B	1.520(14)
O1	C1	1.266(4)	C6	C5A	1.566(6)
O3	C7	1.263(4)	C6	C4A	1.541(6)
O5	C8	1.246(3)	C6	C3A	1.545(6)
O2	C1	1.261(4)	C6	C5B	1.508(16)
N1	C9	1.458(4)	C6	C4B	1.557(16)
N1	C8	1.315(4)	C6	C3B	1.556(15)
N1	C10	1.465(4)			

Symmetry codes: [1]+Y-X, 1-X, 1/3+Z; [2]-1+Y, -X+Y, 1/6+Z; [3]+Y, -X+Y, 1/6+Z

Table S2.6 Selected bond angles for **3DL-MOF-3β**.

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
O4[1]	Cd1	O3[2]	87.15(8)	C6	C7	Cd1[4]	169.31(19)
O4[1]	Cd1	O3[1]	54.03(8)	O5	C8	N1	123.5(3)
O4[1]	Cd1	O2[3]	124.13(8)	C1	C2	C5A	126.2(3)
O4[1]	Cd1	C7[1]	26.91(9)	C1	C2	C4A	126.4(3)
O1	Cd1	O4[1]	105.63(10)	C1	C2	C3A	128.8(3)
O1	Cd1	O3[2]	86.02(8)	C1	C2	C5B	128.6(7)
O1	Cd1	O3[1]	91.69(8)	C1	C2	C4B	125.4(6)
O1	Cd1	O5	145.03(8)	C1	C2	C3B	127.7(6)
O1	Cd1	O2[3]	98.53(9)	C4A	C2	C5A	87.4(4)
O1	Cd1	C7[1]	98.34(9)	C4A	C2	C3A	87.7(3)
O3[2]	Cd1	O3[1]	138.91(8)	C3A	C2	C5A	86.8(3)
O3[1]	Cd1	C7[1]	27.19(8)	C5B	C2	C4B	84.3(12)
O3[2]	Cd1	C7[1]	112.74(8)	C3B	C2	C5B	89.8(10)
O5	Cd1	O4[1]	104.67(9)	C3B	C2	C4B	87.0(11)
O5	Cd1	O3[2]	78.43(8)	O1	C1	C2	115.5(3)
O5	Cd1	O3[1]	120.43(7)	O2	C1	O1	125.3(3)
O5	Cd1	O2[3]	78.26(9)	O2	C1	C2	119.2(2)
O5	Cd1	C7[1]	116.53(8)	C7	C6	C5A	127.9(3)
O2[3]	Cd1	O3[1]	76.04(8)	C7	C6	C4A	126.2(3)
O2[3]	Cd1	O3[2]	144.88(8)	C7	C6	C3A	126.6(3)
O2[3]	Cd1	C7[1]	101.09(9)	C7	C6	C5B	129.1(7)
C7	O4	Cd1[4]	98.7(2)	C7	C6	C4B	126.8(7)
C1	O1	Cd1	115.0(2)	C7	C6	C3B	127.5(6)
Cd1[5]	O3	Cd1[4]	109.51(9)	C4A	C6	C5A	87.4(3)
C7	O3	Cd1[4]	84.26(16)	C4A	C6	C3A	88.2(4)
C7	O3	Cd1[5]	124.33(17)	C3A	C6	C5A	87.4(4)
C8	O5	Cd1	123.8(2)	C5B	C6	C4B	84.4(11)
C1	O2	Cd1[6]	132.8(2)	C5B	C6	C3B	89.2(10)
C9	N1	C10	116.5(3)	C3B	C6	C4B	85.2(11)
C8	N1	C9	121.8(3)	C6	C5A	C2	73.3(3)
C8	N1	C10	121.6(3)	C2	C4A	C6	74.8(3)
O4	C7	Cd1[4]	54.40(15)	C6	C3A	C2	74.1(3)
O4	C7	O3	122.7(3)	C6	C5B	C2	76.2(8)
O4	C7	C6	117.3(3)	C2	C4B	C6	74.3(7)
O3	C7	Cd1[4]	68.54(15)	C2	C3B	C6	74.9(7)
O3	C7	C6	120.0(3)				

Symmetry codes: [1]+Y-X, 1-X, 1/3+Z; [2]-1+Y, -X+Y, 1/6+Z; [3]+Y, -X+Y, 1/6+Z; [4]1-Y, 1+X-Y, -1/3+Z; [5]1-Y+X, 1+X, -1/6+Z; [6]-Y+X, +X, -1/6+Z

Table 2.7 Crystal data and structure refinement for 3DL-MOF-4.

Empirical formula	$C_{39}H_{39}Cd_3N_3O_{15}$
Formula weight	1126.93
Temperature / K	150(2)
Crystal system	orthorhombic
Space group	$P2_12_12$
a / Å	9.5668(3)
b / Å	23.3692(6)
c / Å	17.0992(3)
Volume / Å^3	3822.85(16)
Z	4
ρ_{calc} / g cm^{-3}	1.958
μ / mm^{-1}	13.928
F(000)	2232.0
Crystal size / mm^3	0.08 × 0.057 × 0.043
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection / °	5.168 to 144.956
Index ranges	-9 ≤ h ≤ 11, -28 ≤ k ≤ 27, -20 ≤ l ≤ 14
Reflections collected	19674
Independent reflections	7285 [R_{int} = 0.1205, R_{sigma} = 0.1091]
Data/restraints/parameters	7285/0/543
Goodness-of-fit on F^2	0.961
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1182
Final R indexes [all data]	R_1 = 0.0724, wR_2 = 0.1266
Largest diff. peak/hole / e Å^{-3}	1.83/-0.99
Flack parameter	-0.026(15)
CCDC Number	2239997

