Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Fe/Ga-CFA-6 – metal organic frameworks featuring trivalent metal centers and the 4,4'-bipyrazolyl ligand

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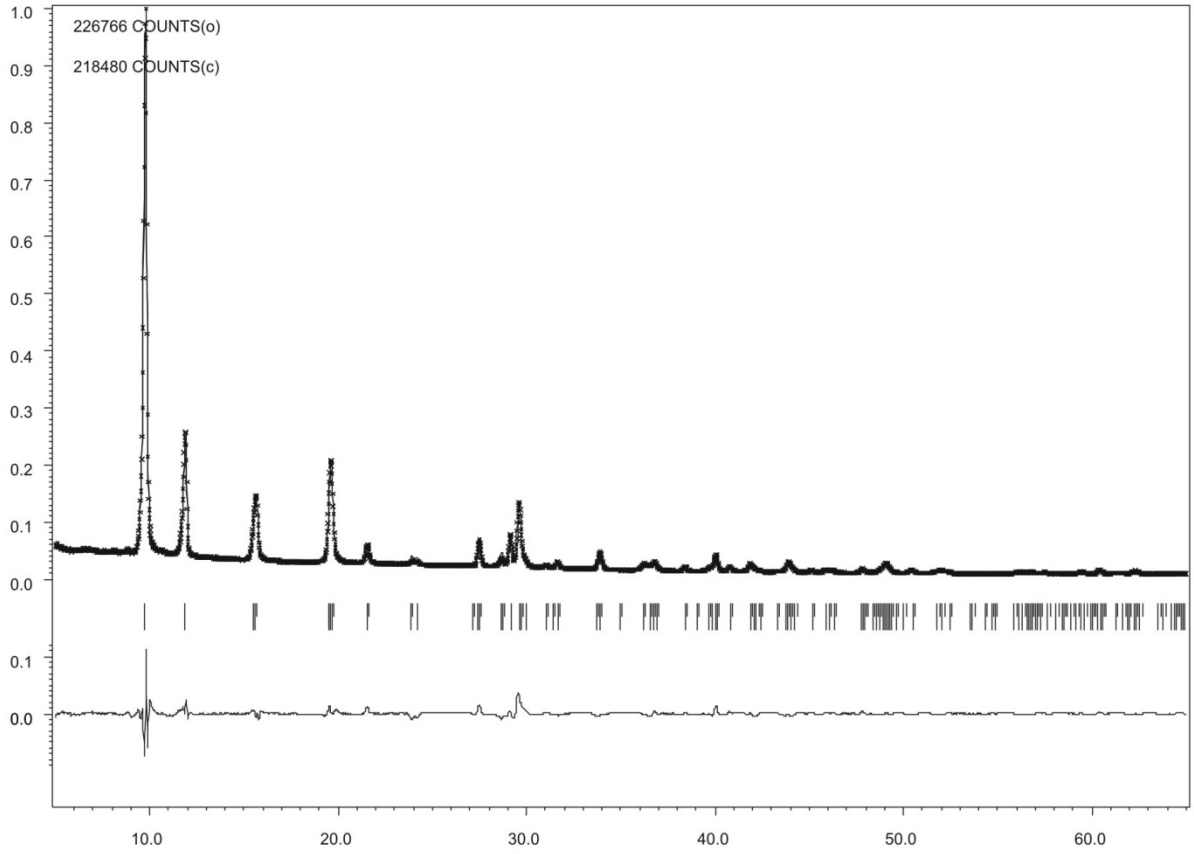

Fig. S1 Rietveld refinement plots for **Ga-CFA-6·2 H_2O**. Dotted and solid lines represent observed and calculated patterns, respectively with peak markers and the difference plot shown at the bottom.

