Supporting Information

Coordination Frameworks assembled from Cu^{II} ions and H_2-1,3-bdpb benzene ligands: X-ray and Magneto Structural Investigations, and Catalytic Activity in the Aerobic Oxidation of Tetralin

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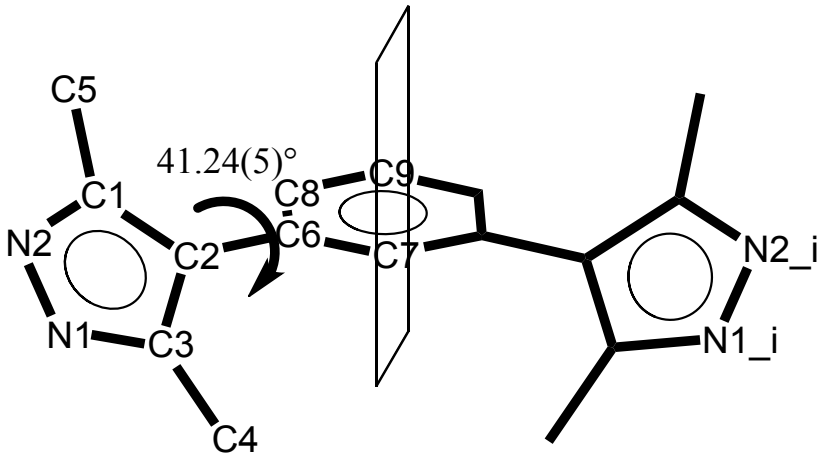
Single Crystal Structure Analysis of H_2-1,3-bdpb·MeOH ($C_{16}H_{22}N_4$·CH_3OH).

The asymmetric unit contains ten carbon, two nitrogen and one oxygen atoms, accounting for one half of H_2-1,3-bdpb and one MeOH molecule. The complete H_2-1,3-bdpb is then generated by the reflection in a mirror plane (Scheme S1). The C7, C9 atoms of the phenyl ring and C10, O1 atoms of MeOH are placed on a crystallographic mirror plane (2e in Wyckoff notation). While the phenyl ring of the molecule is almost parallel to the (100) plane, the pyrazole rings are inclined with respect to the phenyl ring. The two equatorial planes created by C1-C5, N1-N2 and C6-C9 atoms enclose an angle of 41.24(5)° (see Scheme S1). An Ortep style plot of the asymmetric unit of H_2-1,3-bdpb·MeOH with the atom labels is shown in Fig. S1.



Scheme S1 Conformation of H_2-1,3-bdpb in the crystal lattice of H_2-1,3-bdpb·MeOH. (H-atoms omitted for clarity. Symmetry transformation used to generate equivalent atoms: (i) –x, y+1/2, -z.)