Table 2.8 Selected Bond Lengths for **3DL-MOF-4.**

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Cd1	O1[1]	2.287(10)	N3	C39	1.45(2)
Cd1	O1	2.287(10)	C1	C2	1.506(18)
Cd1	O3[1]	2.320(10)	C2	C3	1.568(18)
Cd1	O3	2.320(10)	C2	C5	1.57(2)
Cd1	O5	2.286(10)	C2	C6	1.540(19)
Cd1	O5[1]	2.286(10)	C3	C4	1.56(2)
Cd2	O2	2.260(9)	C3	C7	1.57(2)
Cd2	O3	2.439(10)	C4	C5	1.591(19)
Cd2	O4	2.298(10)	C4	C8	1.54(2)
Cd2	O6	2.347(11)	C5	C9	1.54(2)
Cd2	O8[2]	2.221(12)	C6	C7	1.566(19)
Cd2	O10[2]	2.263(9)	C6	C9	1.54(2)
Cd3	O7	2.253(10)	C7	C8	1.54(2)
Cd3	O9	2.216(11)	C8	C9	1.578(19)
Cd3	O11	2.235(11)	C8	C10	1.517(19)
Cd3	O13	2.289(10)	C11	C12	1.470(19)
Cd3	O14[3]	2.298(10)	C12	C13	1.54(2)
Cd4	O12	2.193(10)	C12	C14	1.585(19)
Cd4	O12[4]	2.193(10)	C12	C15	1.570(19)
Cd4	O14[3]	2.428(10)	C13	C14[6]	1.56(2)
Cd4	O14[5]	2.428(10)	C13	C15[6]	1.54(2)
Cd4	O15[3]	2.295(11)	C14	C14[6]	1.59(3)
Cd4	O15[5]	2.295(11)	C15	C15[6]	1.58(2)
O1	C1	1.265(18)	C22	C23	1.53(2)
O2	C1	1.243(16)	C23	C24	1.56(2)
O3	C11	1.256(17)	C23	C25[1]	1.56(2)
O4	C11	1.276(17)	C23	C26	1.56(2)
O5	C16	1.220(19)	C24	C24[1]	1.58(3)
O6	C19	1.21(2)	C24	C25	1.55(2)
O7	C10	1.27(2)	C25	C26	1.57(2)
O8	C10	1.25(2)	C26	C26[1]	1.55(3)
O9	C27	1.227(19)	C27	C28	1.515(19)
O10	C27	1.288(18)	C28	C29	1.56(2)
O11	C22	1.254(18)	C28	C31	1.59(2)
O12	C22	1.263(17)	C28	C32	1.56(2)
O13	C37	1.241(19)	C29	C30	1.590(19)
O14	C36	1.294(18)	C29	C33	1.56(2)

Table 2.8 Selected Bond Lengths for **3DL-MOF-4.**

Atom	Atom	Length / Å	Atom	Atom	Length / Å
O15	C36	1.257(19)	C30	C31	1.54(3)
N1	C16	1.302(19)	C30	C34	1.54(2)
N1	C17	1.46(2)	C31	C35	1.53(2)
N1	C18	1.47(2)	C32	C33	1.58(2)
N2	C19	1.33(2)	C32	C35	1.579(19)
N2	C20	1.47(2)	C33	C34	1.597(19)
N2	C21	1.44(2)	C34	C35	1.53(2)
N3	C37	1.310(19)	C34	C36	1.49(2)
N3	C38	1.47(2)			

Symmetry codes: [1]1-X,1-Y,+Z; [2]-1/2+X,1/2-Y,1-Z; [3]1/2+X,1/2-Y,-Z; [4]2-X,1-Y,+Z; [5]3/2-X,1/2+Y,-Z; [6]-X,1-Y,+Z

Table 2.9 Selected bond angles for **3DL-MOF-4.**

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
O1	Cd1	O1[1]	90.1(5)	C9	C5	C2	90.0(12)
O1[1]	Cd1	O3[1]	84.7(4)	C9	C5	C4	90.4(11)
O1[1]	Cd1	O3	92.7(4)	C2	C6	C7	90.7(10)
O1	Cd1	O3[1]	92.7(4)	C2	C6	C9	90.8(12)
O1	Cd1	O3	84.7(4)	C9	C6	C7	90.8(10)
O3	Cd1	O3[1]	176.3(5)	C6	C7	C3	89.3(10)
O5[1]	Cd1	O1[1]	97.7(4)	C8	C7	C3	88.0(11)
O5[1]	Cd1	O1	170.8(4)	C8	C7	C6	89.6(11)
O5	Cd1	O1	97.7(4)	C4	C8	C9	90.6(11)
O5	Cd1	O1[1]	170.8(4)	C7	C8	C4	92.9(12)
O5	Cd1	O3	92.7(4)	C7	C8	C9	90.4(11)
O5[1]	Cd1	O3[1]	92.7(4)	C10	C8	C4	126.8(13)
O5[1]	Cd1	O3	90.2(4)	C10	C8	C7	126.1(13)
O5	Cd1	O3[1]	90.2(4)	C10	C8	C9	119.8(13)
O5[1]	Cd1	O5	74.9(5)	C5	C9	C6	90.1(11)
O2	Cd2	O3	81.9(3)	C5	C9	C8	89.8(11)
O2	Cd2	O4	135.4(4)	C6	C9	C8	89.1(12)
O2	Cd2	O6	86.1(4)	O7	C10	C8	119.8(14)
O2	Cd2	O10[2]	86.8(4)	O8	C10	O7	123.6(14)
O4	Cd2	O3	54.7(3)	O8	C10	C8	116.6(14)
O4	Cd2	O6	97.5(4)	O3	C11	O4	119.0(13)
O6	Cd2	O3	83.5(4)	O3	C11	C12	123.0(13)
O8[2]	Cd2	O2	135.6(4)	O4	C11	C12	117.8(13)
O8[2]	Cd2	O3	136.9(4)	C11	C12	C13	128.1(13)
O8[2]	Cd2	O4	88.4(4)	C11	C12	C14	125.7(12)
O8[2]	Cd2	O6	79.8(4)	C11	C12	C15	121.2(12)
O8[2]	Cd2	O10[2]	96.3(4)	C13	C12	C14	91.5(12)
O10[2]	Cd2	O3	108.3(3)	C13	C12	C15	90.6(12)

