Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

CFA-1: The first chiral metal-organic framework containing Kuratowski-type secondary building units

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1. Crystallographic data

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for CFA-1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

(Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x+1,z #2 -y+1, x-y+1,z #3 -x,-x+y,-z+1 #4 -x,-x+y,-z+2)

Atom	x	y	z	U(eq)
Zn(1)	3333	6667	7355(1)	15(1)
Zn(2)	3333	6667	9220(1)	21(1)
Zn(3)	1271(1)	6313(1)	6722(1)	18(1)
O(1A)	555(4)	6221(4)	5675(4)	57(2)
O(2A)	65(4)	6037(7)	6723(4)	73(2)
O(1B)	454(4)	6567(5)	6177(5)	55(2)
O(2B)	-168(4)	5335(5)	6725(4)	46(2)
C(1)	-123(5)	5968(5)	6190(5)	83(2)
C(2)	-1013(4)	5755(6)	5924(5)	113(3)
O(3)	3057(7)	7327(8)	10168(6)	58(3)
O(4)	2928(8)	6602(12)	10167(6)	64(3)
C(3)	3333	6667	10519(8)	142(8)
C(4)	3333	6667	11273(6)	164(8)
N(1)	2557(2)	4935(2)	6471(1)	19(1)
N(2)	2426(2)	5568(2)	6697(1)	19(1)
N(3)	1690(2)	5479(2)	6433(2)	20(1)
C(5)	1327(2)	4765(2)	6025(2)	21(1)
C(6)	1883(2)	4414(2)	6046(2)	22(1)
C(7)	1687(2)	3660(2)	5658(2)	29(1)
C(8)	945(2)	3303(2)	5267(2)	33(1)
C(9)	385(2)	3669(2)	5233(2)	27(1)
C(10)	574(2)	4392(2)	5614(2)	25(1)
N(4)	1474(2)	6327(2)	7767(1)	20(1)
N(5)	2240(2)	6476(2)	8009(1)	20(1)
N(6)	2233(2)	6416(2)	8696(1)	20(1)
C(11)	947(2)	6161(2)	8328(2)	23(1)
C(12)	1427(2)	6220(2)	8921(2)	21(1)
C(13)	1071(2)	6068(2)	9596(2)	26(1)
C(14)	219(2)	5860(2)	9652(2)	29(1)
C(15)	-267(2)	5815(2)	9047(1)	32(1)
C(16)	74(2)	5961(2)	8389(1)	30(1)

Table S2. Bond lengths for CFA-1.

Bonds	Bond lengths (Å)	Bonds	Bond lengths (Å)
Zn(1)-N(5)	2.191(3)	O(4)-C(3)	0.952(12)
Zn(1)-N(5)#1	2.191(3)	O(4)-O(4)#1	1.16(2)
Zn(1)-N(5)#2	2.191(3)	O(4)-O(4)#2	1.16(2)

Zn(1)-N(2)#1	2.203(3)	O(4)-O(3)#2	1.38(2)
Zn(1)-N(2)	2.203(3)	C(3)-O(4)#1	0.952(13)
Zn(1)-N(2)#2	2.203(3)	C(3)-O(4)#2	0.952(12)
Zn(2)-O(4)	1.936(10)	C(3)-C(4)	1.447(17)
Zn(2)-O(4)#1	1.936(10)	C(3)-O(3)#2	1.627(13)
Zn(2)-O(4)#2	1.936(10)	C(3)-O(3)#1	1.627(12)
Zn(2)-N(6)	2.038(3)	N(1)-N(2)	1.328(4)
Zn(2)-N(6)#1	2.038(3)	N(1)-C(6)	1.359(4)
Zn(2)-N(6)#2	2.038(3)	N(1)-Zn(3)#2	2.043(3)
Zn(2)-O(3)	2.345(11)	N(2)-N(3)	1.335(4)
Zn(2)-O(3)#1	2.345(11)	N(3)-C(5)	1.348(4)
Zn(2)-O(3)#2	2.345(11)	C(5)-C(10)	1.401(4)
Zn(2)-C(3)	2.493(15)	C(5)-C(6)	1.406(4)
Zn(3)-O(2A)	1.943(6)	C(6)-C(7)	1.414(5)
Zn(3)-O(1B)	2.013(6)	C(7)-C(8)	1.366(5)
Zn(3)-N(4)	2.037(3)	C(8)-C(9)	1.436(5)
Zn(3)-N(3)	2.038(3)	C(9)-C(10)	1.366(5)
Zn(3)-N(1)#1	2.043(3)	C(9)-C(9)#3	1.482(6)
Zn(3)-O(2B)	2.259(7)	N(4)-N(5)	1.332(4)
Zn(3)-O(1A)	2.339(7)	N(4)-C(11)	1.358(4)
Zn(3)-C(1)	2.455(6)	N(5)-N(6)	1.323(4)
O(1A)-C(1)	1.443(12)	N(6)-C(12)	1.363(4)
O(2A)-C(1)	1.065(10)	C(11)-C(12)	1.394(4)
O(1B)-C(1)	1.045(9)	C(11)-C(16)	1.413(4)
O(2B)-C(1)	1.496(12)	C(12)-C(13)	1.407(4)
C(1)-C(2)	1.518(8)	C(13)-C(14)	1.370(5)
O(3)-O(4)	1.19(2)	C(14)-C(15)	1.423(4)
O(3)-O(4)#1	1.38(2)	C(14)-C(14)#4	1.497(6)
O(3)-C(3)	1.627(12)	C(15)-C(16)	13.684

Table S3. Angles for CFA-1.

Atoms	angle (°)	Atoms	angle (°)	Atoms	angle (°)
N(5)-Zn(1)-N(5)#1	90.49(10)	O(2A)-Zn(3)-N(1)#1	130.2(3)	O(4)#1-C(3)-C(4)	135.3(8)
N(5)-Zn(1)-N(5)#2	90.49(10)	O(1B)-Zn(3)-N(1)#1	96.0(2)	O(4)#2-C(3)-C(4)	135.3(8)
N(5)#1-Zn(1)-N(5)#2	90.49(10)	N(4)-Zn(3)-N(1)#1	98.23(10)	O(4)-C(3)-O(3)	46.3(11)
N(5)-Zn(1)-N(2)#1	89.56(9)	N(3)-Zn(3)-N(1)#1	97.39(10)	O(4)#1-C(3)-O(3)	57.8(12)
N(5)#1-Zn(1)-N(2)#1	89.59(10)	O(2A)-Zn(3)-O(2B)	29.1(3)	O(4)#2-C(3)-O(3)	109.8(13)
N(5)#2-Zn(1)-N(2)#1	179.90(10)	O(1B)-Zn(3)-O(2B)	60.6(3)	C(4)-C(3)-O(3)	114.5(6)
N(5)-Zn(1)-N(2)	89.59(10)	N(4)-Zn(3)-O(2B)	97.5(2)	O(4)-C(3)-O(3)#2	57.8(12)
N(5)#1-Zn(1)-N(2)	179.90(14)	N(3)-Zn(3)-O(2B)	97.2(2)	O(4)#1-C(3)-O(3)#2	109.8(13)
N(5)#2-Zn(1)-N(2)	89.56(9)	N(1)#1-Zn(3)-O(2B)	156.6(2)	O(4)#2-C(3)-O(3)#2	46.3(12)
N(2)#1-Zn(1)-N(2)	90.36(10)	O(2A)-Zn(3)-O(1A)	59.5(3)	C(4)-C(3)-O(3)#2	114.5(6)
N(5)-Zn(1)-N(2)#2	179.90(10)	O(1B)-Zn(3)-O(1A)	30.9(3)	O(3)-C(3)-O(3)#2	104.0(7)
N(5)#1-Zn(1)-N(2)#2	89.56(9)	N(4)-Zn(3)-O(1A)	158.96(19)	O(4)-C(3)-O(3)#1	109.8(13)
N(5)#2-Zn(1)-N(2)#2	89.59(10)	N(3)-Zn(3)-O(1A)	95.71(18)	O(4)#1-C(3)-O(3)#1	46.3(12)
N(2)#1-Zn(1)-N(2)#2	90.36(10)	N(1)#1-Zn(3)-O(1A)	95.07(17)	O(4)#2-C(3)-O(3)#1	57.8(12)

