Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Characterization of a flexible Metal Organic Framework generated from Mn^{III} and the 4,4'-Bipyrazolate-Ligand

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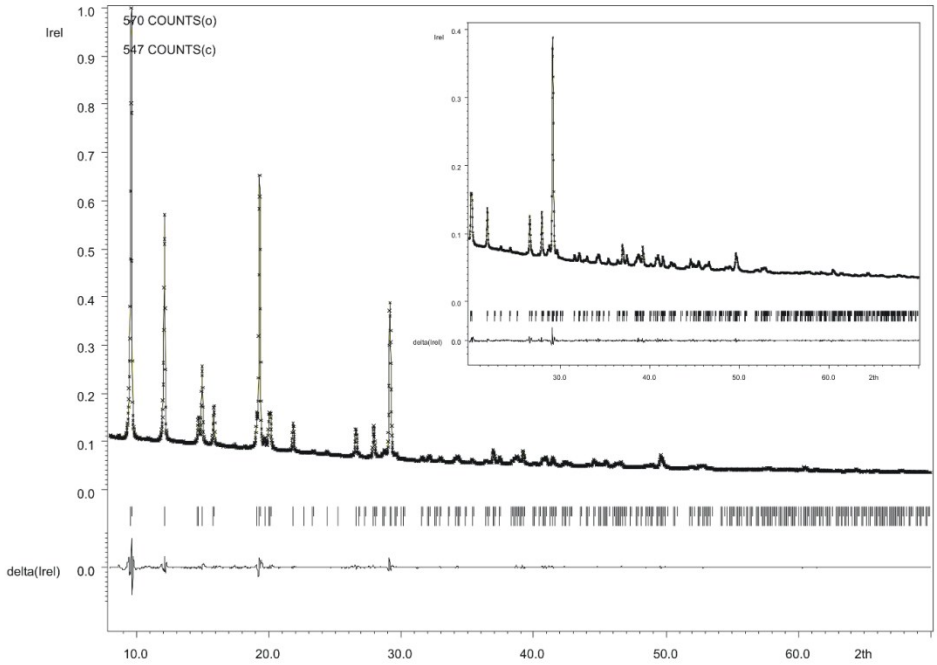

Figure S1: *Le Bail fit of the XRPD pattern of compound Mn-CFA-6. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. Rp=1.24, wRp=2.20.*

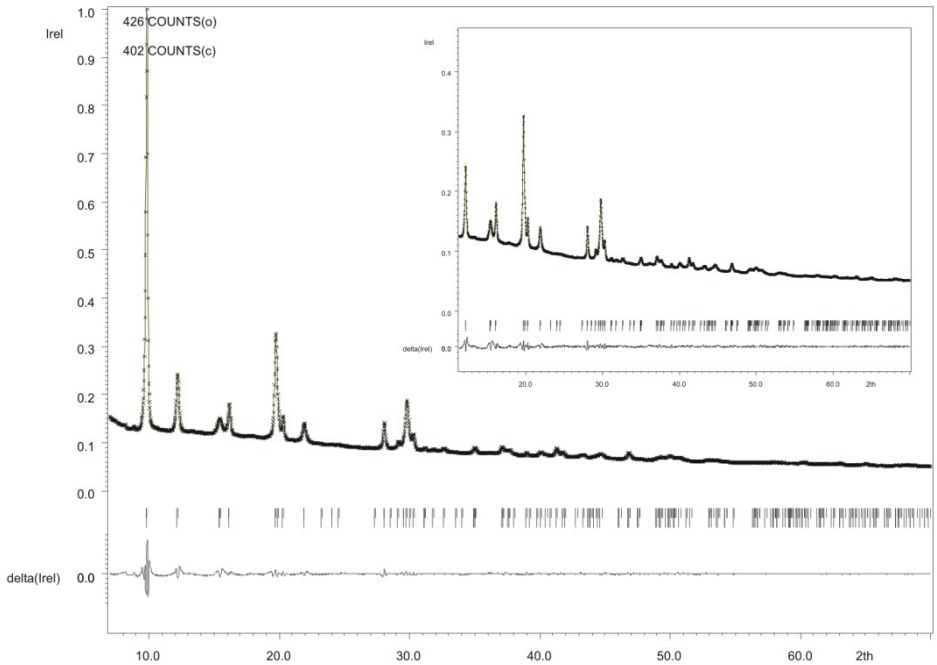

Figure S2: *Le Bail fit of the XRPD pattern of the compound Mn-CFA-6 after the solvent removal. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom. Rp=1.37, wRp=2.17.*