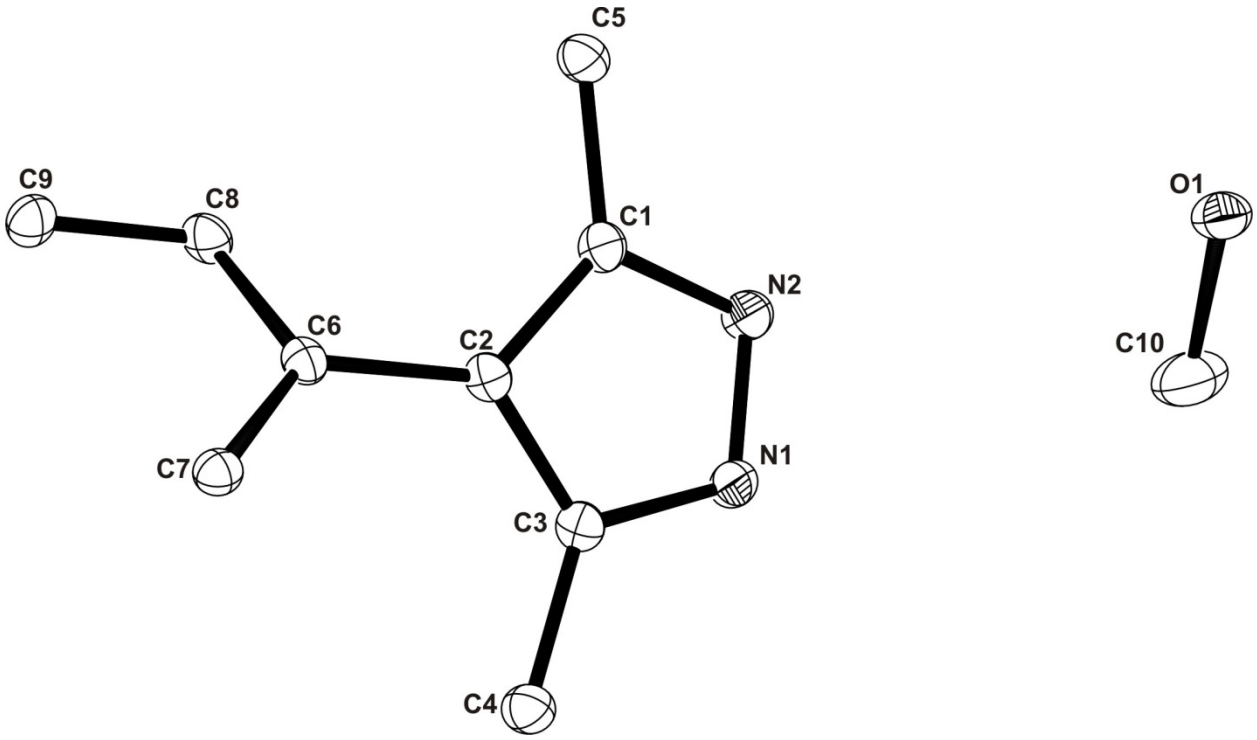


Fig. S1. Ortep-style plot of the asymmetric unit of H_2-1,3-bdpb·MeOH. Thermal ellipsoids probability: 50 %. Hydrogen atoms are omitted for clarity.

H_2-1,3-bdpb·MeOH exhibits a 2D layered packing motif. The first layer is created by H_2-1,3-bdpb molecules while the second one is created by solvent molecules. The whole structure is stabilized by hydrogen bridges formed between MeOH molecules and nitrogen atoms of H_2-1,3-bdpb. The packing diagram of H_2-1,3-bdpb along the *a*-direction is shown in Fig. S2. The atomic coordinates and isotropic thermal parameters, selected bond lengths and angles are presented in Tables S1-S2, respectively.

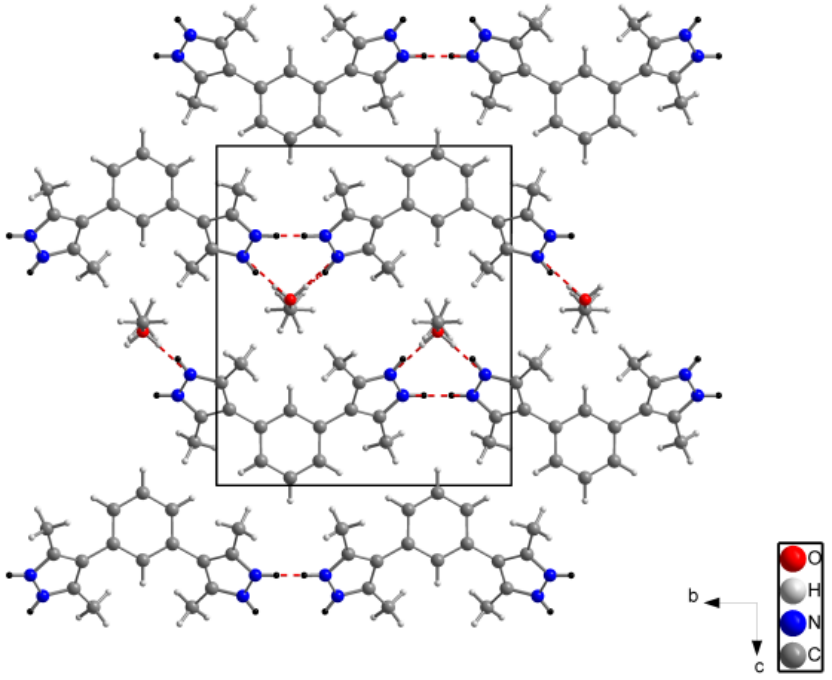


Fig. S2 Packing diagram of H_2-1,3-bdpb·MeOH with hydrogen bonds shown as intercepted red lines. Black hydrogen atoms from H_2-1,3-bdpb molecules are shown with 50 % occupation. (In the crystal structure of H_2-1,3-bdpb·MeOH the acidic NH-protons of H_2-1,3-bdpb have been placed in calculated positions (d(NH) = 0.88 Å). Owing to lattice symmetry both nitrogen atoms of each pyrazole ring appear to be protonated at 50% probability).

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for H_2-1,3-bdpb·MeOH. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1107(3)	2500	5474(1)	17(1)
N(1)	9587(3)	4107(1)	6738(1)	19(1)
N(2)	7797(3)	3685(1)	7352(1)	20(1)
C(1)	7224(4)	4472(1)	7977(1)	16(1)
C(2)	8668(4)	5435(1)	7763(1)	14(1)
C(3)	10128(4)	5160(1)	6967(1)	15(1)
C(4)	12076(4)	5826(1)	6414(1)	18(1)
C(5)	5215(4)	4247(1)	8720(1)	18(1)
C(6)	8710(3)	6495(1)	8278(1)	14(1)

C(7)	8637(5)	7500	7795(2)	14(1)
C(8)	8852(4)	6510(1)	9282(1)	16(1)
C(9)	8916(5)	7500	9775(2)	17(1)
C(10)	3905(6)	2500	5196(2)	29(1)

Table S2. Bond lengths [Å] and angles [°] for H_2-1,3-bdpb·MeOH.