Table 2.9 Selected bond angles for **3DL-MOF-4.**

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
O10[2]	Cd2	O4	96.7(4)	C15	C12	C14	88.6(10)
O10[2]	Cd2	O6	165.2(4)	C12	C13	C14[9]	90.6(12)
O7	Cd3	O13	82.7(4)	C12	C13	C15[9]	91.0(12)
O7	Cd3	O14[3]	145.0(4)	C15[9]	C13	C14[9]	90.6(11)
O9	Cd3	O7	119.4(4)	C12	C14	C14[9]	87.7(11)
O9	Cd3	O11	88.7(4)	C13[9]	C14	C12	89.7(10)
O9	Cd3	O13	119.8(4)	C13[9]	C14	C14[9]	90.2(11)
O9	Cd3	O14[3]	95.6(4)	C12	C15	C15[9]	88.3(11)
O11	Cd3	O7	91.6(4)	C13[9]	C15	C12	91.1(10)
O11	Cd3	O13	150.0(4)	C13[9]	C15	C15[9]	90.1(11)
O11	Cd3	O14[3]	87.5(4)	O5	C16	N1	124.7(14)
O13	Cd3	O14[3]	80.9(4)	O6	C19	N2	125.7(17)
O12[4]	Cd4	O12	92.5(5)	O11	C22	O12	125.2(14)
O12[4]	Cd4	O14[5]	84.2(4)	O11	C22	C23	115.6(13)
O12[4]	Cd4	O14[3]	134.2(4)	O12	C22	C23	119.1(12)
O12	Cd4	O14[3]	84.2(4)	C22	C23	C24	123.4(12)
O12	Cd4	O14[5]	134.2(4)	C22	C23	C25[1]	125.9(14)
O12	Cd4	O15[3]	132.4(4)	C22	C23	C26	124.9(12)
O12	Cd4	O15[5]	98.0(4)	C25[1]	C23	C24	91.3(12)
O12[4]	Cd4	O15[5]	132.4(4)	C25[1]	C23	C26	91.6(12)
O12[4]	Cd4	O15[3]	98.0(4)	C26	C23	C24	89.3(11)
O14[3]	Cd4	O14[5]	128.9(4)	C23	C24	C24[1]	88.3(12)
O15[5]	Cd4	O14[3]	93.1(4)	C25	C24	C23	91.1(10)
O15[3]	Cd4	O14[3]	55.9(4)	C25	C24	C24[1]	90.7(12)
O15[5]	Cd4	O14[5]	55.9(4)	C23[1]	C25	C26	88.3(12)
O15[3]	Cd4	O14[5]	93.1(4)	C24	C25	C23[1]	89.6(12)
O15[5]	Cd4	O15[3]	107.8(6)	C24	C25	C26	89.2(11)
C1	O1	Cd1	126.7(8)	C23	C26	C25	90.4(10)
C1	O2	Cd2	115.8(9)	C26[1]	C26	C23	88.8(12)
Cd1	O3	Cd2	125.0(4)	C26[1]	C26	C25	91.3(13)
C11	O3	Cd1	145.1(9)	O9	C27	O10	124.1(13)
C11	O3	Cd2	89.7(8)	O9	C27	C28	117.6(14)
C11	O4	Cd2	95.7(8)	O10	C27	C28	118.3(13)
C16	O5	Cd1	134.9(9)	C27	C28	C29	123.7(13)
C19	O6	Cd2	129.3(11)	C27	C28	C31	120.8(13)
C10	O7	Cd3	115.5(9)	C27	C28	C32	131.0(13)
C10	O8	Cd2[6]	118.6(11)	C29	C28	C31	88.7(11)
C27	O9	Cd3	108.1(9)	C29	C28	C32	91.0(11)
C27	O10	Cd2[6]	120.0(9)	C32	C28	C31	89.8(11)
C22	O11	Cd3	117.1(10)	C28	C29	C30	90.7(11)
C22	O12	Cd4	119.3(8)	C33	C29	C28	89.7(12)
C37	O13	Cd3	118.1(10)	C33	C29	C30	89.8(10)
Cd3[7]	O14	Cd4[8]	112.4(4)	C31	C30	C29	89.3(11)
C36	O14	Cd3[7]	130.3(9)	C34	C30	C29	90.4(12)

Table 2.9 Selected bond angles for **3DL-MOF-4.**

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
C36	O14	Cd4[8]	88.3(9)	C34	C30	C31	89.1(13)
C36	O15	Cd4[8]	95.3(10)	C30	C31	C28	91.3(13)
C16	N1	C17	122.2(14)	C35	C31	C28	89.7(12)
C16	N1	C18	121.9(14)	C35	C31	C30	90.6(13)
C17	N1	C18	115.9(13)	C28	C32	C33	88.8(11)
C19	N2	C20	121.5(15)	C28	C32	C35	89.1(11)
C19	N2	C21	120.9(16)	C33	C32	C35	88.8(10)
C21	N2	C20	117.6(14)	C29	C33	C32	90.5(11)
C37	N3	C38	121.9(14)	C29	C33	C34	89.5(11)
C37	N3	C39	123.1(13)	C32	C33	C34	89.6(11)
C39	N3	C38	115.0(13)	C30	C34	C33	90.2(12)
O1	C1	C2	117.0(12)	C35	C34	C30	90.6(13)
O2	C1	O1	125.7(12)	C35	C34	C33	89.7(11)
O2	C1	C2	117.2(13)	C36	C34	C30	129.1(14)
C1	C2	C3	125.3(12)	C36	C34	C33	122.0(13)
C1	C2	C5	127.6(12)	C36	C34	C35	124.2(14)
C1	C2	C6	123.9(13)	C31	C35	C32	91.4(12)
C5	C2	C3	89.2(11)	C31	C35	C34	89.6(13)
C6	C2	C3	90.3(10)	C34	C35	C32	91.9(11)
C6	C2	C5	89.0(11)	O14	C36	Cd4[8]	63.3(7)
C2	C3	C7	89.6(11)	O14	C36	C34	118.4(14)
C4	C3	C2	91.6(11)	O15	C36	Cd4[8]	57.3(8)
C4	C3	C7	91.0(11)	O15	C36	O14	120.5(14)
C3	C4	C5	88.6(10)	O15	C36	C34	120.9(14)
C8	C4	C3	88.2(12)	C34	C36	Cd4[8]	174.8(10)
C8	C4	C5	89.1(11)	O13	C37	N3	122.7(14)
C2	C5	C4	90.6(11)				

Symmetry codes: [1]1-X,1-Y,+Z; [2]-1/2+X,1/2-Y,1-Z; [3]1/2+X,1/2-Y,-Z; [4]2-X,1-Y,+Z; [5]3/2-X,1/2+Y,-Z; [6]1/2+X,1/2-Y,1-Z; [7]-1/2+X,1/2-Y,-Z; [8]3/2-X,-1/2+Y,-Z; [9]-X,1-Y,+Z

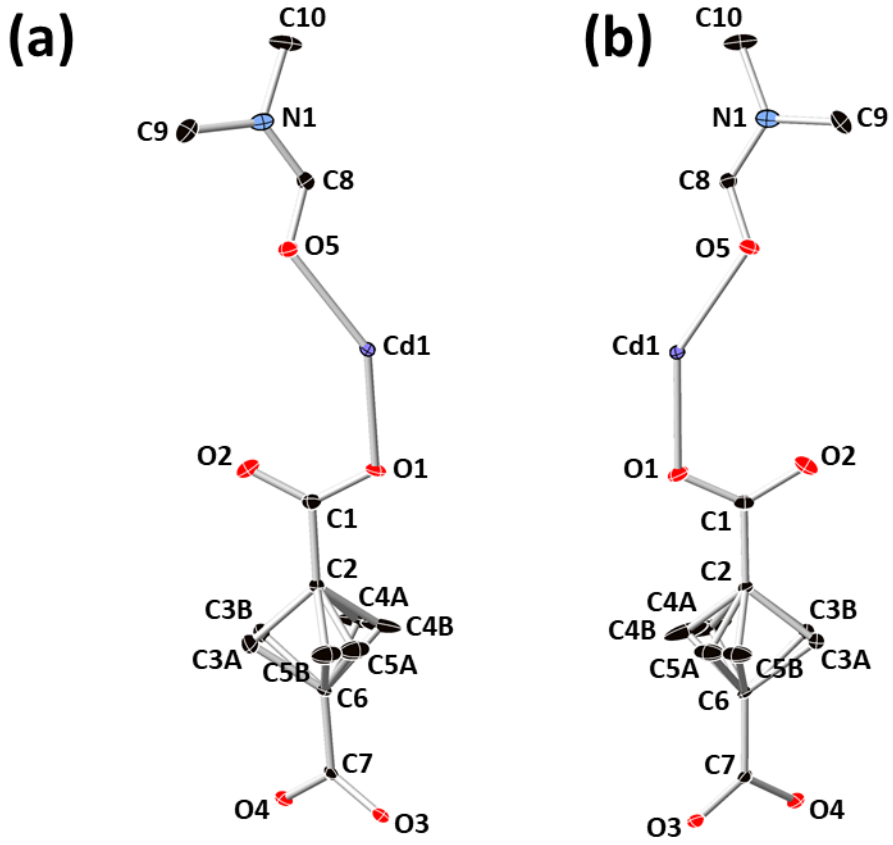

Figure S2.1 Asymmetric units of (a) **3DL-MOF-3α** and (b) **3DL-MOF-3β**. Displacement ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Atom colours: C (black), N (blue), O (red), Cd (lavender).