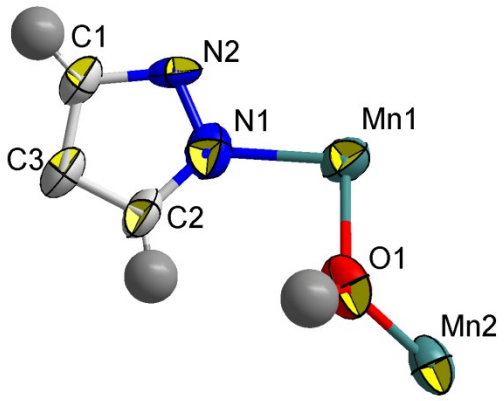

Figure S3: *ORTEP-style plot of the asymmetric unit of Mn-CFA-6 showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.*

Table S1: *Atomic coordinates (·10⁴) and equivalent isotropic displacement parameters (Å²·10³) for twin4a_sq. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.*

Atom	x	y	z	U(eq)
Mn(1)	0	0	0	55(3)
Mn(2)	0	0	5000	58(3)
O(1)	1041(14)	0	3730(40)	67(7)
N(1)	937(14)	975(12)	-580(40)	65(5)
N(2)	951(14)	981(11)	7500(30)	50(5)
C(1)	1691(16)	1664(13)	-2500(40)	56(5)
C(2)	1619(16)	1643(13)	710(40)	56(4)
C(3)	2075(16)	2090(13)	-440(40)	58(5)

Table S2: *Bond lengths [Å] and angles [°] for twin4a_sq.*

Mn(1)-N(1)#1	2.017(19)
Mn(1)-N(1)#2	2.017(19)
Mn(1)-N(1)#3	2.017(19)
Mn(1)-N(1)	2.017(19)
Mn(1)-O(1)	2.25(2)
Mn(1)-O(1)#1	2.25(2)
Mn(2)-O(1)	1.87(2)
Mn(2)-O(1)#4	1.87(2)

Mn(2)-N(2)	2.143(17)
Mn(2)-N(2)#2	2.143(17)
Mn(2)-N(2)#4	2.143(17)
Mn(2)-N(2)#5	2.143(17)
N(1)-N(2)#6	1.29(2)
N(1)-C(2)	1.35(3)
N(2)-C(1)#7	1.39(2)
C(1)-C(3)	1.39(3)
C(3)-C(2)	1.32(3)
C(3)-C(3)#8	1.56(4)
N(1)#1-Mn(1)-N(1)#2	89.3(10)
N(1)#1-Mn(1)-N(1)#3	90.7(10)
N(1)#2-Mn(1)-N(1)#3	180.0(10)
N(1)#1-Mn(1)-N(1)	180.0
N(1)#2-Mn(1)-N(1)	90.7(10)
N(1)#3-Mn(1)-N(1)	89.3(10)
N(1)#1-Mn(1)-O(1)	85.1(8)
N(1)#2-Mn(1)-O(1)	94.9(8)
N(1)#3-Mn(1)-O(1)	85.1(8)
N(1)-Mn(1)-O(1)	94.9(8)
N(1)#1-Mn(1)-O(1)#1	94.9(8)
N(1)#2-Mn(1)-O(1)#1	85.1(8)
N(1)#3-Mn(1)-O(1)#1	94.9(8)
N(1)-Mn(1)-O(1)#1	85.1(8)
O(1)-Mn(1)-O(1)#1	180.0
O(1)-Mn(2)-O(1)#4	180.0
O(1)-Mn(2)-N(2)#4	86.2(7)
O(1)#4-Mn(2)-N(2)#4	93.8(7)
O(1)-Mn(2)-N(2)#2	93.8(7)
O(1)#4-Mn(2)-N(2)#2	86.2(7)
N(2)#4-Mn(2)-N(2)#2	95.4(10)
O(1)-Mn(2)-N(2)#5	86.2(7)
O(1)#4-Mn(2)-N(2)#5	93.8(7)
N(2)#4-Mn(2)-N(2)#5	84.6(10)
N(2)#2-Mn(2)-N(2)#5	180.0
O(1)-Mn(2)-N(2)	93.8(7)
O(1)#4-Mn(2)-N(2)	86.2(7)
N(2)#4-Mn(2)-N(2)	180.0
N(2)#2-Mn(2)-N(2)	84.6(10)