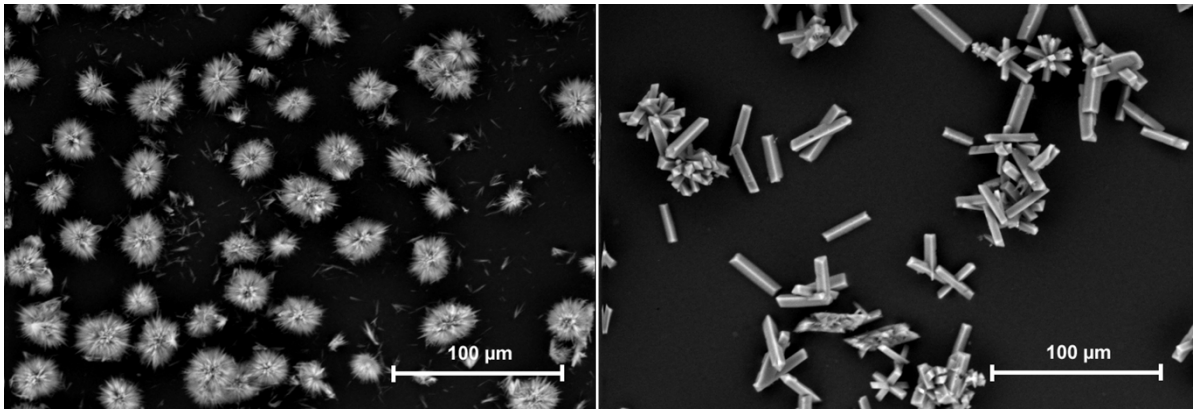

Fig. S2 ESEM images of compounds **Ga-CFA-6** (left) and **Fe-CFA-6** (right) revealing the morphology of the polycrystalline powder of **Ga-CFA-6** and the block-shaped morphology of the crystals of **Fe-CFA-6**.

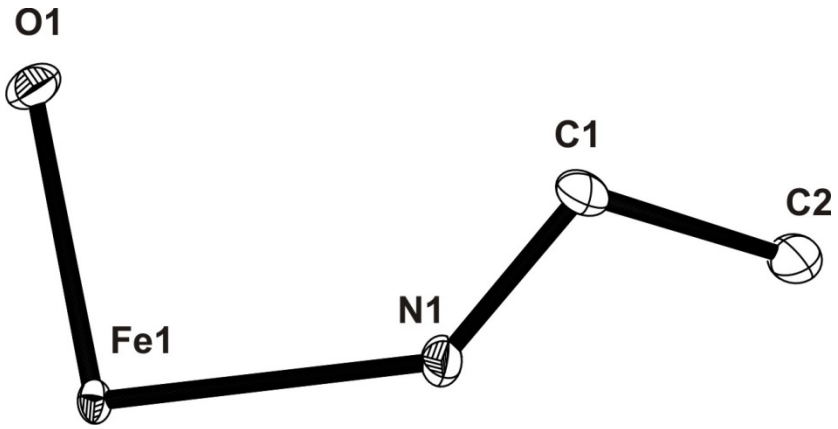

Fig. S3 Ortep-style plot of the asymmetric unit of **Fe-CFA-6·0.6 DMAc**. Thermal ellipsoids probability: 50 %. Hydrogen atoms are omitted.

Table S1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **Fe-CFA-6·0.6 DMAc**. *U(eq)* is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	*U(eq)*
Fe(1)	5000	5000	5000	5(1)
C(1)	6652(2)	5855(6)	6651(3)	16(1)
C(2)	7118(4)	7500	7114(4)	15(1)

N(1)	5984(2)	6469(4)	5982(2)	11(1)
O(1)	5000	2500	5929(4)	11(1)