O(1)-C(10)	1.416(3)	C(2)-C(6)	1.473(2)
N(1)-C(3)	1.337(2)	C(2)-C(6)	1.473(2)
N(1)-N(2)	1.360(2)	C(3)-C(4)	1.494(2)
N(2)-C(1)	1.339(2)	C(6)-C(7)	1.3932(19)
C(1)-C(2)	1.400(2)	C(6)-C(8)	1.402(2)
C(1)-C(5)	1.498(2)	C(7)-C(6)#1	1.3932(19)
C(2)-C(3)	1.403(2)	C(8)-C(9)	1.384(2)
C(8)-C(9)	1.384(2)	C(9)-C(8)#1	1.384(2)
C(3)-N(1)-N(2)	108.99(15)	N(1)-C(3)-C(4)	120.41(15)
C(1)-N(2)-N(1)	108.57(15)	C(2)-C(3)-C(4)	130.91(15)
N(2)-C(1)-C(2)	108.89(15)	C(7)-C(6)-C(8)	118.18(15)
N(2)-C(1)-C(5)	120.14(15)	C(7)-C(6)-C(2)	121.84(15)
C(2)-C(1)-C(5)	130.92(15)	C(8)-C(6)-C(2)	119.98(14)
C(1)-C(2)-C(3)	104.88(14)	C(6)#1-C(7)-C(6)	122.1(2)
C(1)-C(2)-C(6)	127.52(15)	C(9)-C(8)-C(6)	120.55(16)
C(3)-C(2)-C(6)	127.58(15)	C(8)-C(9)-C(8)#1	120.4(2)
N(1)-C(3)-C(2)	108.67(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z

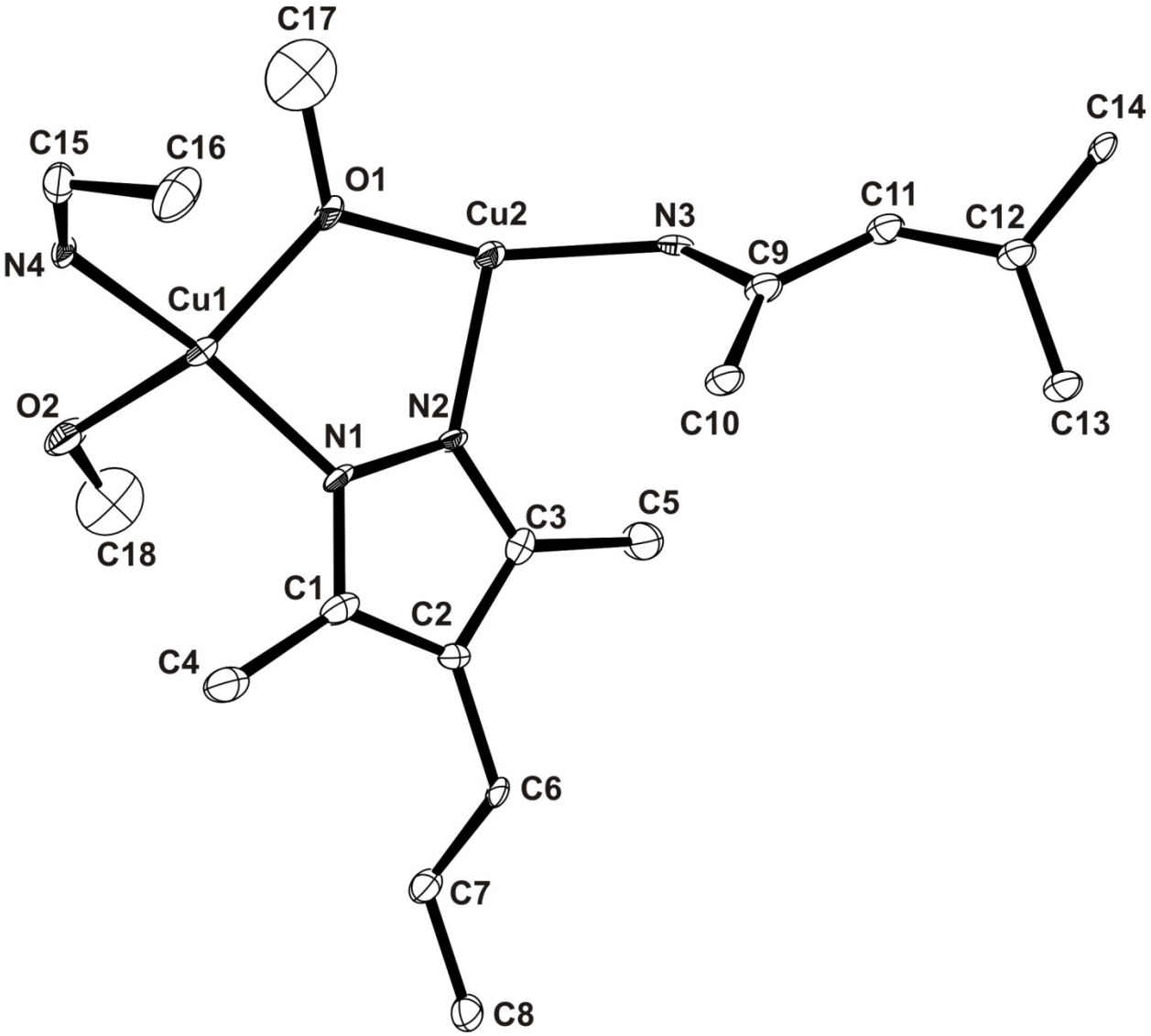


Fig. S3. Ortep-style plot of the asymmetric unit of **CFA-5**. Thermal ellipsoids probability: 50 %. Hydrogen atoms are omitted for clarity.