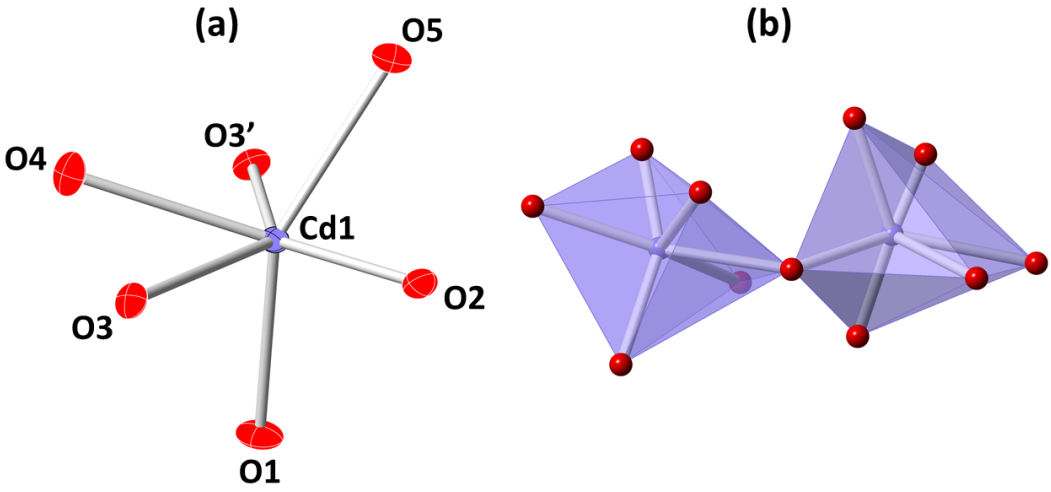

Figure S2.2 (a) Local coordination environment of Cd in **3DL-MOF-3** with displacement ellipsoids set at 50% probability. (b) Structural motif containing two corner-sharing distorted trigonal prismatic Cd centres. Atom colours: O (red), Cd (lavender).

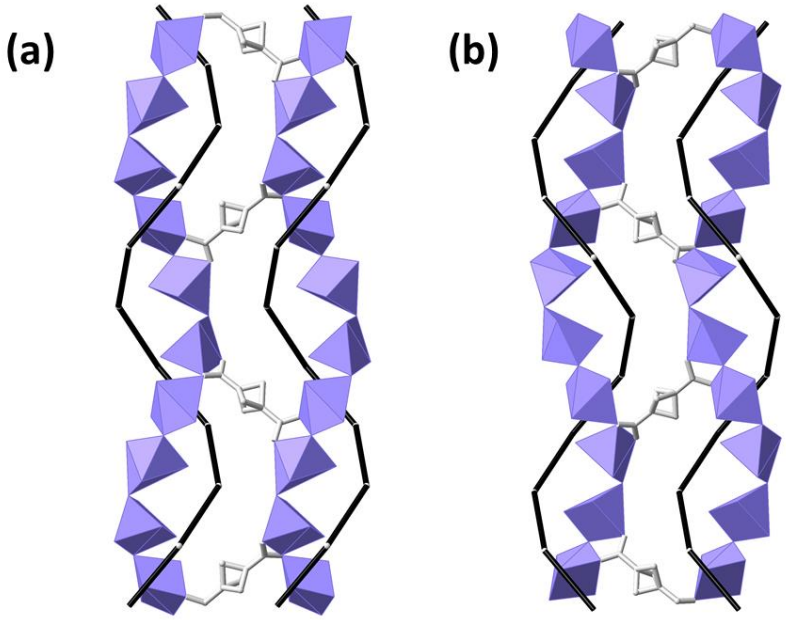

Figure S2.3 Helical twists in simplified $[Cd]_n$ chains with bridging bicyclo[1.1.1]pentane-1,3-dicarboxylic acid units: (a) **3DL-MOF-3α** (clockwise; **P**), (b) **3DL-MOF-3β** (anti-clockwise; **M**).

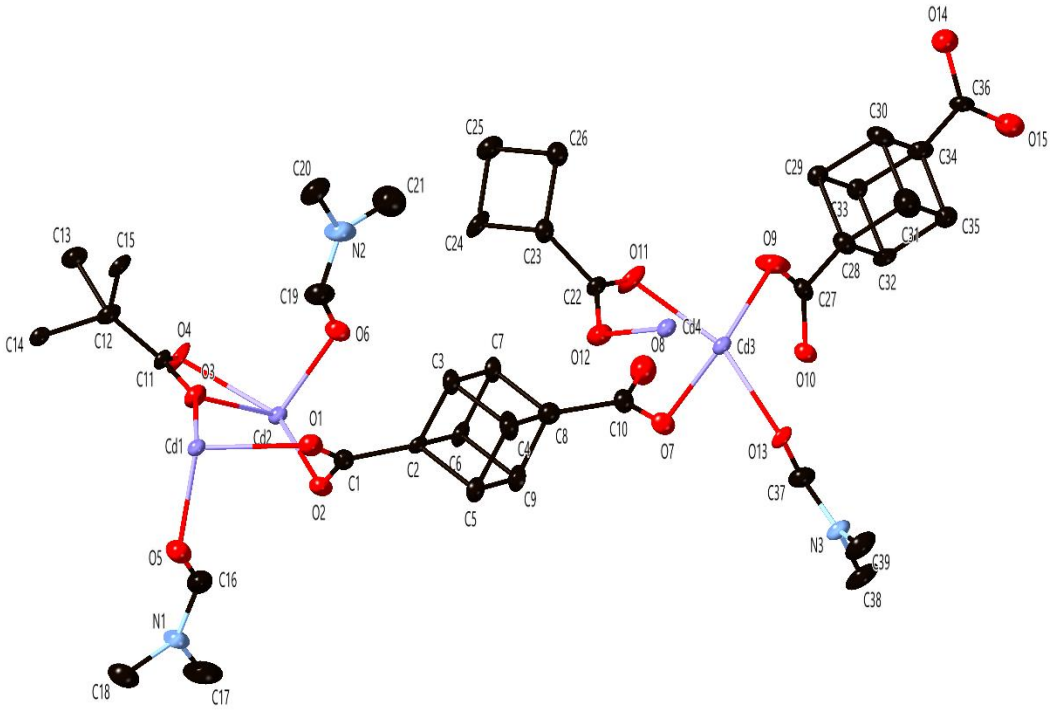

Figure S2.4 Asymmetric unit of **3DL-MOF-4** at 100 K with displacement ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Atom colours: C (black), N (blue), O (red), Cd (lavender).