Table S2 Bond lengths [Å] and angles [°] for **Fe-CFA-6·0.6 DMAc.**

Fe(1)-O(1)	1.983(3)
Fe(1)-O(1)#1	1.983(3)
Fe(1)-N(1)#1	2.100(3)
Fe(1)-N(1)#2	2.100(3)
Fe(1)-N(1)#3	2.100(3)
Fe(1)-N(1)	2.100(3)
C(1)-N(1)	1.328(4)
C(1)-C(2)	1.401(5)
C(2)-C(1)#4	1.401(5)
C(2)-C(2)#5	1.452(10)
N(1)-N(1)#4	1.366(6)
O(1)-Fe(1)#6	1.983(3)
O(1)-Fe(1)-O(1)#1	180.0
O(1)-Fe(1)-N(1)#1	85.15(11)
O(1)#1-Fe(1)-N(1)#1	94.84(11)
O(1)-Fe(1)-N(1)#2	94.85(11)
O(1)#1-Fe(1)-N(1)#2	85.16(11)
N(1)#1-Fe(1)-N(1)#2	91.85(16)
O(1)-Fe(1)-N(1)#3	85.15(11)
O(1)#1-Fe(1)-N(1)#3	94.84(11)
N(1)#1-Fe(1)-N(1)#3	88.15(15)
N(1)#2-Fe(1)-N(1)#3	180.0
O(1)-Fe(1)-N(1)	94.85(11)
O(1)#1-Fe(1)-N(1)	85.16(11)
N(1)#1-Fe(1)-N(1)	180.0
N(1)#2-Fe(1)-N(1)	88.16(16)
N(1)#3-Fe(1)-N(1)	91.84(16)
N(1)-C(1)-C(2)	111.1(3)
C(1)#4-C(2)-C(1)	102.2(4)
C(1)#4-C(2)-C(2)#5	128.9(2)
C(1)-C(2)-C(2)#5	128.9(2)
C(1)-N(1)-N(1)#4	107.8(2)
C(1)-N(1)-Fe(1)	134.6(3)
N(1)#4-N(1)-Fe(1)	117.59(8)
Fe(1)#6-O(1)-Fe(1)	113.2(2)
Fe(1)-O(1)	1.983(3)
Fe(1)-O(1)#1	1.983(3)
Fe(1)-N(1)#1	2.100(3)
Fe(1)-N(1)#2	2.100(3)
Fe(1)-N(1)#3	2.100(3)
Fe(1)-N(1)	2.100(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1; #2 -x+1,y,z; #3 x,-y+1,-z+1; #4 x,-y+3/2,z; #5 -x+3/2,-y+3/2,-z+3/2; #6 -x+1,y-1/2,-z+1.

Table S3 Atomic coordinates and equivalent isotropic displacement parameters for **Ga-CFA-6·2 H_2O.**

	x	y	z	*U(iso)*
Ga(1)	; 0.5	; 0.5	; 0.5	0.0090(10)
C(1)	0.6650(5)	0.5864(2)	0.6657(9)	0.009(2)
C(2)	0.71171(10)	0.75	0.7112(2)	0.009(2)
N(1)	0.5988(4)	0.6412(10)	0.5960(7)	0.009(2)
O(1)	0.5	0.25	0.5872(2)	0.009(2)
O(2)	0	0.25	0.367(2)	0.009(2)
O3(3)	0	0.25	0.597(2)	0.009(2)

Table S4 Bond lengths [Å] and angles [°] for **Ga-CFA-6·2 H_2O**.

Ga1-N1	2.043(7)
Ga1-N1^{i}	2.043(7)
Ga1-N1^{ii}	2.043(7)
Ga1-N1^{iii}	2.043(7)
Ga1-O1	1.8998(12)
Ga1-O1^{iv}	1.8998(12)
C1-C1^{v}	2.1232(19)
C1-C2	1.369(6)
C1-N1	1.310(11)
C1-N1^{v}	2.171(8)
C2-C2^{vi}	1.437(3)
C2-N1	2.239(7)
C2-N1^{v}	2.239(7)
N1-N1^{v}	1.412(9)
N1-Ga1-N1^{i}	88.4(3)
N1-Ga1-N1^{ii}	180.0(5)
N1-Ga1-N1^{iii}	91.6(3)