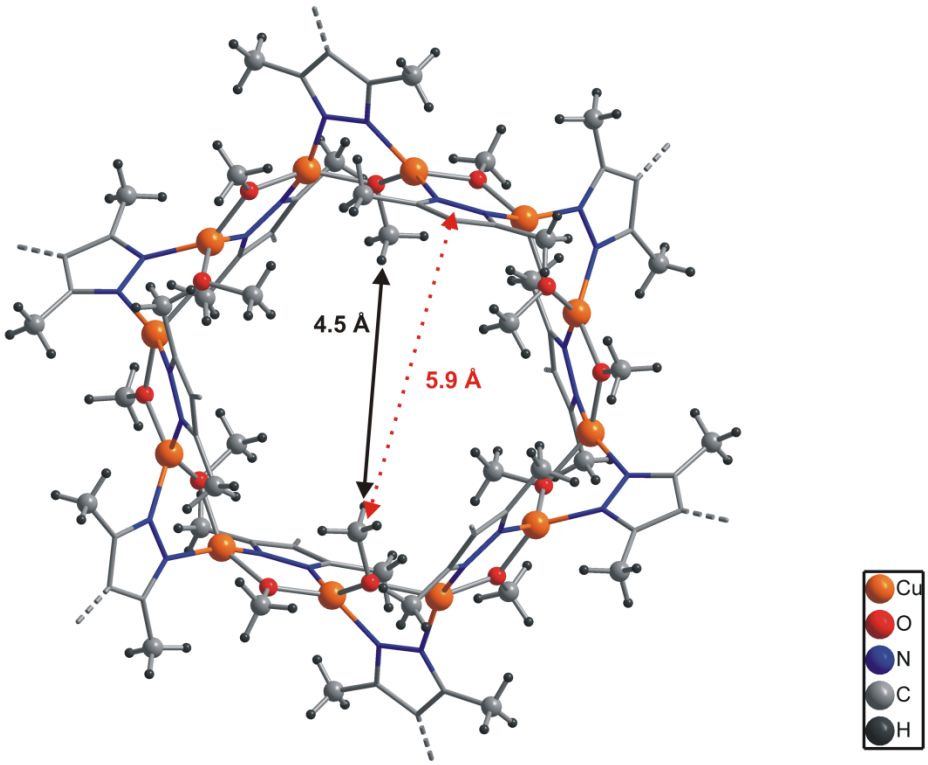


Fig. S4. Channel diameter in the **CFA-5** structure.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **CFA-5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5251(1)	6091(1)	1177(1)	14(1)
Cu(2)	5811(1)	7490(1)	1302(1)	13(1)
O(1)	5715(2)	6796(2)	1782(3)	18(1)
O(2)	4469(2)	5473(2)	1035(3)	22(1)
N(1)	5323(2)	6525(2)	172(3)	15(1)
N(2)	5485(2)	7092(2)	229(3)	11(1)
N(3)	6394(2)	8259(2)	962(3)	10(1)
N(4)	5380(2)	5593(2)	1908(3)	13(1)
C(1)	5187(3)	6359(3)	-632(4)	18(2)
C(2)	5244(3)	6816(3)	-1116(4)	13(2)
C(3)	5432(3)	7271(3)	-544(4)	16(2)
C(4)	5020(4)	5760(3)	-910(5)	31(2)
C(5)	5538(3)	7868(3)	-711(5)	26(2)
C(6)	5173(3)	6828(3)	-2041(4)	13(2)
C(7)	4655(3)	6453(3)	-2452(4)	15(2)
C(8)	4633(3)	6460(3)	-3327(4)	15(2)
C(9)	6847(3)	8460(3)	424(4)	13(1)
C(10)	6932(3)	8069(3)	-141(4)	13(1)
C(11)	7201(3)	9053(3)	552(4)	13(1)
C(12)	7714(3)	9450(3)	69(4)	13(1)
C(13)	7688(3)	9463(3)	-810(4)	13(1)
C(14)	8233(3)	9832(3)	470(4)	10(1)
C(15)	5853(3)	5591(3)	2141(4)	17(2)
C(16)	6423(3)	5978(3)	1727(5)	25(2)
C(17)	5926(5)	6825(5)	2626(6)	68(2)
C(18)	4041(5)	5640(5)	680(7)	68(2)

Table S4. Bond lengths [Å] and angles [°] for **CFA-5**.