N(2)-Zn(1)-N(2)#2	90.36(10)
O(4)-Zn(2)-O(4)#1	34.9(7)
O(4)-Zn(2)-O(4)#2	34.9(6)
O(4)#1-Zn(2)-O(4)#2	34.9(6)
O(4)-Zn(2)-N(6)	99.4(4)
O(4)#1-Zn(2)-N(6)	129.2(5)
O(4)#2-Zn(2)-N(6)	126.5(5)
O(4)-Zn(2)-N(6)#1	126.5(5)
O(4)#1-Zn(2)-N(6)#1	99.4(4)
O(4)#2-Zn(2)-N(6)#1	129.2(5)
N(6)-Zn(2)-N(6)#1	97.71(9)
O(4)-Zn(2)-N(6)#2	129.2(5)
O(4)#1-Zn(2)-N(6)#2	126.5(5)
O(4)#2-Zn(2)-N(6)#2	99.4(4)
N(6)-Zn(2)-N(6)#2	97.71(9)
N(6)#1-Zn(2)-N(6)#2	97.71(9)
O(4)-Zn(2)-O(3)	30.4(6)
O(4)#1-Zn(2)-O(3)	36.0(6)
O(4)#2-Zn(2)-O(3)	59.3(5)
N(6)-Zn(2)-O(3)	94.3(3)
N(6)#1-Zn(2)-O(3)	98.3(3)
N(6)#2-Zn(2)-O(3)	158.5(3)
O(4)-Zn(2)-O(3)#1	59.3(5)
O(4)#1-Zn(2)-O(3)#1	30.4(6)
O(4)#2-Zn(2)-O(3)#1	36.0(6)
N(6)-Zn(2)-O(3)#1	158.5(3)
N(6)#1-Zn(2)-O(3)#1	94.3(3)
N(6)#2-Zn(2)-O(3)#1	98.3(3)
O(3)-Zn(2)-O(3)#1	66.3(4)
O(4)-Zn(2)-O(3)#2	36.0(6)
O(4)#1-Zn(2)-O(3)#2	59.3(5)
O(4)#2-Zn(2)-O(3)#2	30.4(6)
N(6)-Zn(2)-O(3)#2	98.3(3)
N(6)#1-Zn(2)-O(3)#2	158.5(3)
N(6)#2-Zn(2)-O(3)#2	94.3(3)
O(3)-Zn(2)-O(3)#2	66.3(4)
O(3)#1-Zn(2)-O(3)#2	66.3(4)
O(4)-Zn(2)-C(3)	20.3(4)
O(4)#1-Zn(2)-C(3)	20.3(4)
O(4)#2-Zn(2)-C(3)	20.3(4)
N(6)-Zn(2)-C(3)	119.59(7)
N(6)#1-Zn(2)-C(3)	119.59(7)
N(6)#2-Zn(2)-C(3)	119.59(7)
O(3)-Zn(2)-C(3)	39.2(3)
O(3)#1-Zn(2)-C(3)	39.2(3)
O(3)#2-Zn(2)-C(3)	39.2(3)
O(2A)-Zn(3)-O(1B)	39.7(3)
O(2B)-Zn(3)-O(1A)	65.3(3)
O(2A)-Zn(3)-C(1)	24.7(3)
O(1B)-Zn(3)-C(1)	24.6(3)
N(4)-Zn(3)-C(1)	124.2(2)
N(3)-Zn(3)-C(1)	113.24(17)
N(1)#1-Zn(3)-C(1)	120.1(2)
O(2B)-Zn(3)-C(1)	36.7(3)
O(1A)-Zn(3)-C(1)	34.9(3)
C(1)-O(1A)-Zn(3)	76.9(4)
C(1)-O(2A)-Zn(3)	105.6(6)
C(1)-O(1B)-Zn(3)	102.1(6)
C(1)-O(2B)-Zn(3)	78.8(4)
O(1B)-C(1)-O(2A)	79.3(8)
O(1B)-C(1)-O(1A)	55.0(7)
O(2A)-C(1)-O(1A)	117.3(7)
O(1B)-C(1)-O(2B)	115.9(7)
O(2A)-C(1)-O(2B)	47.2(7)
O(1A)-C(1)-O(2B)	115.3(5)
O(1B)-C(1)-C(2)	127.9(8)
O(2A)-C(1)-C(2)	125.4(9)
O(1A)-C(1)-C(2)	116.7(8)
O(2B)-C(1)-C(2)	112.7(7)
O(1B)-C(1)-Zn(3)	53.3(5)
O(2A)-C(1)-Zn(3)	49.7(4)
O(1A)-C(1)-Zn(3)	68.1(4)
O(2B)-C(1)-Zn(3)	64.5(4)
C(2)-C(1)-Zn(3)	175.1(7)
O(4)-O(3)-O(4)#1	53.1(11)
O(4)-O(3)-C(3)	35.4(6)
O(4)#1-O(3)-C(3)	35.7(6)
O(4)-O(3)-Zn(2)	55.4(6)
O(4)#1-O(3)-Zn(2)	55.6(5)
C(3)-O(3)-Zn(2)	75.3(7)
C(3)-O(4)-O(4)#1	52.4(6)
C(3)-O(4)-O(4)#2	52.4(6)
O(4)#1-O(4)-O(4)#2	60.000(8)
C(3)-O(4)-O(3)	98.3(15)
O(4)#1-O(4)-O(3)	71.9(19)
O(4)#2-O(4)-O(3)	131.9(19)
C(3)-O(4)-O(3)#2	86.5(12)
O(4)#1-O(4)-O(3)#2	115.0(16)
O(4)#2-O(4)-O(3)#2	55.0(16)
O(3)-O(4)-O(3)#2	173.1(11)
C(3)-O(4)-Zn(2)	115.0(11)
O(4)#1-O(4)-Zn(2)	72.6(3)
O(4)#2-O(4)-Zn(2)	72.6(3)
O(3)-O(4)-Zn(2)	94.2(9)
C(4)-C(3)-O(3)#1	114.5(6)
O(3)-C(3)-O(3)#1	104.0(7)
O(3)#2-C(3)-O(3)#1	104.0(7)
O(4)-C(3)-Zn(2)	44.7(8)
O(4)#1-C(3)-Zn(2)	44.7(8)
O(4)#2-C(3)-Zn(2)	44.7(8)
C(4)-C(3)-Zn(2)	180.000(5)
O(3)-C(3)-Zn(2)	65.5(6)
O(3)#2-C(3)-Zn(2)	65.5(6)
O(3)#1-C(3)-Zn(2)	65.5(6)
N(2)-N(1)-C(6)	107.8(2)
N(2)-N(1)-Zn(3)#2	119.39(19)
C(6)-N(1)-Zn(3)#2	132.6(2)
N(1)-N(2)-N(3)	110.5(2)
N(1)-N(2)-Zn(1)	125.21(19)
N(3)-N(2)-Zn(1)	124.13(19)
N(2)-N(3)-C(5)	108.1(2)
N(2)-N(3)-Zn(3)	120.2(2)
C(5)-N(3)-Zn(3)	131.6(2)
N(3)-C(5)-C(10)	131.7(3)
N(3)-C(5)-C(6)	106.8(3)
C(10)-C(5)-C(6)	121.5(3)
N(1)-C(6)-C(5)	106.8(3)
N(1)-C(6)-C(7)	132.6(3)
C(5)-C(6)-C(7)	120.6(3)
C(8)-C(7)-C(6)	116.9(3)
C(7)-C(8)-C(9)	122.7(3)
C(10)-C(9)-C(8)	120.0(3)
C(10)-C(9)-C(9)#3	119.5(2)
C(8)-C(9)-C(9)#3	120.4(2)
C(9)-C(10)-C(5)	118.2(3)
N(5)-N(4)-C(11)	106.9(2)
N(5)-N(4)-Zn(3)	120.09(19)
C(11)-N(4)-Zn(3)	132.9(2)
N(6)-N(5)-N(4)	111.4(2)
N(6)-N(5)-Zn(1)	123.66(19)
N(4)-N(5)-Zn(1)	124.72(19)
N(5)-N(6)-C(12)	107.6(2)
N(5)-N(6)-Zn(2)	120.42(19)
C(12)-N(6)-Zn(2)	131.9(2)
N(4)-C(11)-C(12)	107.7(3)
N(4)-C(11)-C(16)	132.0(3)
C(12)-C(11)-C(16)	120.3(3)
N(6)-C(12)-C(11)	106.5(3)
N(6)-C(12)-C(13)	130.9(3)
C(11)-C(12)-C(13)	122.6(3)
C(14)-C(13)-C(12)	116.9(3)

O(2A)-Zn(3)-N(4)	99.6(2)	O(3)#2-O(4)-Zn(2)	88.3(8)	C(13)-C(14)-C(15)	120.5(3)
O(1B)-Zn(3)-N(4)	130.6(3)	O(4)-C(3)-O(4)#1	75.1(12)	C(13)-C(14)-C(14)#4	119.9(4)
O(2A)-Zn(3)-N(3)	125.0(3)	O(4)-C(3)-O(4)#2	75.1(12)	C(15)-C(14)-C(14)#4	119.5(3)
O(1B)-Zn(3)-N(3)	126.0(3)	O(4)#1-C(3)-O(4)#2	75.1(12)	C(16)-C(15)-C(14)	122.99(16)
N(4)-Zn(3)-N(3)	98.65(11)	O(4)-C(3)-C(4)	135.3(8)	C(15)-C(16)-C(11)	116.66(16)

Table S4. Crystal data and structure refinement for Co-CFA-1 **(3)**.