S3 – Powder X-Ray Diffraction

Variable temperature powder X-ray diffraction (PXRD) patterns were measured on a STOE STADI P diffractometer operating in Debye-Scherrer geometry with monochromated Mo-Kα (λ = 0.70930 Å) radiation and three Mythen 1K strip detectors in stationary mode, covering a 2θ range of 0–55°. Temperature control was achieved using an Oxford Cryostreams nitrogen cryostream system. Single crystals of **3DL-MOF-3** or **3DL-MOF-4** were first washed with DMF to remove any residual ligand or metal salts and then ground to produce a bulk polycrystalline sample before being loaded as a solid suspension into a 0.5 mm glass capillary. Centrifugation was applied to concentrate the powder before the capillary was flame-sealed to prevent solvent loss.

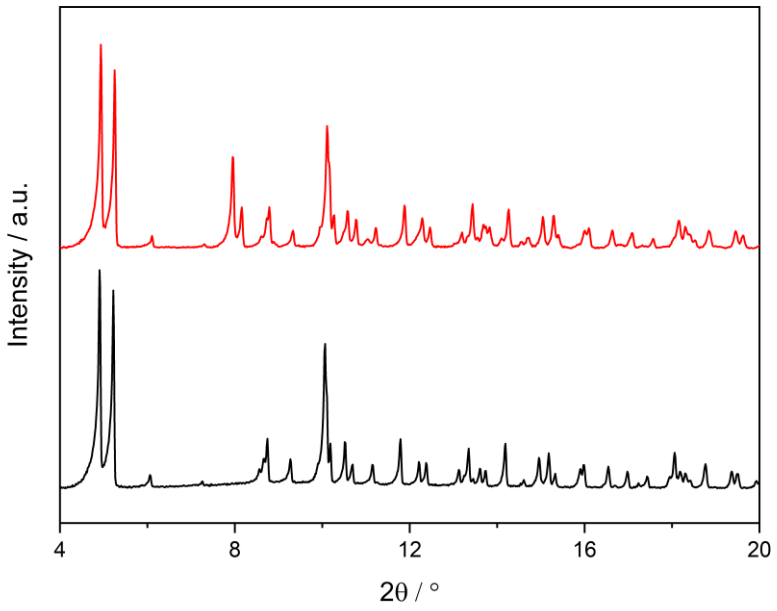

Figure S3.1 Comparison of experimental PXRD patterns of **3DL-MOF-3** at room temperature (black) and 100 K (red). The same impurity peak at 2θ ≈ 8° in the 100 K pattern is due to frozen *N*,*N*-dimethylformamide.

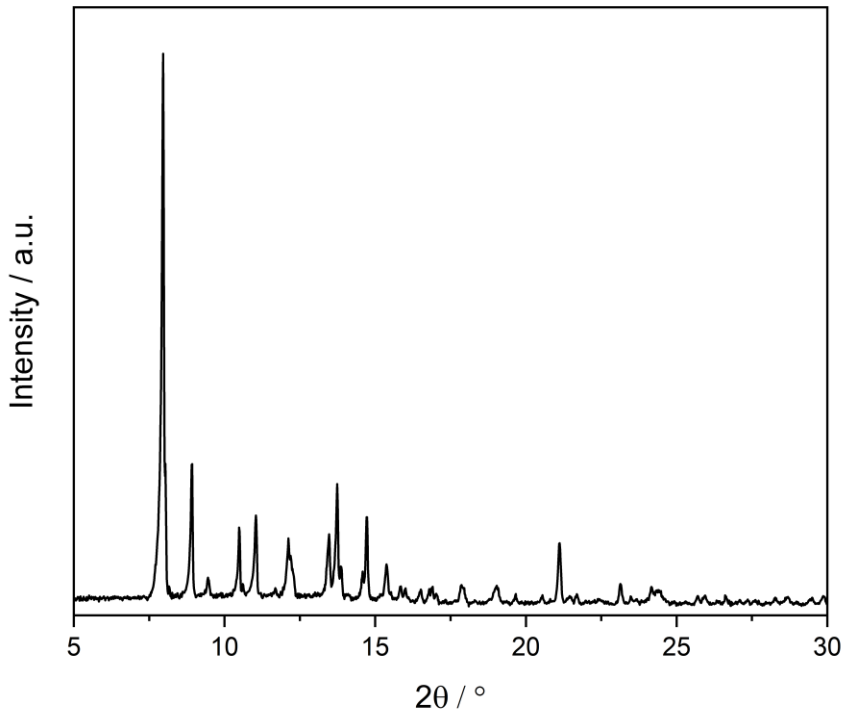

Figure S3.2 Experimental PXRD pattern of slow-cooled frozen *N*,*N*-dimethylformamide at 100 K.

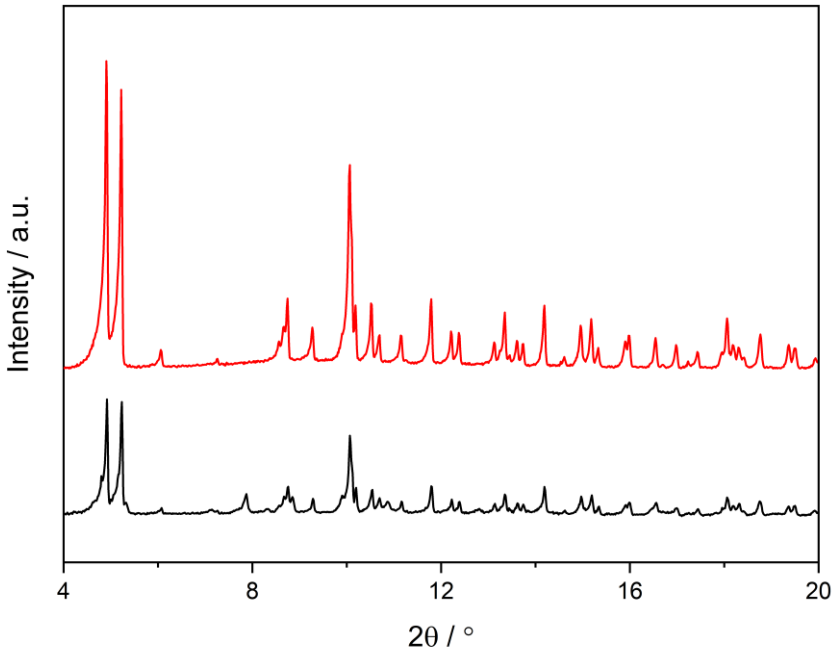

Figure S3.3 Experimental PXRD patterns of air-dried (black) and solvated (red) **3DL-MOF-3** measured at room temperature. For the desorbed sample, the crystallisation mother liquor was first exchanged with dichloromethane to remove all residual *N*,*N*-dimethylformamide before the sample was allowed to air-dry for six hours.