Cu(1)-O(1)	1.923(4)	C(1)-C(4)	1.502(9)
Cu(1)-N(4)	1.924(5)	C(2)-C(3)	1.396(9)
Cu(1)-N(1)	1.925(5)	C(2)-C(6)	1.480(9)
Cu(1)-O(2)	1.929(5)	C(3)-C(5)	1.504(9)
Cu(2)-O(1)	1.904(4)	C(6)-C(13)#3	1.388(9)
Cu(2)-O(2)#1	1.921(4)	C(6)-C(7)	1.403(9)
Cu(2)-N(3)	1.942(5)	C(7)-C(8)	1.387(9)
Cu(2)-N(2)	1.963(5)	C(8)-C(14)#3	1.375(9)
O(1)-C(17)	1.439(11)	C(9)-C(11)	1.402(9)
O(2)-C(18)	1.531(11)	C(9)-C(10)	1.481(9)
O(2)-Cu(2)#2	1.921(4)	C(11)-C(15)#1	1.396(9)
N(1)-C(1)	1.337(8)	C(11)-C(12)	1.466(9)
N(1)-N(2)	1.359(7)	C(12)-C(13)	1.394(9)
N(2)-C(3)	1.349(8)	C(12)-C(14)	1.403(9)
N(3)-C(9)	1.355(8)	C(13)-C(6)#3	1.388(9)
N(3)-N(4)#1	1.363(7)	C(14)-C(8)#3	1.375(9)
N(4)-C(15)	1.326(8)	C(15)-C(11)#2	1.396(9)
N(4)-N(3)#2	1.363(7)	C(15)-C(16)	1.503(9)
C(1)-C(2)	1.386(9)		

O(1)-Cu(1)-N(4)	97.5(2)	N(3)#2-N(4)-Cu(1)	117.6(4)
O(1)-Cu(1)-N(4)	97.5(2)	N(1)-C(1)-C(2)	109.8(6)
O(1)-Cu(1)-N(1)	89.7(2)	N(1)-C(1)-C(4)	121.4(6)
N(4)-Cu(1)-N(1)	156.9(2)	C(2)-C(1)-C(4)	128.7(6)
O(1)-Cu(1)-O(2)	142.6(2)	C(1)-C(2)-C(3)	104.3(6)
N(4)-Cu(1)-O(2)	88.3(2)	C(1)-C(2)-C(6)	127.4(6)
N(1)-Cu(1)-O(2)	99.2(2)	C(3)-C(2)-C(6)	128.0(6)
O(1)-Cu(2)-O(2)#1	98.2(2)	N(2)-C(3)-C(2)	109.4(6)
O(1)-Cu(2)-N(3)	142.5(2)	N(2)-C(3)-C(5)	122.8(6)
O(2)#1-Cu(2)-N(3)	89.8(2)	C(2)-C(3)-C(5)	127.7(6)
O(1)-Cu(2)-N(2)	90.5(2)	C(13)#3-C(6)-C(7)	118.8(6)
O(2)#1-Cu(2)-N(2)	144.6(2)	C(13)#3-C(6)-C(2)	118.7(6)
N(3)-Cu(2)-N(2)	104.0(2)	C(7)-C(6)-C(2)	122.4(6)

C(17)-O(1)-Cu(2)	117.5(5)	C(8)-C(7)-C(6)	119.2(6)
C(17)-O(1)-Cu(1)	124.0(5)	C(14)#3-C(8)-C(7)	121.8(6)
Cu(2)-O(1)-Cu(1)	117.9(2)	N(3)-C(9)-C(11)	109.0(6)
C(18)-O(2)-Cu(2)#2	109.9(5)	N(3)-C(9)-C(10)	121.5(6)
C(18)-O(2)-Cu(1)	116.4(5)	C(11)-C(9)-C(10)	129.4(6)
Cu(2)#2-O(2)-Cu(1)	113.3(2)	C(15)#1-C(11)-C(9)	104.6(6)
C(1)-N(1)-N(2)	108.6(5)	C(15)#1-C(11)-C(12)	127.9(6)
C(1)-N(1)-Cu(1)	131.0(5)	C(9)-C(11)-C(12)	127.3(6)
N(2)-N(1)-Cu(1)	120.1(4)	C(13)-C(12)-C(14)	118.5(6)
C(3)-N(2)-N(1)	107.8(5)	C(13)-C(12)-C(11)	119.9(6)
C(3)-N(2)-Cu(2)	133.6(4)	C(14)-C(12)-C(11)	121.5(6)
N(1)-N(2)-Cu(2)	118.2(4)	C(11)#2-C(15)-C(16)	129.2(6)
C(9)-N(3)-N(4)#1	107.6(5)	C(6)#3-C(13)-C(12)	121.9(6)
C(9)-N(3)-Cu(2)	133.1(4)	C(8)#3-C(14)-C(12)	119.7(6)
N(4)#1-N(3)-Cu(2)	118.2(4)	N(4)-C(15)-C(11)#2	109.5(6)
C(15)-N(4)-N(3)#2	109.4(5)	N(4)-C(15)-C(16)	121.4(6)
C(15)-N(4)-Cu(1)	132.5(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x-y+2/3,x+1/3,-z+1/3, #2 y-1/3,-x+y+1/3,-z+1/3, #3 -x+4/3,-y+5/3,-z-1/3