N1-Ga1-O1	96.0(2)
N1-Ga1-O1^{iv}	84.0(2)
N1^{i}-Ga1-N1^{ii}	91.6(3)
N1^{i}-Ga1-N1^{iii}	180.0(5)
N1^{i}-Ga1-O1	84.0(2)
N1^{i}-Ga1-O1^{iv}	96.0(2)
N1^{ii}-Ga1-N1^{iii}	88.4(3)
N1^{ii}-Ga1-O1	84.0(2)
N1^{ii}-Ga1-O1^{iv}	96.0(2)
N1^{iii}-Ga1-O1	96.0(2)
N1^{iii}-Ga1-O1^{iv}	84.0(2)
O1-Ga1-O1^{iv}	180.0(5)
C1^{v}-C1-C2	39.1(2)
C1^{v}-C1-N1	74.2(4)
C1^{v}-C1-N1^{v}	35.5(3)
C2-C1-N1	113.4(4)
C2-C1-N1^{v}	74.6(2)
N1-C1-N1^{v}	38.7(3)
C1-C2-C1^{v}	101.7(4)
C1-C2-C2^{vi}	129.1(3)
C1-C2-N1	32.5(3)
C1-C2-N1^{v}	69.2(3)
C1^{v}-C2-C2^{vi}	129.1(3)
C1^{v}-C2-N1	69.2(3)
C1^{v}-C2-N1^{v}	32.5(3)
C2^{vi}-C2-N1	161.62(17)

C2^{vi}-C2-N1^{v}	161.62(17)
N1-C2-N1^{v}	36.8(2)
Ga1-N1-C1	137.6(5)
Ga1-N1-C1^{v}	152.1(4)
Ga1-N1-C2	171.7(4)
Ga1-N1-N1^{v}	116.6(5)
C1-N1-C1^{v}	70.3(4)
C1-N1-C2	34.1(2)
C1-N1-N1^{v}	105.8(5)
C1^{v}-N1-C2	36.1(2)
C1^{v}-N1-N1^{v}	35.5(4)
C2-N1-N1^{v}	71.6(4)
Ga1-O1-Ga1^{vii}	117.23(12)

Symmetry transformations used to generate equivalent atoms:

(i) x,-y+1,-z+1; (ii) -x+1,-y+1,-z+1; (iii) -x+1,y,z; (iv) -x+1,y+1/2,-z+1; (v) x,-y+3/2,z; (vi) -x+3/2,y+1,-z+3/2; (vii) -x+1,-y+1/2,z

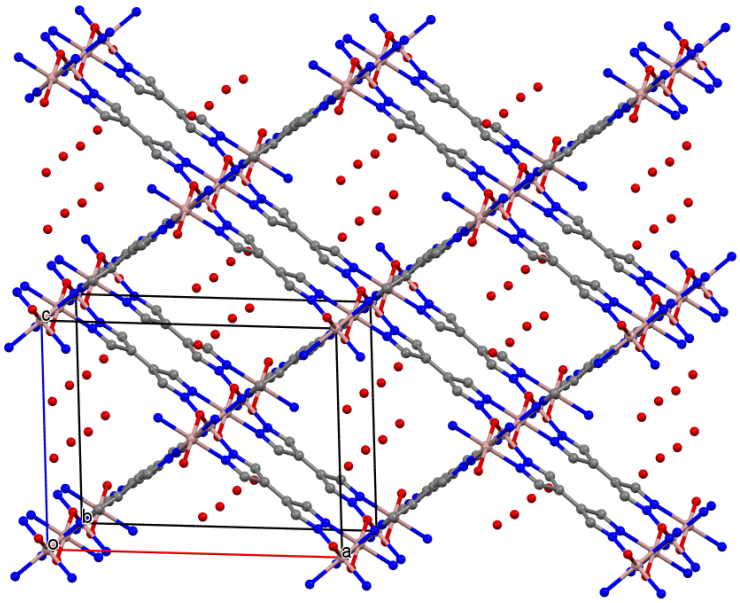

Fig. S4 Packing plot of **Ga-CFA-6·2 H_2O.** Octahedrally coordinated Ga atoms (pink), nitrogen (blue) and carbon (grey) atoms of the 4,4'-bipyrazolyl ligand and oxygen atoms (red) of bridging hydroxyl groups form the framework. Oxygen atoms of water molecules inside the pores complete the structure.