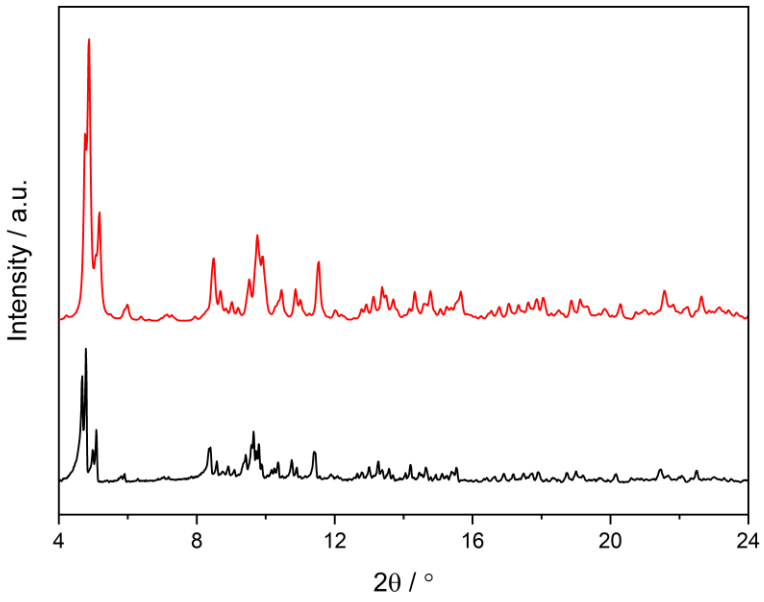

Figure S3.4 Experimental (black) and predicted (red) PXRD patterns of **3DL-MOF-4**.

S4 – Raman Spectroscopy

Raman scattering spectra were acquired using a Renishaw InVia Qontor confocal spectrometer. Samples were excited using a Renishaw plc RL785 red diode laser outputting an excitation wavelength of 785 nm (25% laser power, 40–50 mW) and were referenced internally with respect to silicon at 520.5 ± 0.1 cm^{-1}. Single crystalline samples of **3DL-MOF-3** and **3DL-MOF-4** were loaded onto a Linkam FTIR 600 cryostage fitted with a glass window. A Leica 20× objective was used to focus the laser beam perpendicularly onto the sample. Spectra were recorded on a Renishaw Centrus 2957N7 CCD detector using 10 second exposure times averaged over 10 accumulations. Data were processed (WiRE 5.0, Renishaw) with baseline subtractions and cosmic ray removal as required.

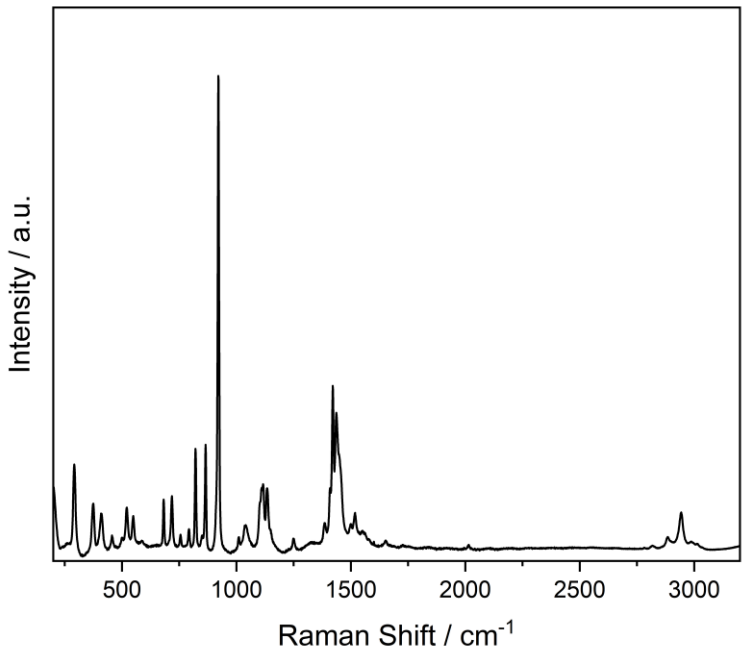

Figure S4.1 Raman spectrum of **3DL-MOF-3** between 200–3200 cm^{-1}.

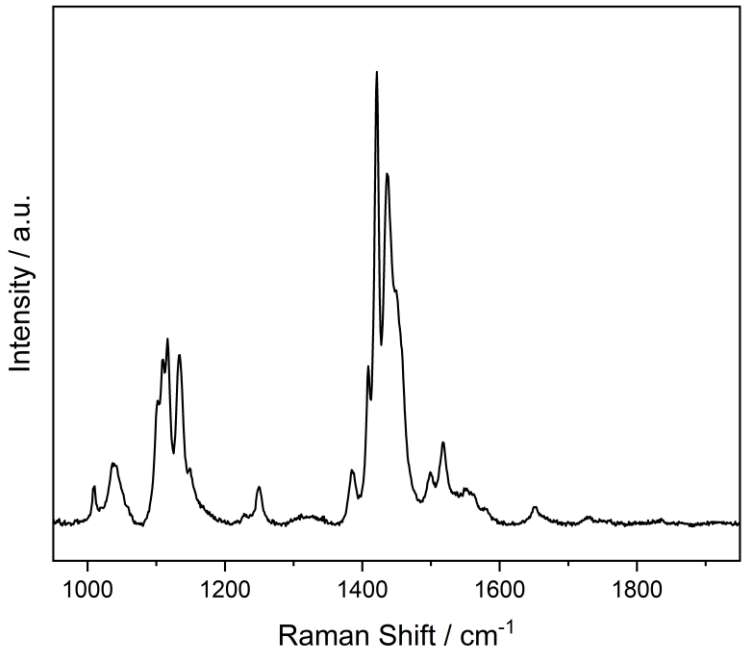

Figure S4.2 Expanded Raman spectrum of **3DL-MOF-3** between 950–1950 cm^{-1}.