Compound	**Co-CFA-1 (3)**
Diffractometer	Bruker D8 Advance
X–ray source/ wavelength/ Å	Cu, 1.5425
T/K	293(3)
Empirical formula	$[Zn_{3.66}Co_{1.34}(OAc)_4(bibta)_3]$
Formula	$C_{44}H_{30}Co_{1.34}N_{18}O_8Zn_{3.66}$
M_r	1257.1
Crystal system	trigonal
Space group (no)	*P*321 (no.150)
a/Å	17.7771(7)
c/Å	19.1129(16)
V/Å^3	5230.9(5)
Z	2
D_c/g cm^{-3}	0.7801
F(000)	1195
Sample	light red powder
2θ Range/°	4.4–70.00
Number of observation	3799
R_{wp}	6.43
R_P	3.54

Table S5. Bond lengths for Co-CFA-1 **(3)**. Symmetry transformations used to generate equivalent atoms:

(i) -y+1,x-y+1,z
(ii) -x+y,-x+1,z
(iii) x-y+1,-y+2,-z+1
(iv) -x,-x+y,-z+2

Bonds	**Bond lengths (Å)**	**Bonds**	**Bond lengths (Å)**
Zn1-N2	2.20(6)	O3-O4^ii^	1.2(6)
Zn1-N2^i^	2.20(6)	O4-C3	1.20(10)
Zn1-N2^ii^	2.20(6)	C3-C4	1.441(14)
Zn1-N5	2.20(6)	N1-N2	1.33(4)

Zn1-N5^i^	2.20(16)	N1-C6	1.36(10)
Zn1-N5^ii^	2.20(5)	N2-N3^ii^	1.38(5)
Co1-O4	2.00(6)	N3-C5^i^	1.35(10)
Co1-O4^i^	2.0(3)	C5-C6	1.45(5)
Co1-O4^ii^	2.00(7)	C5-C7	1.40(11)
Co1-N6	2.03(3)	C6-C9	1.40(10)
Co1-N6^i^	2.03(8)	C7-C10	1.41(14)
Co1-N6^ii^	2.03(2)	C8-C9	1.37(10)
Zn3-O1a	2.20(10)	C8-C10	1.43(3)
Zn3-O2b	2.16(10)	C10-C10^iii^	1.40(18)
Zn3-N1	2.03(3)	N4-N5	1.33(9)
Zn3-N3	2.03(5)	N4-C11	1.37(4)
Zn3-N4	2.036(17)	N5-N6	1.339(19)
Zn3-O1b	2.00(13)	N6-C12	1.36(4)
Zn3-O2a	2.041(17)	C11-C12	1.41(4)
O1a-C1	1.44(10)	C11-C15	1.40(8)
O2b-C1	1.54(16)	C12-C13	1.43(3)
O2b-O2a	1.03(18)	C13-C14	1.38(12)
C1-C2	1.508(17)	C14-C14^iv^	1.54(5)
C1-O1b	1.03(10)	C14-C16	1.43(7)
C1-O2a	1.077(18)	C15-C16	1.37(5)
O3-O4	1.3(7)	O1b-O2a	1.01(12)

Table S6. Angles for Co-CFA-1 **(3)**.

Atoms	angle (°)	Atoms	angle (°)	Atoms	angle (°)
N2-Zn1-N2^i^	86(2)	N1-Zn3-O1b	105(3)	N2^i^-N3-C5^i^	107(7)
N2-Zn1-N2^ii^	86(2)	N1-Zn3-O2a	132.8(12)	N3^ii^-C5-C6	107(7)
N2-Zn1-N5	93(4)	N3-Zn3-N4	103(3)	N3^ii^-C5-C7	129(5)
N2-Zn1-N5^i^	177(4)	N3-Zn3-O1b	134(4)	C6-C5-C7	121(7)
N2-Zn1-N5^ii^	90(3)	N3-Zn3-O2a	126.7(9)	N1-C6-C5	106(6)
N2^i^-Zn1-N2^ii^	86(2)	N4-Zn3-O1b	115(5)	N1-C6-C9	134(3)
N2^i^-Zn1-N5	90(3)	N4-Zn3-O2a	97.7(15)	C5-C6-C9	120(7)
N2^i^-Zn1-N5^i^	93(3)	O1b-Zn3-O2a	29(3)	C5-C7-C10	118(5)
N2^i^-Zn1-N5^ii^	177(2)	Zn3-O1a-C1	82(4)	C9-C8-C10	125(8)
N2^ii^-Zn1-N5	177(2)	Zn3-O2b-C1	81(5)	C6-C9-C8	117(3)
N2^ii^-Zn1-N5^i^	90(4)	Zn3-O2b-O2a	69(5)	C7-C10-C8	118(10)
N2^ii^-Zn1-N5^ii^	93(4)	C1-O2b-O2a	44(6)	C7-C10-C10^iii^	118(6)
N5-Zn1-N5^i^	91(5)	O1a-C1-O2b	109(7)	C8-C10-C10^iii^	124(11)
N5-Zn1-N5^ii^	91(4)	O1a-C1-C2	121(4)	Zn3-N4-N5	120(3)
N5^i^-Zn1-N5^ii^	91(4)	O1a-C1-O1b	81(9)	Zn3-N4-C11	133(4)
O4-Co1-O4^i^	50(15)	O1a-C1-O2a	117(4)	N5-N4-C11	107(2)
O4-Co1-O4^ii^	50(12)	O2b-C1-C2	117(4)	Zn1-N5-N4	124.7(13)
O4-Co1-N6	94(5)	O2b-C1-O1b	94(9)	Zn1-N5-N6	123(5)
O4-Co1-N6^i^	117(15)	O2b-C1-O2a	42(6)	N4-N5-N6	112(5)

O4-Co1-N6^ii^	142(13)	C2-C1-O1b	127(7)	Co1-N6-N5	122(3)
O4^i^-Co1-O4^ii^	50(19)	C2-C1-O2a	121.1(13)	Co1-N6-C12	132.1(9)
O4^i^-Co1-N6	142(12)	O1b-C1-O2a	58(9)	N5-N6-C12	106(4)
O4^i^-Co1-N6^i^	94(17)	O4-O3-O4^ii^	80(30)	N4-C11-C12	106(4)
O4^i^-Co1-N6^ii^	117(11)	Co1-O4-O3	82(16)	N4-C11-C15	133(3)
O4^ii^-Co1-N6	117(16)	Co1-O4-O3^i^	82(12)	C12-C11-C15	121(2)
O4^ii^-Co1-N6^i^	142(14)	Co1-O4-C3	96(7)	N6-C12-C11	108.5(18)
O4^ii^-Co1-N6^ii^	94(4)	O3-O4-O3^i^	150(20)	N6-C12-C13	129(4)
N6-Co1-N6^i^	97(2)	O3-O4-C3	80(30)	C11-C12-C13	122(4)
N6-Co1-N6^ii^	97(2)	O3^i^-O4-C3	80(20)	C12-C13-C14	114(5)
N6^i^-Co1-N6^ii^	97.3(19)	O4-C3-O4^i^	90(20)	C13-C14-C14^iv^	123(6)
O1a-Zn3-O2b	68(4)	O4-C3-O4^ii^	90(30)	C13-C14-C16	123(4)
O1a-Zn3-N1	94(3)	O4-C3-C4	126(4)	C14^iv^-C14-C16	113(6)
O1a-Zn3-N3	92(4)	O4^i^-C3-O4^i^	90(30)	C11-C15-C16	118(6)
O1a-Zn3-N4	159(3)	O4^i^-C3-C4	126(18)	C14-C16-C15	120(5)
O1a-Zn3-O1b	45(6)	O4^ii^-C3-C4	126(4)	Zn3-O1b-C1	104(8)
O1a-Zn3-O2a	61(3)	Zn3-N1-N2	120(4)	Zn3-O1b-O2a	78(8)
O2b-Zn3-N1	158(5)	Zn3-N1-C6	131.4(19)	C1-O1b-O2a	64(4)
O2b-Zn3-N3	101(5)	N2-N1-C6	108(3)	Zn3-O2a-O2b	82(7)
O2b-Zn3-N4	94(3)	Zn1-N2-N1	125(3)	Zn3-O2a-C1	99.4(10)
O2b-Zn3-O1b	55(5)	Zn1-N2-N3^ii^	124(3)	Zn3-O2a-O1b	73(7)
O2b-Zn3-O2a	28(5)	N1-N2-N3^ii^	111(5)	O2b-O2a-C1	93(6)
N1-Zn3-N3	90.0(15)	Zn3-N3-N2^i^	118(3)	O2b-O2a-O1b	138(10)
N1-Zn3-N4	101(2)	Zn3-N3-C5^i^	134(5)	C1-O2a-O1b	59(8)