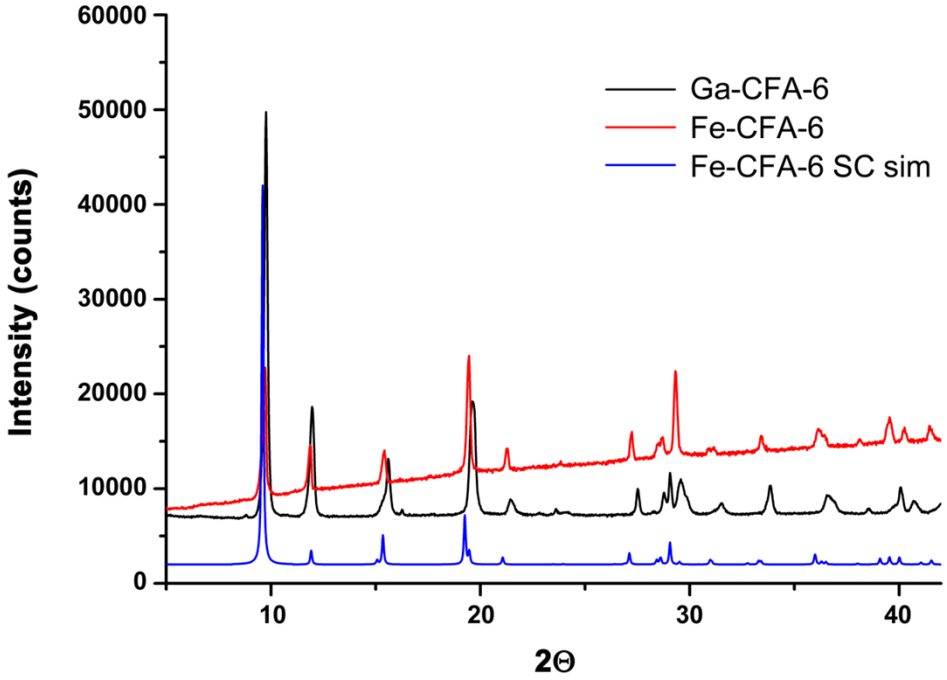

Fig. S5 X-ray powder patterns of **Ga-CFA-6** (black), **Fe-CFA-6** (red) and the XRPD pattern calculated from the single crystal data of **Fe-CFA-6** (blue).