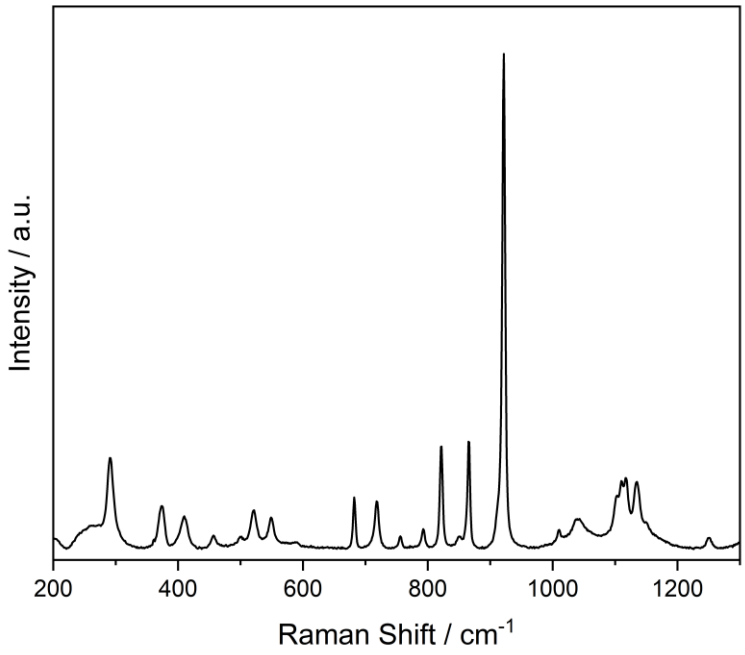

Figure S4.3 Expanded Raman spectrum of **3DL-MOF-3** between 200–1300 cm^{-1}.

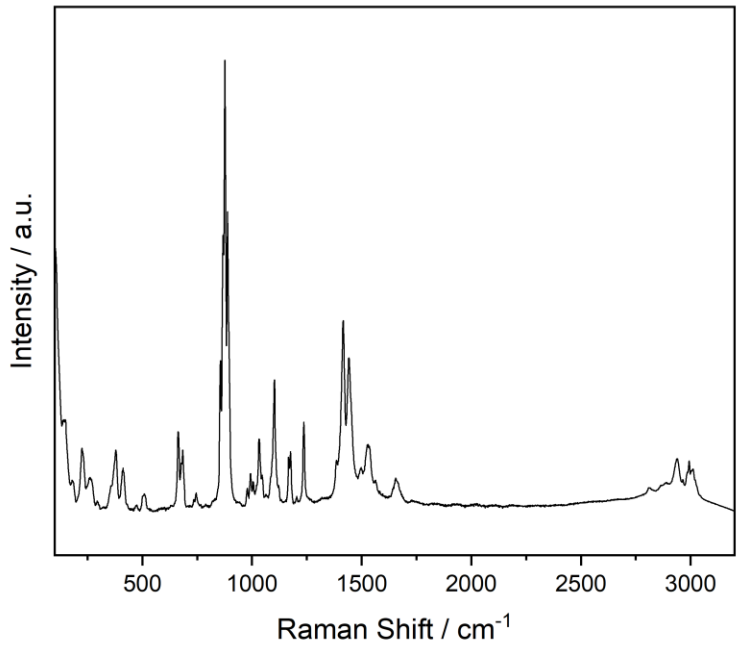

Figure S4.4 Raman spectrum of **3DL-MOF-4** between 200–3200 cm^{-1}.

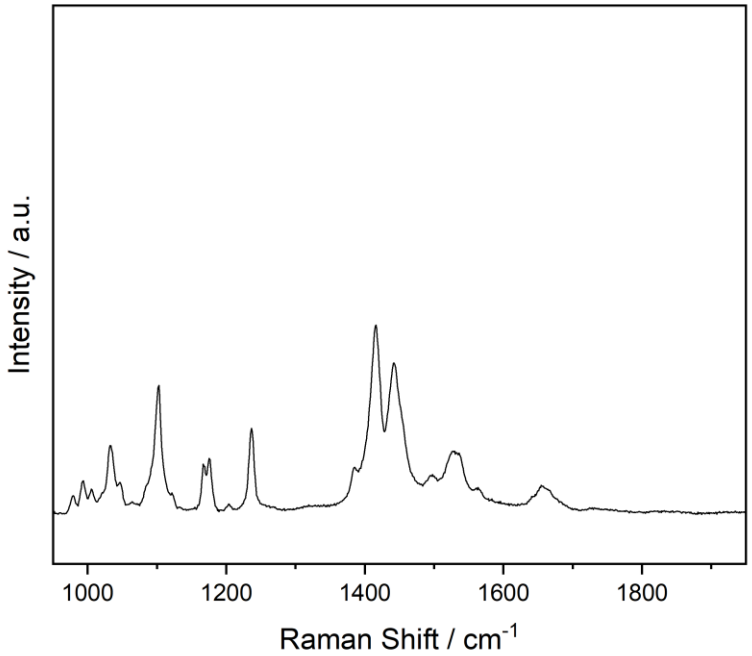

Figure S4.5 Expanded Raman spectrum of **3DL-MOF-4** between 950–1950 cm^{-1}.

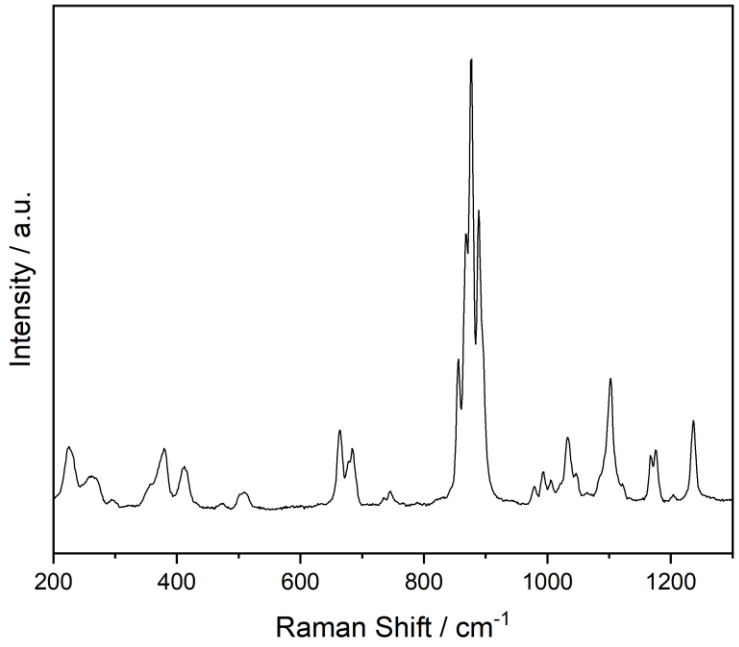

Figure S4.6 Expanded Raman spectrum of **3DL-MOF-4** between 200–1300 cm^{-1}.

S5 – Thermogravimetric Analysis

TGA data were acquired from a TA Instruments Discovery TGA Thermogravimetric Analyser. Samples (ca. 5–20 mg) were first loaded onto a pre-tared Pt pan sample holder and then isothermally heated at 30 °C for 10 minutes and under a constant stream of dry nitrogen with a flow rate of 0.1 L min^{-1}. Ramping steps were conducted to a final temperature of 650 °C and at a rate of 5 °C min^{-1}.