Table S7. Atomic coordinates and equivalent isotropic displacement parameters for Co-CFA-1 **(3).**

Atomic coordinates, U	
Zn1	0.3333; 0.6667; 0.7350(6); 0.028(4)
Zn2	0.3333; 0.6667; 0.9237(9); 0.01(2)
Zn3	0.1275(7); 0.6319(6); 0.6715(5); 0.028(4)
Co1	0.3333; 0.6667; 0.9237(9); 0.01(2)
Co2	0.1275(7); 0.6319(6); 0.6715(5); 0.028(4)
O1a	0.059(6); 0.622(7); 0.573(5); 0.05(3)
O2b	-0.010(7); 0.540(10); 0.678(6); 0.05(3)
C1	-0.0124(7); 0.5980(10); 0.6195(8); 0.02(2)
C2	-0.1009(6); 0.5757(2); 0.5925(2); 0.02(2)
O3	0.27(2); 0.70(2); 1.0122(6); 0.05(3)
O4	0.271(6); 0.63(3); 1.0152(5); 0.05(3)
C3	0.3333; 0.6667; 1.0517(5); 0.02(2)
C4	0.3333; 0.6667; 1.1271(5); 0.02(2)
N1	0.2389(8); 0.739(2); 0.640(3); 0.04(3)
N2	0.3153(10); 0.754(3); 0.664(4); 0.04(3)
N3	0.173(2); 0.555(3); 0.6340(5); 0.04(3)
C5	0.345(3); 0.859(5); 0.591(5); 0.02(2)

C6 0.2525(10); 0.808(4); 0.600(6); 0.02(2)
C7 0.383(2); 0.940(4); 0.557(6); 0.02(2)
C8 0.2366(10); 0.902(4); 0.522(5); 0.02(2)
C9 0.198(2); 0.827(3); 0.560(5); 0.02(2)
C10 0.3282(10); 0.961(7); 0.519(9); 0.02(2)
N4 0.147(2); 0.633(7); 0.7765(5); 0.04(3)
N5 0.222(3); 0.644(9); 0.8008(7); 0.04(3)
N6 0.2240(10); 0.641(4); 0.8707(5); 0.04(3)
C11 0.096(2); 0.624(5); 0.8334(5); 0.02(2)
C12 0.1453(10); 0.628(4); 0.8926(5); 0.02(2)
C13 0.110(3); 0.612(10); 0.9616(9); 0.02(2)
C14 0.026(4); 0.598(9); 0.9657(9); 0.02(2)
C15 0.011(3); 0.607(8); 0.840(2); 0.02(2)
C16 -0.026(3); 0.587(9); 0.9056(10); 0.02(2)
O1b 0.033(6); 0.655(5); 0.643(9); 0.05(3)
O2a 0.0010(6); 0.6027(6); 0.6748(5); 0.05(3)

2. NMR spectroscopy

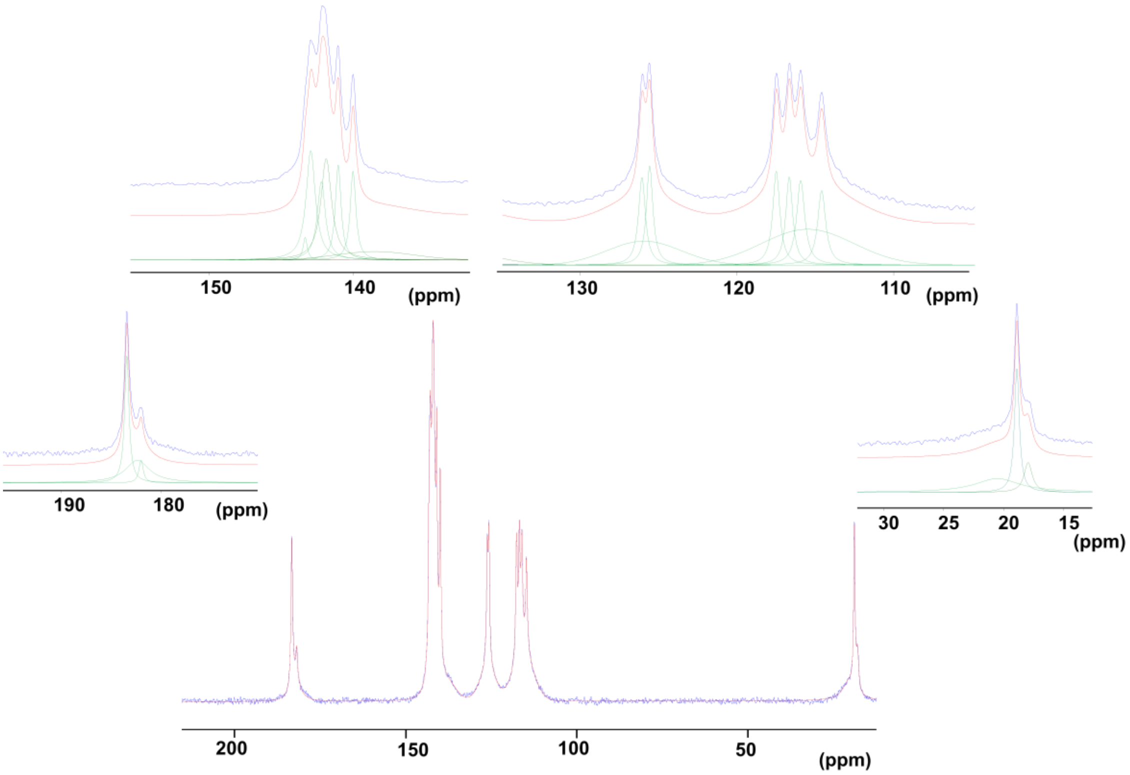


Fig. S1 ^{13}C CPMAS spectrum of CFA-1 **(2)**; blue curve: ^{13}C CPMAS spectrum of **(2)**; green curves: Gauss-functions; red curve: resulting graph of the different Gauss fits.

Graph		**amp**	**pos (ppm)**	**relative share**
"Gaus/Lor"	"#1"	89.88	17.96	1,74
"Gaus/Lor"	"#2"	41.65	20.52	4,39

"Gaus/Lor"	"#3"	372.66	18.89	4,31
"Gaus/Lor"	"#4"	61.33	181.98	0,74
"Gaus/Lor"	"#5"	61.77	182.34	4,18
"Gaus/Lor"	"#6"	344.35	183.41	4,34
"Gaus/Lor"	"#7"	217.90	114.81	3,13
"Gaus/Lor"	"#8"	247.88	116.15	3,61
"Gaus/Lor"	"#9"	258.15	116.88	3,20
"Gaus/Lor"	"#10"	275.14	117.70	3,50
"Gaus/Lor"	"#11"	290.58	125.78	3,38
"Gaus/Lor"	"#12"	256.82	126.27	3,24
"Gaus/Lor"	"#13"	441.39	140.01	4,93
"Gaus/Lor"	"#14"	471.86	141.04	5,29
"Gaus/Lor"	"#15"	503.27	141.87	10,71
"Gaus/Lor"	"#16"	388.94	142.21	6,30
"Gaus/Lor"	"#17"	544.00	142.95	9,93
"Gaus/Lor"	"#18"	112.55	143.34	0,90
"Gaus/Lor"	"#19"	104.90	115.70	11,62
"Gaus/Lor"	"#20"	41.75	138.49	4,27
"Gaus/Lor"	"#21"	70.43	126.14	6,30

3. Computational Studies

FT-IR Spectra of cluster-1 and cluster-2.

The most characteristic vibrations of CFA-1, present in both cluster-1 and cluster-2 are those associated to Zn-N vibrations. We have classified these vibrations in two types which we call 'skeleton' and 'Zn-BTA' and, by analysis of the normal vibrational modes, they are distinguished by a participation of most of the Zn and N atoms of the cluster ('skeleton' vibrations) and by a participation of Zn and the BTA ligand as a whole ('Zn-BTA' vibrations). The bending and rotating modes involving both Zn and BTA linkers are infrared active vibrations are calculated at 189, 242 and 266 cm^{-1} (cluster-1), which compare to the experimental peaks at 204, 257 and 278 cm^{-1}. A broad band between 210-216 cm^{-1} in cluster-2 is also in good agreement with the experimental peaks. On the other hand, 'Zn-BTA' peaks are calculated (cluster-1) at 555 and 1227-1247 cm^{-1}, which compare to the experimental peaks at 559, 1190 and 1203 cm^{-1}. The calculated 'Zn-BTA' peak at 1227-1247 cm^{-1} involves a considerable contribution from the BTA ligand and hence this could be the reason of the ca. 35 cm^{-1} disagreement with respect to the experimental values in CFA-1 (1190 and 1203 cm^{-1}) where the ligand is not a single BTA but two (BTA-BTA) ligands bonded. In cluster-2, similar results are obtained, with 'Zn-BTA' peaks at 560 and 1220-1230 cm^{-1}, the latter more in agreement with the experimental values at 1190 and 1203 cm^{-1}.