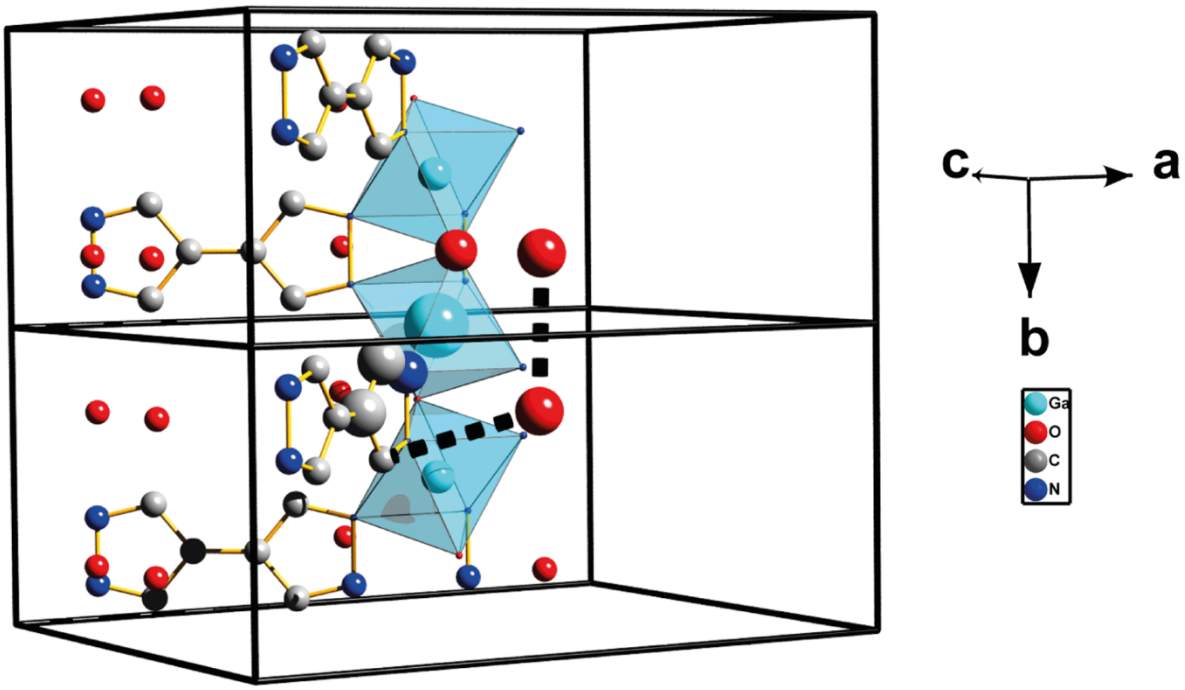

Fig. S6 Out-take of the structure solution of **Ga-CFA-6**. The coordination octahedrons around the Ga atoms are indicated and for clarity some parts of the structure are omitted. The atoms drawn with larger radius correspond to the content of the asymmetric unit. The conjunction lines between one oxygen of a water molecule to a second oxygen atom of a water molecule and to a carbon atom of the pyrazolate ring are drawn dashed and black. The angle between those is approximately 109°. On the other side of the pyrazolate ring no similarly oriented oxygen atoms are present.

Table S5. Unit cell parameters for the **Ga-** and **Fe-CFA-6** heated at the temperature range of 300 – 400 °C.

Sample	Temp. (°C)	a (Å)	b (Å)	c (Å)	α=β=γ = 90 (°)	V (Å^3)	Figure of merits
Ga-CFA-6	300	14.768(8)	6.525(3)	11.482(3)	90	1106.4(2)	M_{20}=11 F_{20}=13
Ga-CFA-6	350	15.009(8)	6.528(3)	11.115(9)	90	1088.9(5)	M_{20}=10 F_{20}=12
Ga-CFA-6	400	15.341(5)	6.534(3)	10.598(1)	90	1062.3(7)	M_{20}=11 F_{20}=19
Fe-CFA-6	300	14.361(6)	6.438(6)	9.069(3)	90	838.5(4)	M_8=86.0 F_8=72.9