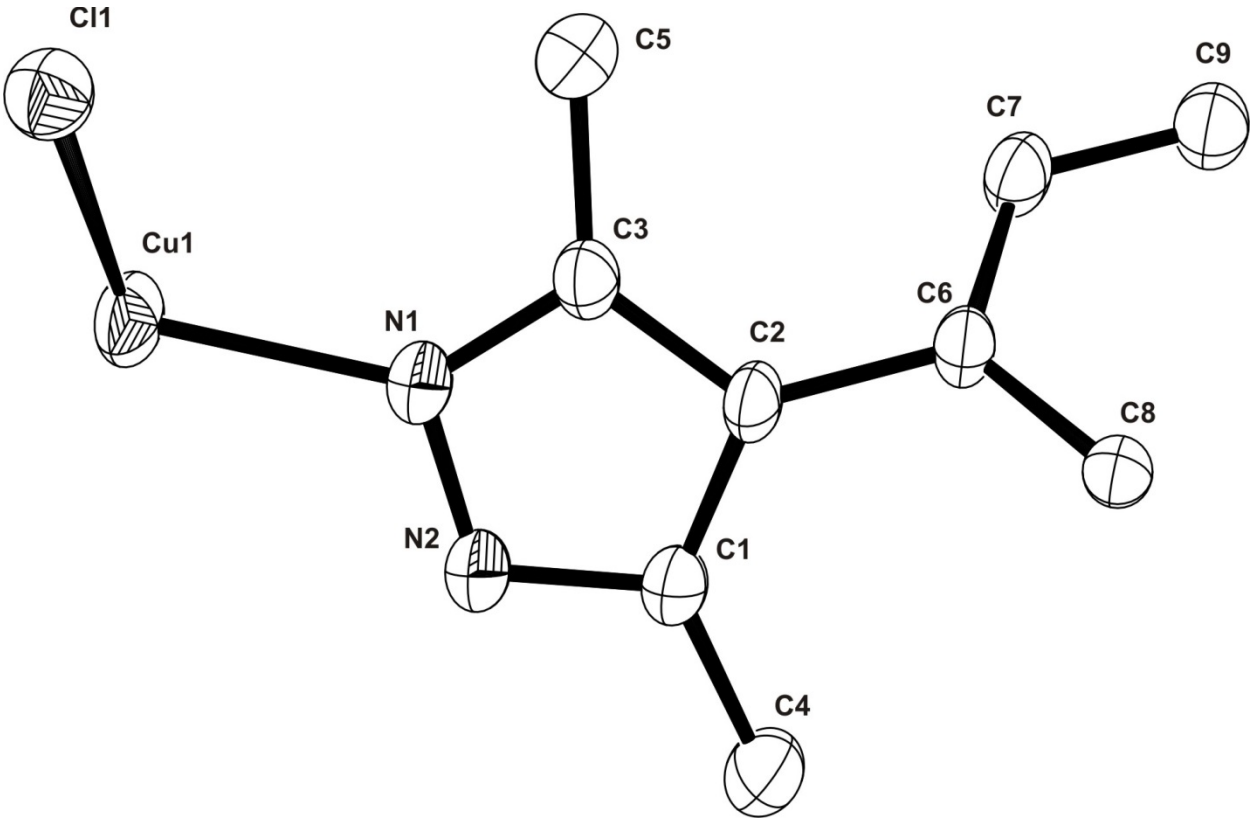


Fig. S5. Ortep-style plot of the asymmetric unit of [CuCl(H_2-1,3-bdpb)]. Thermal ellipsoids probability: 50 %. Hydrogen atoms are omitted for clarity.