Another characteristic feature of CFA-1 is the Zn-acetate vibration, and here an experimental peak at 320 cm^{-1} is assigned on the basis of inspection of the calculated normal mode analysis. The corresponding calculated peak appears at 305 cm^{-1} (cluster-1), and 295 cm^{-1} (cluster-2), both in reasonable agreement with the experiment.

Following these assignations, the rest of the spectrum is characterised by peaks assigned to localised vibrations at the ligands, either in the acetate group or in the BTA ligand.

Among these localised vibrations are the following: 692 cm^{-1}, calculated in cluster-1 at 679 cm^{-1}, and in cluster-2 at 689 cm^{-1}, due to the acetate group; 796 cm^{-1} due to the BTA ligand, calculated at 797 cm^{-1} in cluster-1, and 800 cm^{-1} in cluster-2.

A special attention is required for the latest two bands, due to the acetate groups, experimentally observed at 1446 and 1570 cm^{-1}, which are not well reproduced by cluster-1 (calculated at 1381, 1436 and 1648 cm^{-1}). As said above this is due to the fact that cluster-1 does not contain two interacting acetate groups. However, cluster-2 which does contain two interacting acetate groups, gives two bands centred at 1414 and 1590 cm^{-1}, much in agreement with the experimental values 1446 and 1570 cm^{-1}. All frequencies are well reproduced by our cluster-2 model, within 20 cm^{-1} error, as can be seen from Table G1. None of the calculated frequencies has been scaled.

Another interesting feature of cluster-2 is the fact that it gives a symmetric geometry for the Zn-acetate binding, which is in agreement with the XRD results (Fig. 9 and 10). Cluster-2 on the other hand is the only containing the biphenyl ligand of CFA-1. This allows to build around the two neighbour acetates in the same environment than the real material CFA-1, and this also contributes to obtain the correct Zn-acetate binding.

FT-IR spectrum of cluster-3.

Each Kuratowski-type Zn pentanuclear SBU is connected to the other SBUs by 6 BTA linkers and has 4 acetate ligands. There are two types of BTA ligands. Three equivalent ligands of type A are oriented along the c-axis, and three of type B are oriented along a- and b-axis. BTA-A ligands are slightly longer and that is why c-axis is larger. More importantly, there are two types of acetate ligands, one along c-axis (type A) and the other along a- and b-axis (type B). Acetate ligands of type A are surrounded with three BTAs of type A while acetate ligands of type B are close to an acetate ligand of type B and one BTA of type B.

In order to reproduce the full IR spectra, all of this representative elements need to be present in the cluster and thus we propose cluster-3, consisting of 221 atoms (Figure S8). Cluster-3 has three pentanuclear building units (PBU), one central and two adjacents.

The central PBU contains one acetate ligand of type B, and is connected to the adjacents through a BTA-A linker and a BTA-B linker. The side-BTU connected with the central through a BTA-A linker has an acetate ligand of type A, and the other side-BTU (also connected with the central through a BTA-A linker) has an acetate ligand of type B. Due to the inherent truncation in any cluster, we do not expect to obtain exactly the same peaks as in the experimental IR spectrum, but we expect to observe all the peaks. Also, additional peaks are expected due to the H and Cl saturation.

Two BTA types are slightly different due to the different connections to the N atoms of the pentanuclear BTU units. The differences between the two acetate types are larger. First, due to the different BTA ligands, Zn(octahedral)–Zn (tetrahedral) distances are not the same. Because of this, different tetrahedral Zn will probably have slightly different electronic states. Also, two acetate ligands of type B are close to each other while the acetate of type A is surrounded by BTA linkers only. Because of this, O–Zn–O bonds are quite different for the acetate ligand of type A and less different for the acetate of type B. Also, the C–C distance in the acetate ligand type A is just slightly longer compared to the same bond in the acetate ligand type B. It is expected that due to these differences, vibrational modes that involve stretching of the acetate ligands will be different for the two types of ligands. The same argument holds for the BTA linkers.

The calculated spectra (Fig. 14) reproduces the experimental one quite well. Frequencies at low wavenumbers (experimental 205, 256 and 277 cm^{-1} and calculated 207, 248, 261, 285 cm^{-1}) agree well and they correspond to the bending and rotating modes involving both Zn and BTA linkers. The calculated frequency of 310 (320 cm^{-1} in experiments) corresponds to the acetate bending mode, with some contribution of the Zn atom.

The peak at 371 cm^{-1} in the calculated spectra corresponds to the Zn-Cl stretching mode. This peak does not exist in the experimental spectra. The smaller peak in the calculated spectra at 376 cm^{-1} corresponds to the 382 cm^{-1} and it belongs to the BTA (1,2,3-benzotriazolate) mode. Peaks at 431, 506, 560 cm^{-1}, belong to the BTA modes and experimental equivalents are 432, 502, 559 cm^{-1}. The next peak in the experimental spectra at 608 cm^{-1} (calculated at 603 cm^{-1}) corresponds to the acetate mode. 657 cm^{-1} is a BTA vibrational mode (663 cm^{-1} calculated) and 693 cm^{-1} belongs again to the acetate ligand (679 cm^{-1} calculated). Next two peaks, 749 cm^{-1} and the intense at 796 cm^{-1} belong to the BTA vibrational modes (752 and 797 cm^{-1} are the calculated values).

In the experimental spectra there is a larger peak at 930 cm^{-1} but there are smaller peaks next to it as well. In the calculated spectra there are two corresponding peaks, at 920 and 931 cm^{-1}. Both peaks belong to the acetate mode, but one at 920 cm^{-1} belongs to the acetate type-A and the 931 cm^{-1} to the same vibrational mode but of the acetate type-B. Exactly the same holds for the experimental peak at 1011 cm^{-1}, which are actually two very close peaks. In the calculated spectra there are peaks at 1004 and 1027 cm^{-1} and again, they belong to the same vibrational mode but of the two acetate types.
The same situation is present in the two broadened peaks at 1446 and 1570 cm^{-1} in the experimental spectra. The calculated value of 1365 cm^{-1} belongs to the combined CH_3 umbrella and C-C stretching mode of the acetate type-A, and the 1397 cm^{-1} corresponds to the same mode of the acetate type-B. The experimental peak at 1570 cm^{-1} corresponds to the 1558 cm^{-1} calculated peak, and it is the Zn-O stretching mode of the acetate ligand type-B, and the one at 1591 cm^{-1} to the same mode of the acetate type-A. In the experimental spectra both peaks are quite broadened, especially that at 1446 cm^{-1}, since all the acetate ligands are not completely equivalents and they are quite sensitive to the geometry and environment, much more than the other acetate vibrational modes, because they involve a stretching type of motion. Also, modes that include CH_3 umbrella motion of the acetate ligand start at around 1320 cm^{-1}.

The experimentally observed frequencies at 1190 and 1203 cm^{-1} belong to the BTA ligand mode, with some contribution of the Zn-BTA bonds. Similar to some of the acetate modes, these two modes belong to the same stretching mode but for the two different BTA types. Since there is the same amount of the two linkers in the structure, they are expected to have peaks with the same intensities, and, since differences are small, the positions of the two peaks are close to each other. In the calculated spectra, peaks are at 1189 and 1192 cm^{-1}. Due to the less constraints and symmetry in the cluster, the two modes do not have the same intensity, they have closer values and in the broadened spectra, where they appear as one peak.

As expected, two BTAs and especially two types of acetate ligands give two different values for the vibrational stretching modes. Vibrational modes that involve ligand bending or slight rotation are mostly the same for the two ligand types (modes below 900 cm^{-1}). Also, values of the experimental and calculated frequencies overlap quite well. Only larger differences are for the broadened peak at 1446 cm^{-1}. This is not a surprise because the same stretching mode calculated for the cluster is reduced approximately by 30 cm^{-1} compared to the periodic case. Other modes are not sensitive to the type of calculation, either cluster or periodic.

Further considerations on the number and types of acetate groups of CFA-1.