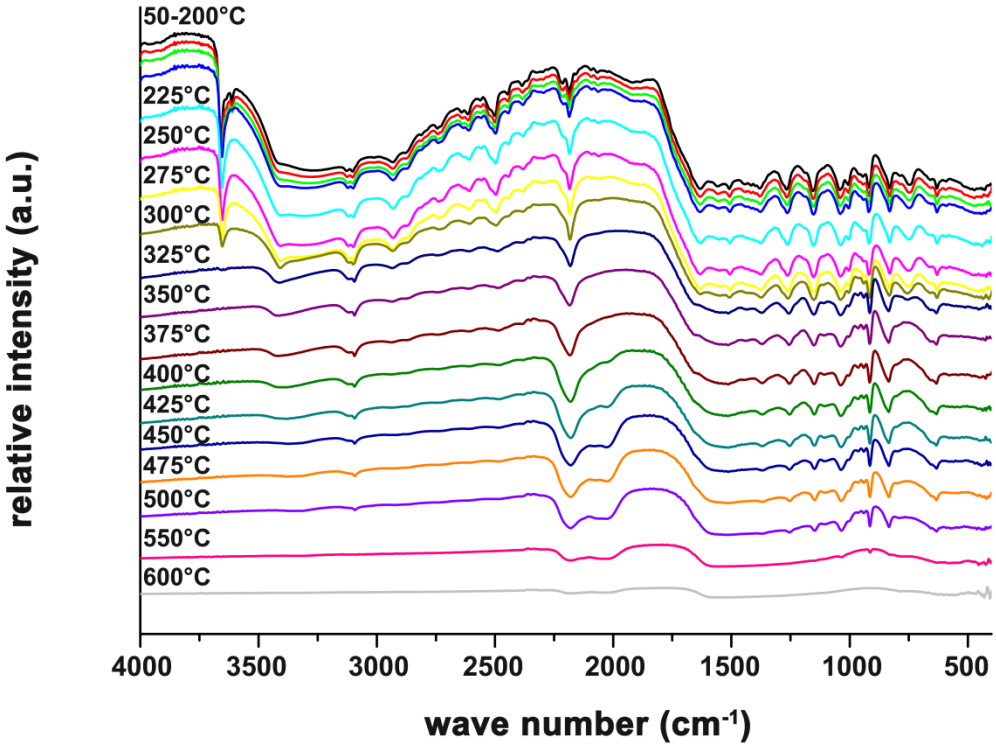

Fig. S7 DRIFT-spectra of **Fe-CFA-6** were recorded under N_2-atmosphere from 50 °C to 600 °C. No significant changes in the spectra can be found in the range of 50°C to 300 °C. First changes in connectivity appear above 300 °C with the disappearance of the O-H stretch at 3680 cm^{-1} and the disappearance of the band at 750 °C (Fe-OH stretch). A new IR-band at *ca.* 2025 cm^{-1} appears above 350 °C, indicating the formation of a ketene imine species, due to the decomposition of the ligand. At higher temperatures, the signal intensities of the spectra decrease due to decomposition of the framework. Above 500 °C a broad band at 580 cm^{-1} appears, possibly representing a Fe-O stretch.

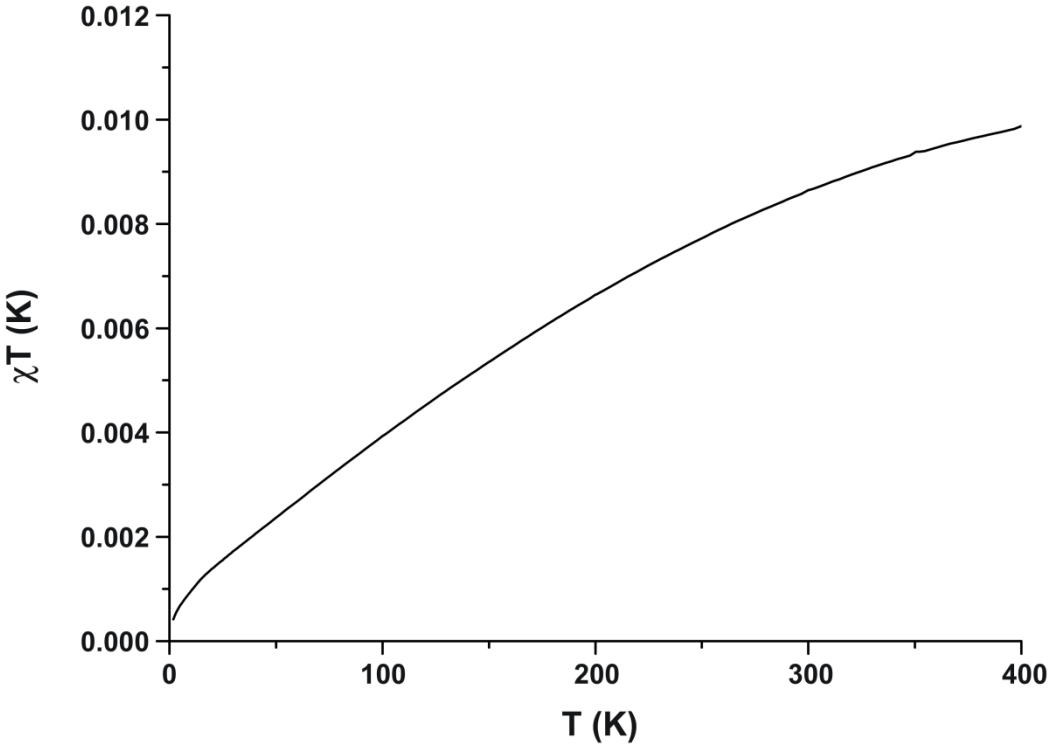

Fig. S8 χT vs. T plot of **Fe-CFA-6** recorded from 400 to 4 K. No abrupt jumps typical for hysteretic spin crossover can be observed.