N(2)#5-Mn(2)-N(2)	95.4(10)
Mn(2)-O(1)-Mn(1)	106.9(7)
N(2)#6-N(1)-C(2)	110.0(19)
N(2)#6-N(1)-Mn(1)	117.3(15)
C(2)-N(1)-Mn(1)	133(2)
N(1)#7-N(2)-C(1)#7	107.8(18)
N(1)#7-N(2)-Mn(2)	121.2(14)
C(1)#7-N(2)-Mn(2)	130.9(17)
N(2)#6-C(1)-C(3)	106.5(19)
C(2)-C(3)-C(1)	107(2)
C(2)-C(3)-C(3)#8	126(3)
C(1)-C(3)-C(3)#8	128(2)
C(3)-C(2)-N(1)	109(2)

Symmetry transformations used to generate equivalent atoms:

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

#5 -x,y,-z+1; #6 x,y,z-1; #7 x,y,z+1; #8 -x+1/2,-y+1/2,-z

Table S3: *Anisotropic displacement parameters ($Å^2 \cdot 10^3$) for twin4a_sq. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	48(4)	75(5)	47(6)	0	24(4)	0
Mn(2)	44(4)	44(4)	78(7)	0	17(4)	0
O(1)	25(9)	78(13)	80(17)	0	6(10)	0
N(1)	58(9)	68(10)	76(13)	2(9)	36(9)	-5(6)
N(2)	56(10)	68(12)	31(15)	-13(10)	23(9)	5(9)
C(1)	60(9)	66(11)	58(12)	8(9)	40(9)	-6(9)
C(2)	56(8)	66(9)	62(12)	6(8)	42(8)	-7(6)
C(3)	62(8)	69(10)	59(12)	7(8)	42(8)	-5(7)

Calculation of the bond valence sums of Mn-CFA-6

The bond valence sum V represents the sum of the bond valences v_i of each coordination bond. The bond valence is calculated from a tabulated standard value for the coordination bond length R_0 which is dependent on the oxidation state of the metal center and the ligand atoms, the observed coordination bond length R_i and a tabulated constant b, in most cases 0.37. The calculated values for the BVS of Mn-CFA-6 is shown in **Table S4**, the parameters applied for the calculations of the BVS are presented in **Table S5**.

$$V = \sum v_i;\ v_i = e^{\left(\frac{R_0 - R_i}{b}\right)}$$

Table S4: *Bond valence sums (BVS) of Mn-CFA-6 calculated for manganese centers with oxidation states of +II, +III und +IV.*

	Mn(II)	Mn(III)	Mn(IV)
BVS Mn1	2.692	2.946	2.565
BVS Mn2	2.618	3.130	3.145

Table S5: *Parameters for the calculation of the BVS.*[1]

Metal center	Ligand atom	R_0 [Å]	b
Mn^{II}	O^{2-}	1.849	0.37
Mn^{II}	N^{3-}	1.765	0.37
Mn^{III}	O^{2-}	1.732	0.37
Mn^{III}	N^{3-}	1.837	0.37
Mn^{IV}	O^{2-}	1.822	0.37
Mn^{IV}	N^{3-}	1.750	0.37

1. Liu, W.; Thorp, H. H. Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. 2. Refined distances and other enzymes. *Inorg. Chem.* **1993,** *32*, 4102-4105.