Regarding the acetate groups of CFA-1, the symmetry of the unit cell indicates two different types of C (COO) atoms, labelled C1 and C3, and two different types of C (CH$_3$) atoms, labelled C2 and C4. There are eight acetate groups in the unit cell, six of them containing C1, C2 atoms, and two of them containing C3, C4 atoms. It is enlightening to calculate the shortest distances between the acetate groups, which we have made considering CH$_3$···CH$_3$ distances in the unit cell of P321 symmetry. If we label 1-8 the eight acetate groups, the distances between them are schematised in Figure S9, top. It can be seen that acetate groups can be classified according to their relative distances, and this allows to explain better the experimental number of C1/C3 and C2/C4 NMR peaks (Figure S9, bottom).

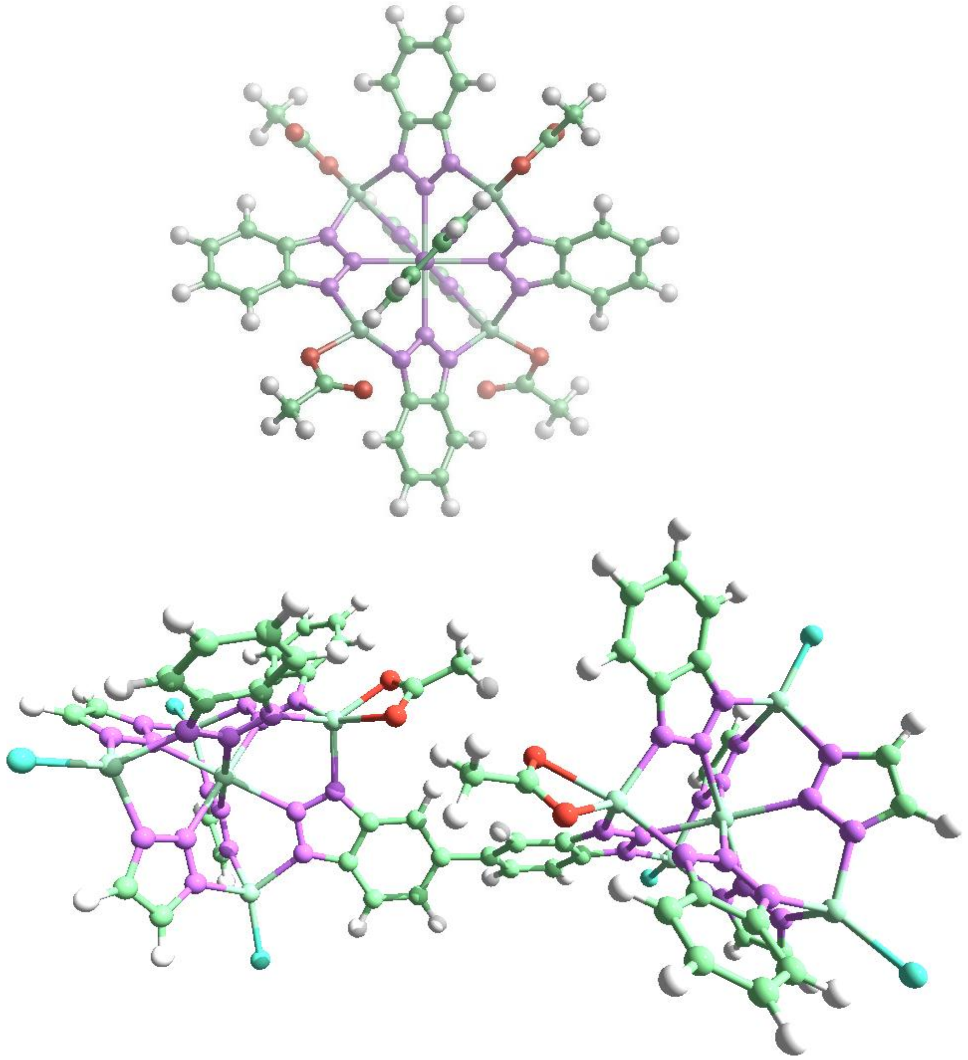


Figure S2. Top: **cluster-1**; [Zn$_5$ac$_4$(L)$_6$], with ac$^-$ = acetate and L$^-$ = bta$^-$ (1,2,3-benzotriazolate). Bottom: **cluster-2**; representing a larger part of the CFA-1 network centred in two interacting acetate groups.

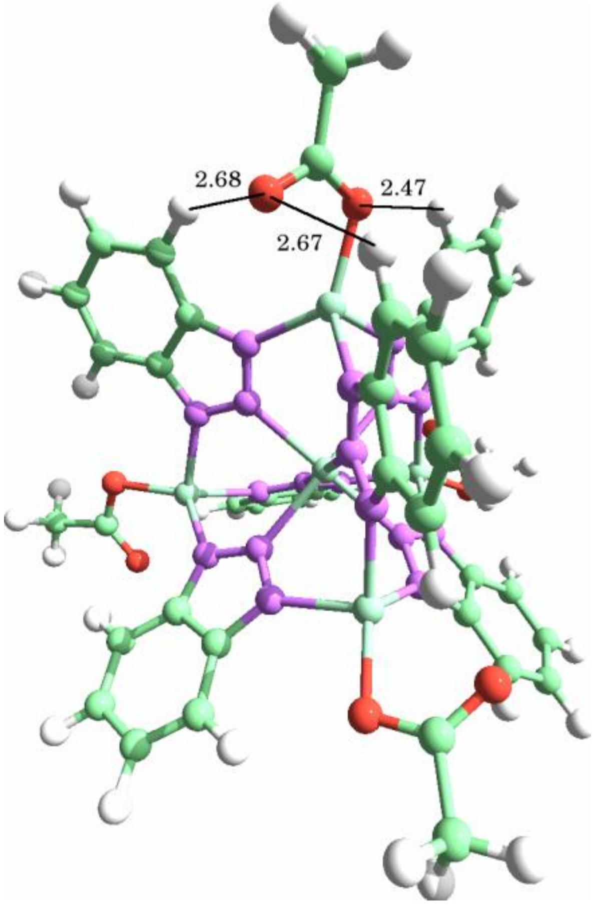


Figure S3. HCTH/TZVP optimised geometry with selected O---H interactions highlighted (distances in Å) in **cluster-1**. This model does not correctly reproduce the acetate environment of CFA-1. For a more correct model see Figure S4.

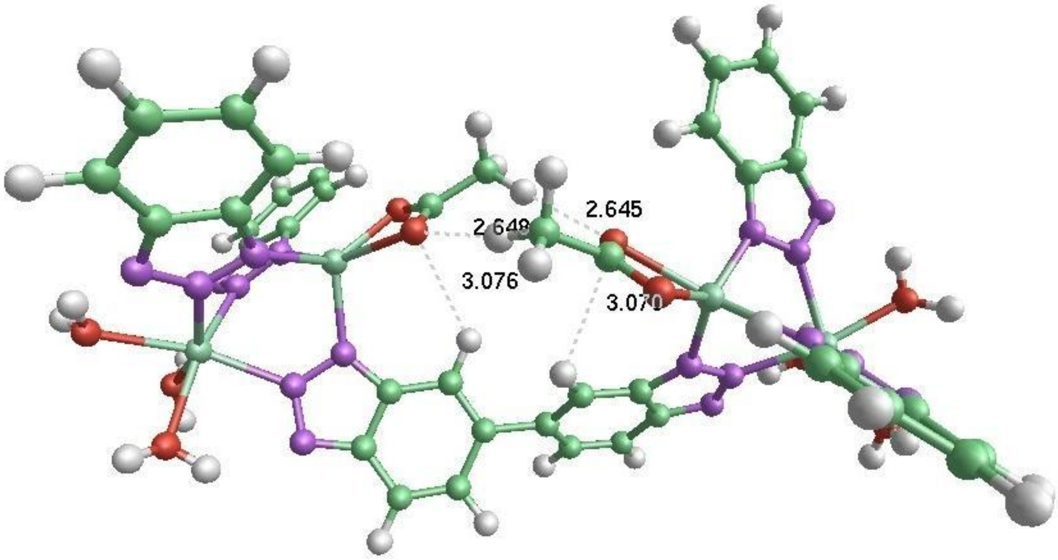


Figure S4. **cluster-2**: HCTH/TZVP optimised geometry with selected O---H interactions highlighted (distances in Å). This model reflects more accurately than **cluster-1** the acetate environment of CFA-1.