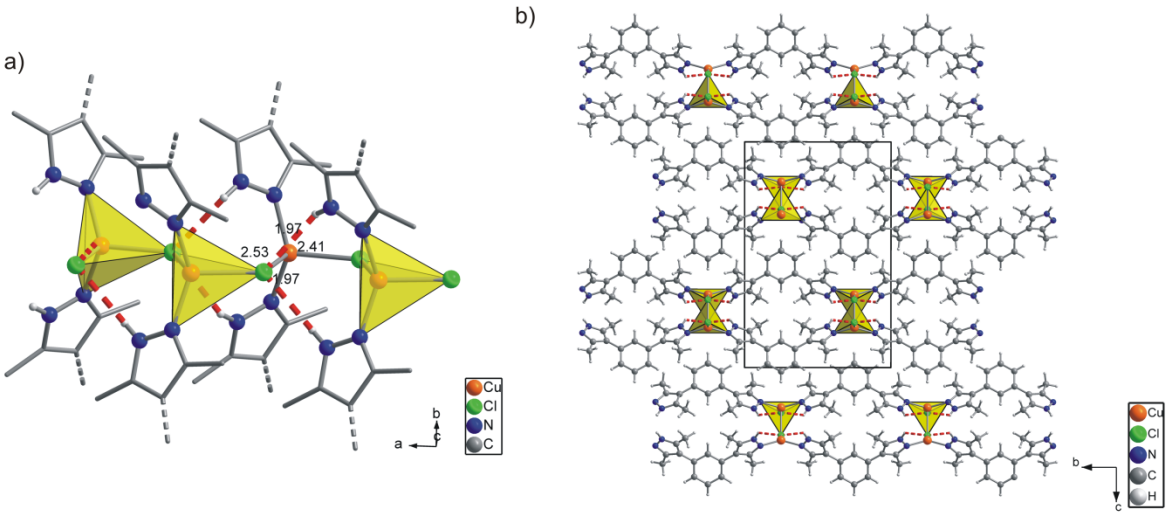


Fig. S6 (a) Schematic representation of a selected part of the crystal structure of [Cu^{I}Cl(H_2-1,3-bdpb)] showing the coordination of Cu(I) ions within zigzag chains expanding in [100] direction. Hydrogen bonds shown as intercepted red lines (b) Crystal packing diagram of [Cu^{I}Cl(H_2-1,3-bdpb)].

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [CuCl(H_2-1,3-bdpb)]. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Cu(1)	6632(1)	12500	6778(1)	35(1)
Cl(1)	10474(2)	12500	6999(1)	31(1)
N(1)	5750(5)	11085(2)	6528(2)	31(1)
C(1)	3707(6)	9660(3)	6617(2)	31(1)
N(2)	3993(5)	10645(2)	6818(2)	33(1)
C(2)	5384(6)	9435(2)	6179(2)	27(1)
C(3)	6595(5)	10358(3)	6140(2)	27(1)
C(4)	1825(7)	9044(3)	6867(2)	47(1)
C(5)	8557(6)	10598(3)	5731(2)	41(1)
C(6)	5766(6)	8444(2)	5830(2)	27(1)
C(7)	6403(6)	8431(3)	5153(2)	33(1)
C(8)	5497(8)	7500	6157(2)	27(1)
C(9)	6730(9)	7500	4823(3)	37(1)

Table S6. Bond lengths [Å] and angles [º] for [Cu^{I}Cl(H_2-1,3-bdpb)].

Cu(1)-N(1)	1.969(3)	C(1)-C(4)	1.493(5)
Cu(1)-N(1)#1	1.969(3)	C(2)-C(3)	1.409(5)
Cu(1)-Cl(1)	2.4136(15)	C(2)-C(6)	1.474(4)
Cu(1)-Cl(1)#2	2.5340(14)	C(3)-C(5)	1.492(5)
Cl(1)-Cu(1)#3	2.5340(14)	C(6)-C(8)	1.391(4)
N(1)-C(3)	1.322(4)	C(6)-C(7)	1.400(5)
N(1)-N(2)	1.353(4)	C(7)-C(9)	1.385(4)
C(1)-N(2)	1.344(5)	C(8)-C(6)#4	1.391(4)
C(1)-C(2)	1.384(5)	C(9)-C(7)#4	1.385(4)

N(1)-Cu(1)-N(1)#1	136.08(18)	C(1)-N(2)-N(1)	112.1(3)
N(1)-Cu(1)-Cl(1)	108.54(9)	C(1)-C(2)-C(3)	104.8(3)
N(1)#1-Cu(1)-Cl(1)	108.54(9)	C(1)-C(2)-C(6)	126.8(3)
N(1)-Cu(1)-Cl(1)#2	99.38(9)	C(3)-C(2)-C(6)	128.4(3)

N(1)#1-Cu(1)-Cl(1)#2	99.38(9)	N(1)-C(3)-C(2)	110.9(3)
Cl(1)-Cu(1)-Cl(1)#2	95.93(4)	N(1)-C(3)-C(5)	119.4(3)
Cu(1)-Cl(1)-Cu(1)#3	116.89(5)	C(2)-C(3)-C(5)	129.6(3)
C(3)-N(1)-N(2)	105.5(3)	C(8)-C(6)-C(7)	118.2(3)
C(3)-N(1)-Cu(1)	134.1(3)	C(8)-C(6)-C(2)	121.3(3)
N(2)-N(1)-Cu(1)	120.2(2)	C(7)-C(6)-C(2)	120.5(3)
N(2)-C(1)-C(2)	106.7(3)	C(9)-C(7)-C(6)	120.4(3)
N(2)-C(1)-C(4)	120.5(3)	C(6)#4-C(8)-C(6)	122.2(4)
C(2)-C(1)-C(4)	132.8(3)	C(7)#4-C(9)-C(7)	120.5(5)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+5/2,z; #2 x-1/2,-y+5/2,-z+3/2; #3 x+1/2,-y+5/2,-z+3/2; #4 x,-y+3/2,z