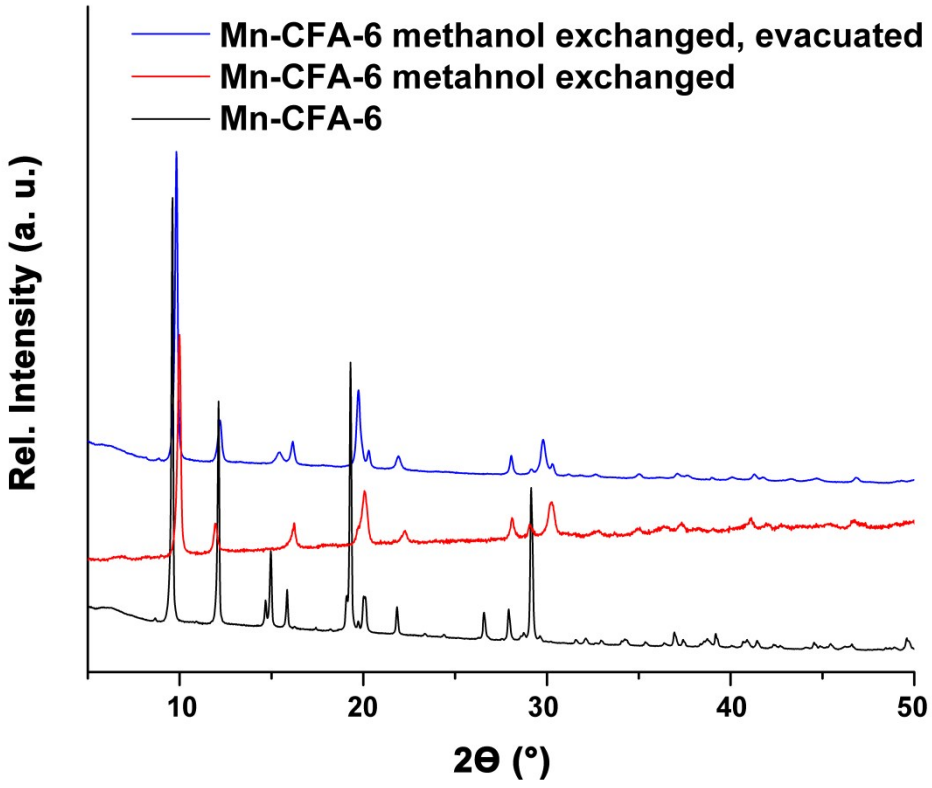

Figure S4: Powder patterns of Mn-CFA-6. Solvent exchange by Soxhlet extraction leads to a change of the unit cell of Mn-CFA-6.

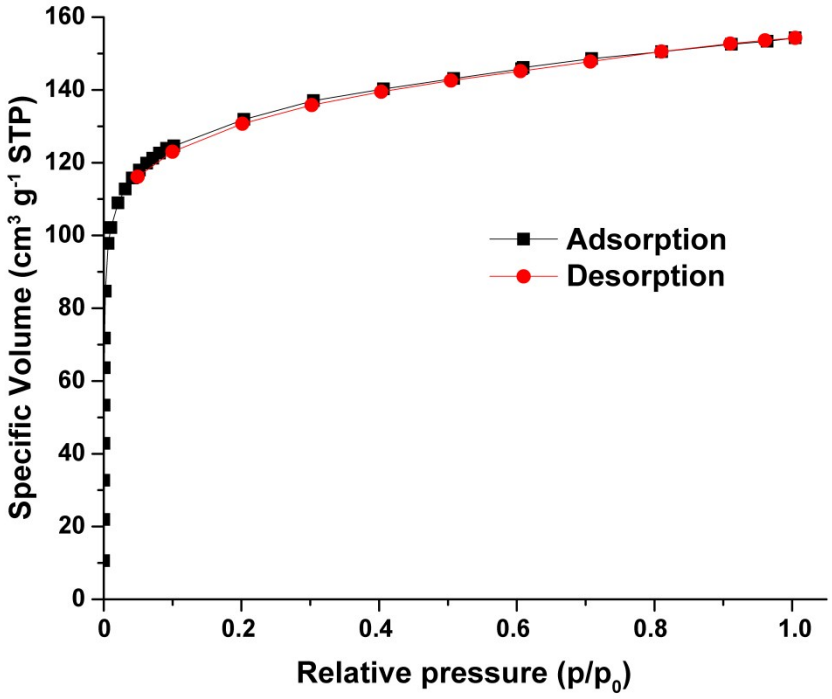

Figure S5: Carbon dioxide sorption measurement of the solvent exchanged and evacuated sample of Mn-CFA-6 at 195 K.