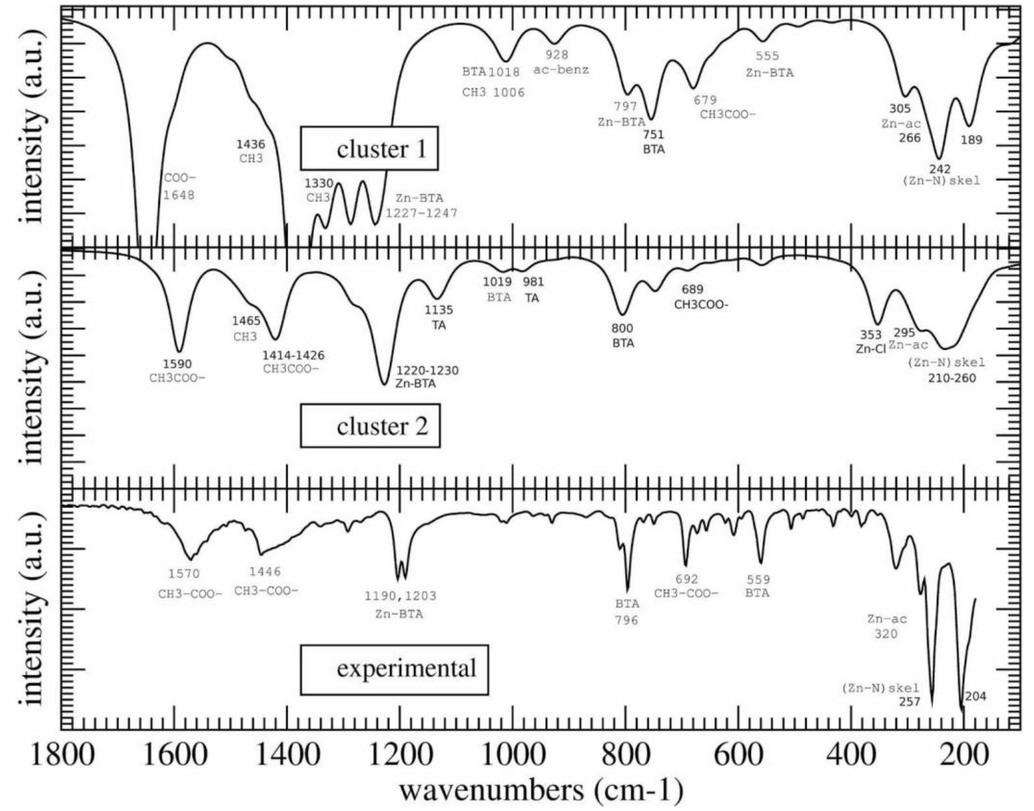


Figure S5. HCTH/TZVP calculated infrared spectrum of **cluster-1** (top) and **cluster-2** (middle), and experimental (bottom). Peaks in blue correspond to vibrational features of terminal atoms in TA and BTA ligands, not expected to be present in CFA-1. Clusters are shown in Figure S2 and S4. Assignations are described in Table 2.

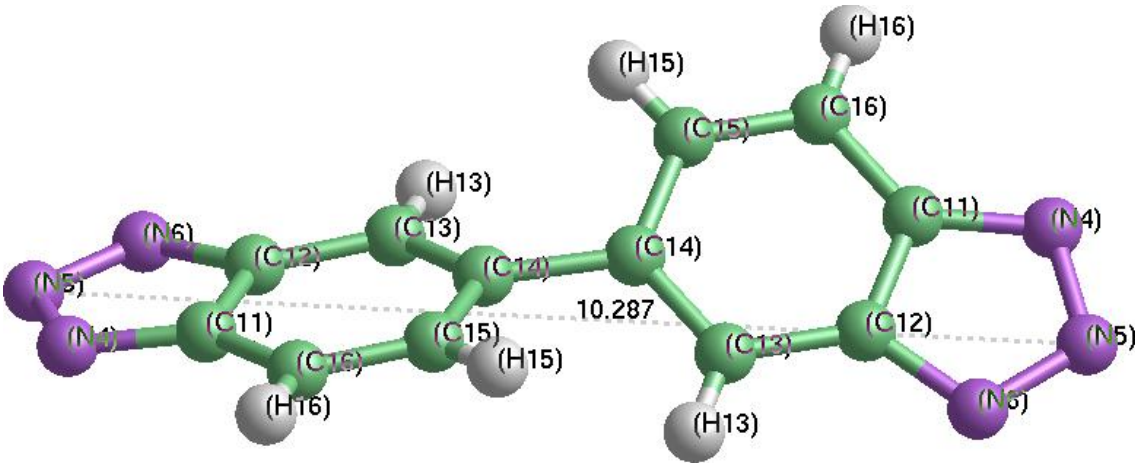


Figure S6. BTA-A type linker. The largest N-N distance is shown in Å. It can be seen that the path from C12 (left part) to C11 (right part) goes through six C-C bonds, and the path from C11 (left) to C12 (right) goes through six C-C bonds as well. This is different to the case of BTA-B linker. Labels according to Figure 3.

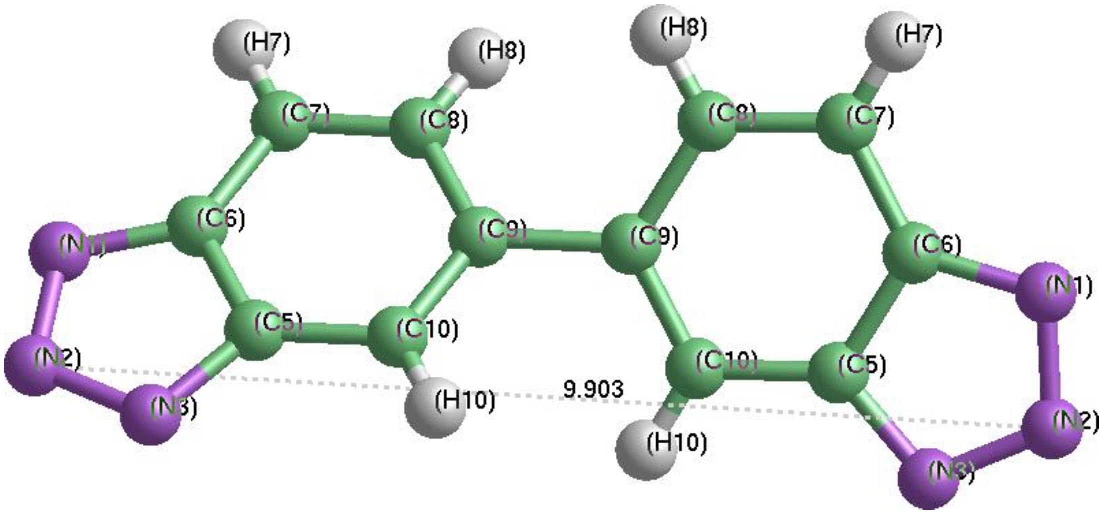


Figure S7. BTA-B type linker. The largest N-N distance is shown in Å. It can be seen that the path from C6 to C6 goes through seven C-C bonds, whilst the path from C5 to C5 goes through five C-C bonds. This is different to the case of BTA-A linker. Labels according to Figure 3.