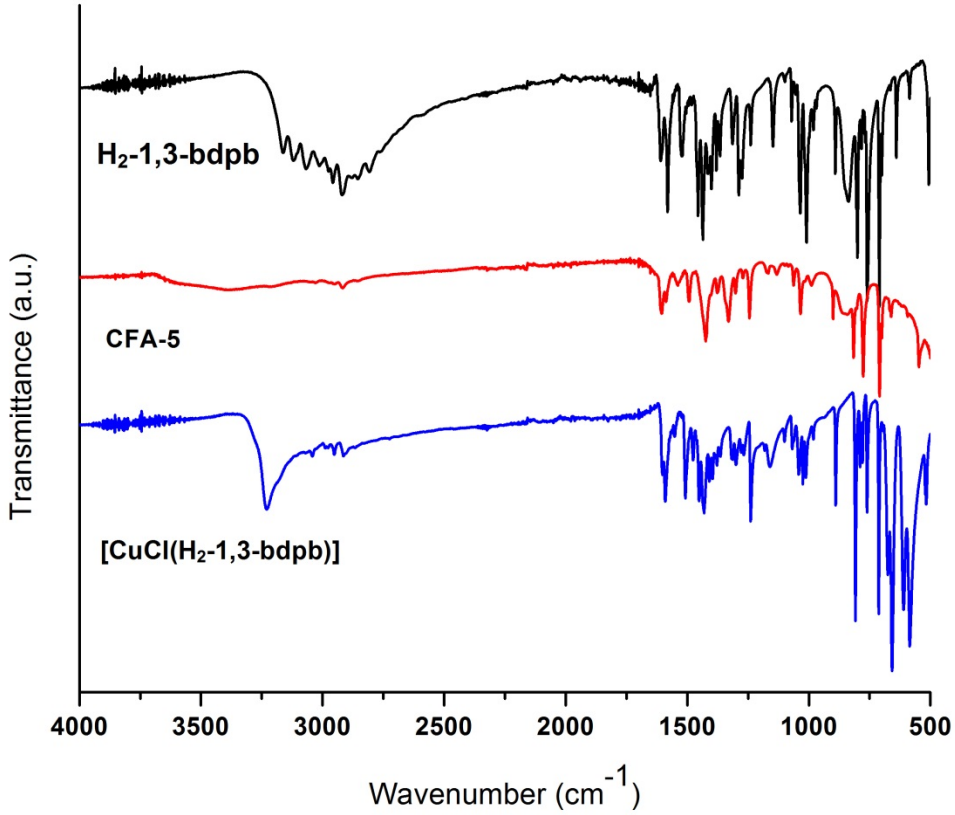


Fig. S7. IR spectra for H_2-1,3-bdpb**, CFA-5** and [CuCl(H_2-1,3-bdpb)].

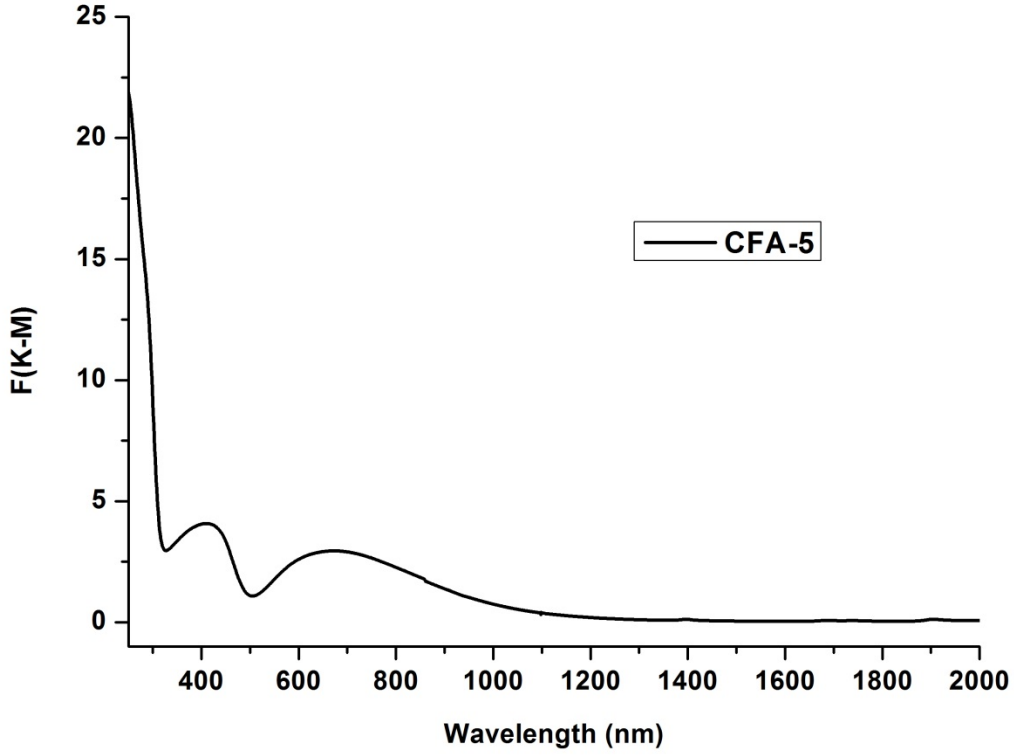


Fig. S8. UV/Vis spectrum of **CFA-5**.