To activate the sample, the bulk crystalline **3DL-MOF-3** or **3DL-MOF-4** was first washed in neat *N*,*N*-dimethylformamide solvent to remove any residual unreacted starting material, and was then washed in anhydrous dichloromethane to remove residual *N*,*N*-dimethylformamide before being air-dried for several hours. Following this, the crystals were heated to 160 °C while under vacuum for 24 hours to completely desorb the coordinated DMF solvent.

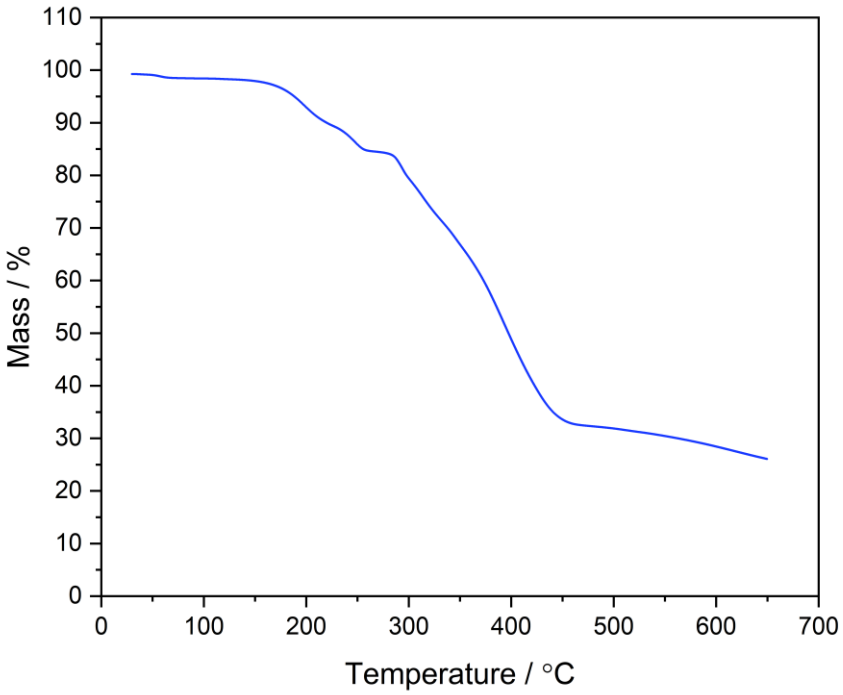

Figure S5.1 TGA plot of **3DL-MOF-3** over the temperature range 30–650 °C.

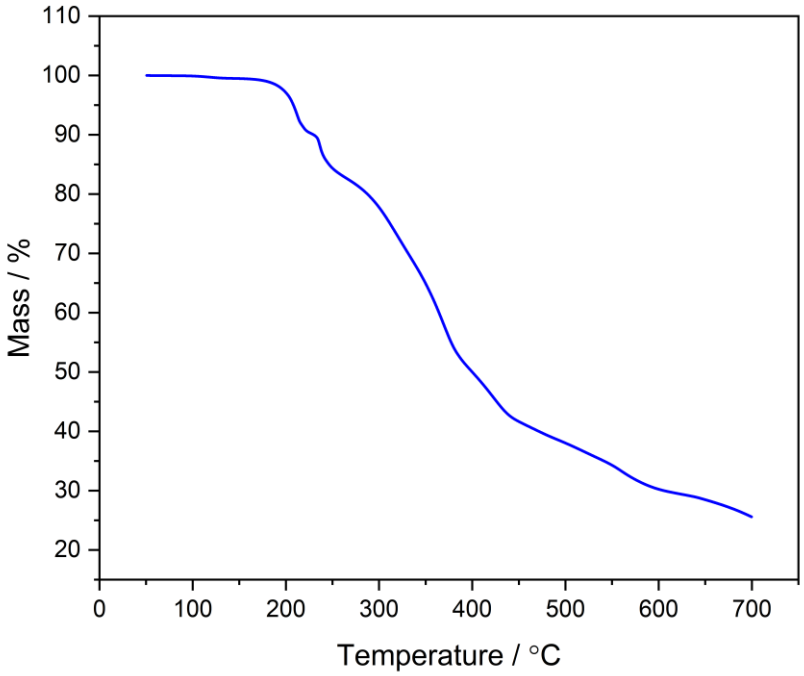

Figure S5.2 TGA plot of **3DL-MOF-4** over the temperature range 50–700 °C.

S6 – Optical Microscopy

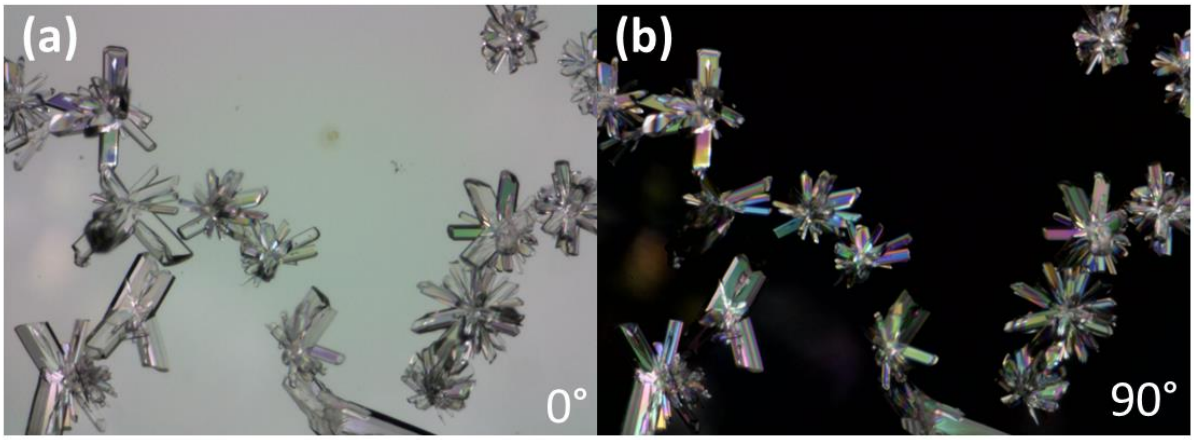

Figure S6.1 Polarised light microscopy view of crystals of **3DL-MOF-3** under (a) 0° and (b) 90° cross-polarised light.

S7 – Elemental Analysis

CHN elemental microanalysis was performed by Dr Rémi Rouquette using a Model PE2400 CHNS/O Elemental Analyser at the Department of Chemistry and Biomolecular Sciences, Macquarie University, New South Wales 2109, Australia. Samples (ca. 2–5 mg) were dried in vacuo for 24 h prior to analysis. Duplicates of samples were obtained and averaged.