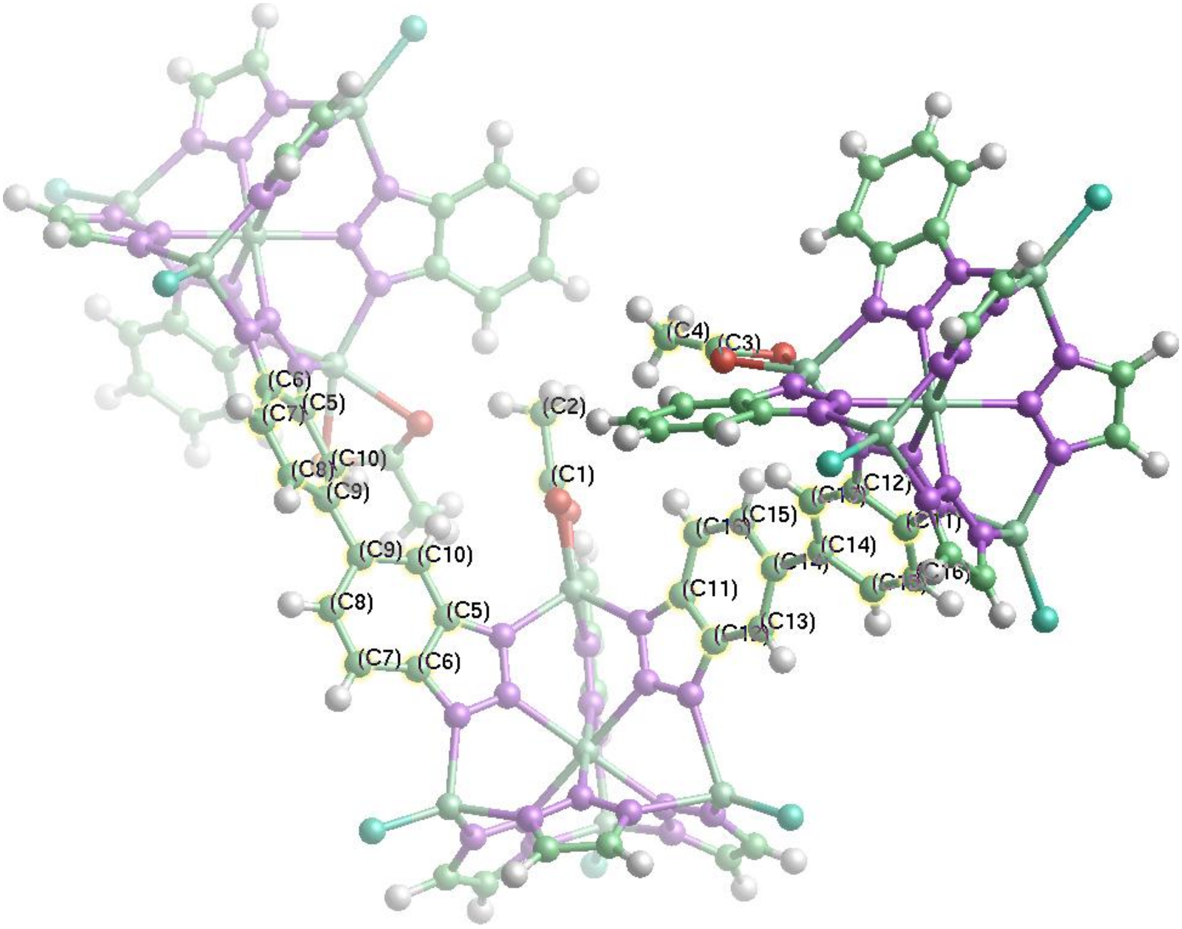
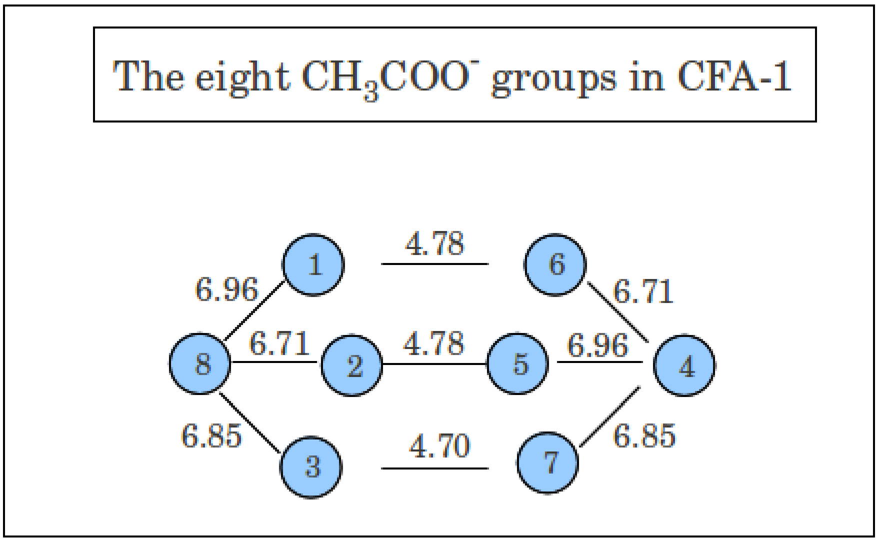


Figure S8. Cluster-3 selected for IR and NMR calculations. This is the largest cluster employed in the current study, containing 221 atoms. It contains three acetate groups: two of them with C1,C2, and one of them with C3,C4 carbon atoms. All labels according to Figure 3. Two linkers, one of type BTA-A and one of type BTA-B (see Figures S6, S7) are contained in the clusters, whose atoms are also highlighted.



Atom label	Atom type	periodic-DFT calculated	Atom label averaged	Atom type averaged
C1	1	163.995	164.3 (C1, 6 values)	164.07
C1	5	164.135		
C1	2	164.455		164.54
C1	6	164.615		
C1	3	163.915		163.95
C3	7	163.975	164.3 (C3, 2values)	
C1	4	164.575		164.56
C3	8	164.545		
C2	1	23.325	23.2 (C2, 6 values)	23.33
C2	5	23.335		
C2	2	23.545		23.57
C2	6	23.585		
C2	3	23.795		23.83
C4	7	23.855	22.8 (C4, 2 values)	
C2	4	21.835		21.82
C4	8	21.805		

Figure S9. (**Top**): Schematic view of the relative distances ($CH_3 \cdots CH_3$) between the eight acetate groups in CFA-1. Calculated using the P321 unit cell. Distances in Å. According to the distances it can be seen that '1'='5', '2'='6', '3'='7', and '4'='8'. Using the atom labelling in Figure 5, carbons '1-6' are C2, and carbons '7,8' are C4. (**Bottom**): The above classification of acetate groups allows a better interpretation of the NMR chemical shifts. Groups of equivalent 'atom types' (with the same background color) have very similar values regardless their 'atom labels'. Groups by 'atom label' tend to show much more scattered values. It is likely that each NMR peak corresponds to each 'atom type'.

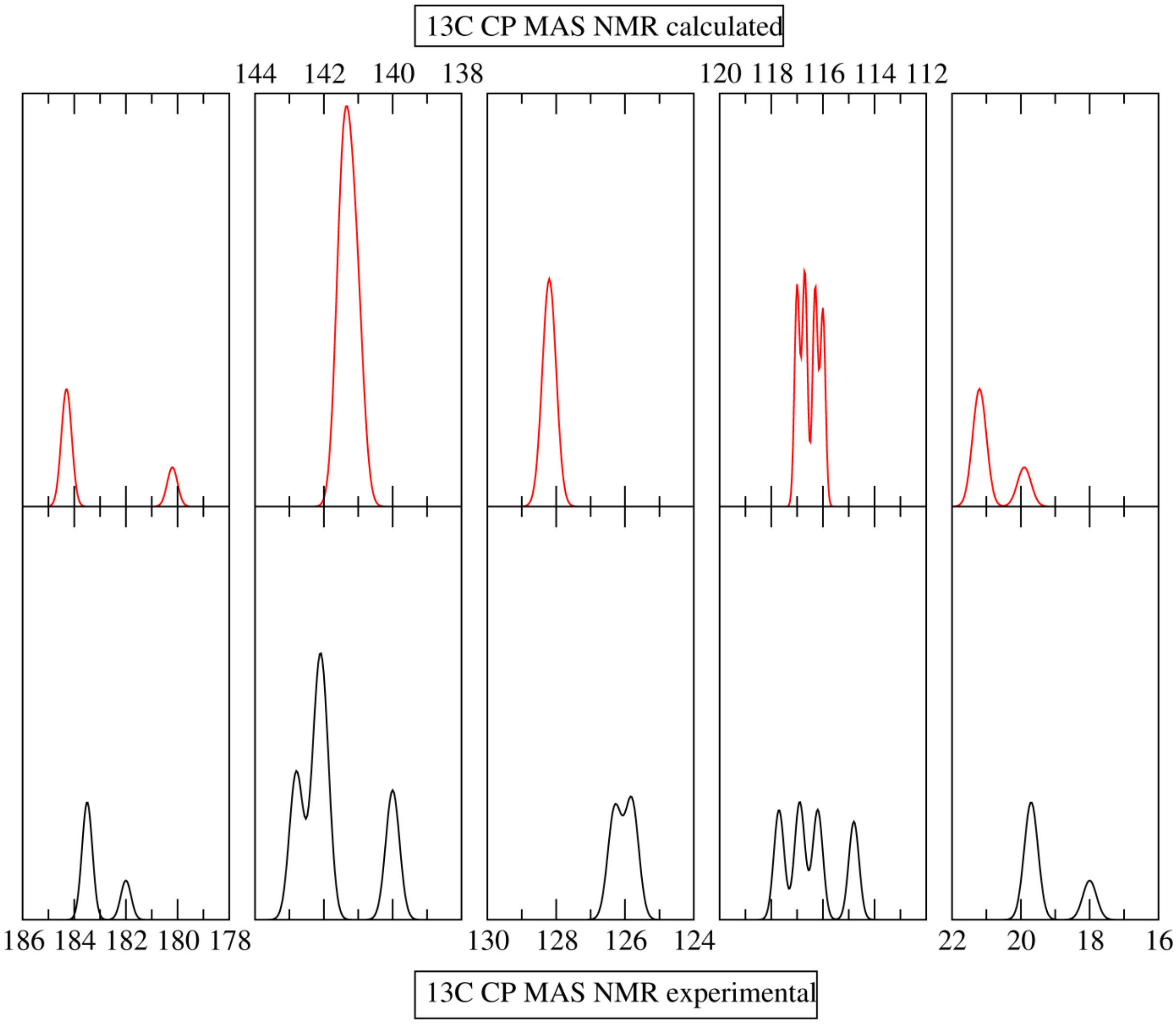


Figure S10. ^{13}C NMR chemical shifts (ppm) of CFA-1 as calculated and from experiment.