Supplementary Information

Synthesis and Breathing Behaviour of a New Member of the Fluoride-substituted Gallium MIL-53 Metal-Organic Framework Solid-Solution Series

A. R. Bonity J. Lutton-Gething,†[a] Ruxuan Lan,[a] Yongkang Huang,[a] Thomas J. Duddles,[a] Carlo Bawn,[a] Daniel Lee,[b] George F.S. Whitehead,[a] and Martin P. Attfield[a]*

[a] Department of Chemistry, School of Natural Sciences, The University of Manchester, Oxford Road, M13 9PL, United Kingdom.

[b] Department of Chemical Engineering, School of Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

† School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom.

* Corresponding Author, e-mail: *m.attfield@manchester.ac.uk*

Table S1: Summary of crystal data and structure refinement for int-**1**·0.7DEF·0.08HF.

Empirical formula	$C_8H_{4.78}F_{0.22}GaO_{4.78}$
Formula weight	254.78
Temperature/K	100(1)
Crystal system	monoclinic
Space group	I2/a
a/Å	6.6882(8)
b/Å	11.009(3)
c/Å	18.045(2)
α/°	90
β/°	92.746(11)
γ/°	90
Volume/Å^3	1327.1(4)
Z	4
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	2.869
F(000)	503.0
Crystal size/mm^3	0.061 × 0.03 × 0.009
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.414 to 91.064
Index ranges	-6 ≤ h ≤ 6, -10 ≤ k ≤ 9, -16 ≤ l ≤ 14
Reflections collected	1528
Independent reflections	554 [R_{int} = 0.0761, R_{sigma} = 0.0850]
Data/restraints/parameters	554/27/44
Goodness-of-fit on F^2	1.187
Final R indexes [I>=2σ (I)]	R_1 = 0.1020, wR_2 = 0.2914
Final R indexes [all data]	R_1 = 0.1305, wR_2 = 0.3103
Largest diff. peak/hole / e Å^{-3}	2.46/-0.60

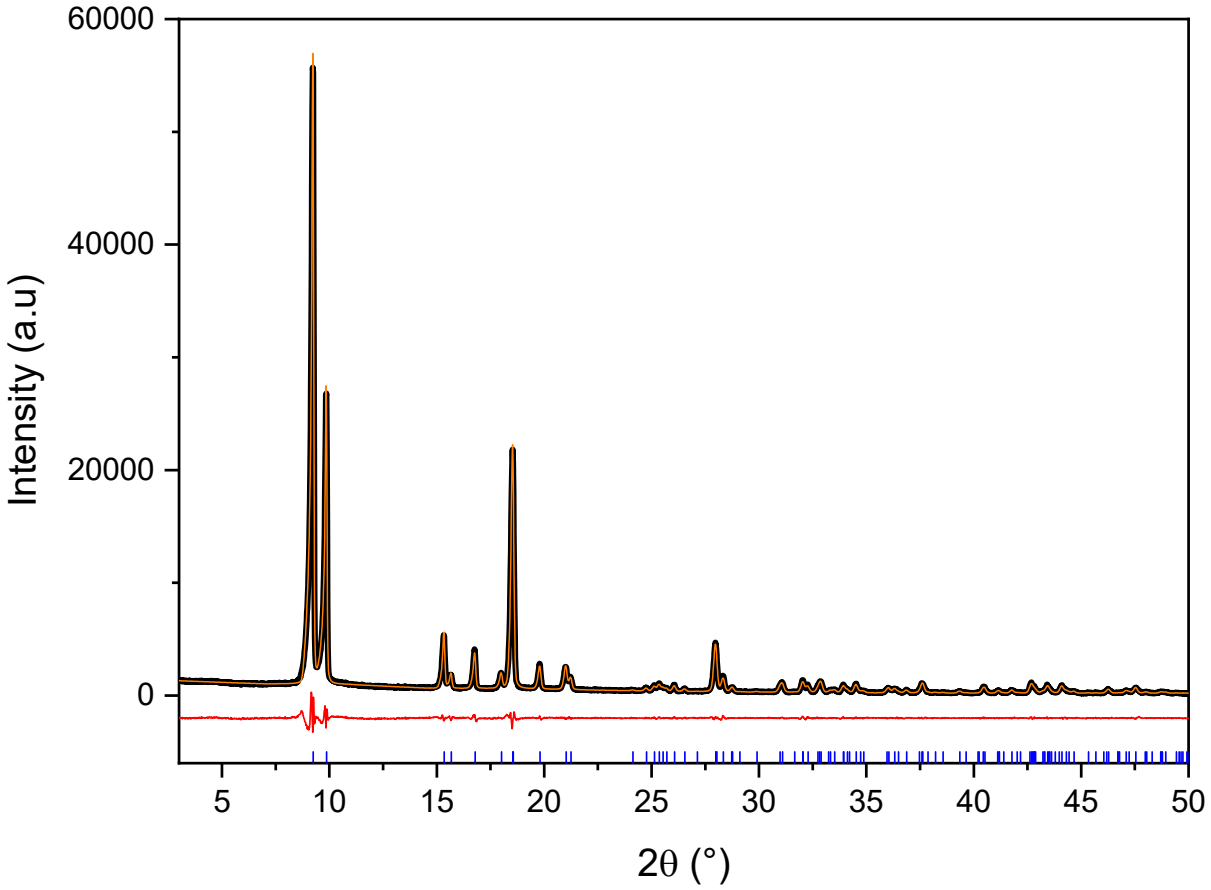

Figure S1: Pawley fit for monophasic int-**1**·0.7DEF·0.08HF. Final refined unit cell parameters: I2/a, a=6.713(3) Å, b =11.294(3) Å, c = 17.922(4) Å, β= 92.095(7)°, R_{wp} = 5.99 %, R_{exp} =2.98 %. Experimental pattern in black, calculated pattern in orange, difference plot in red and *hkl* marks in blue.

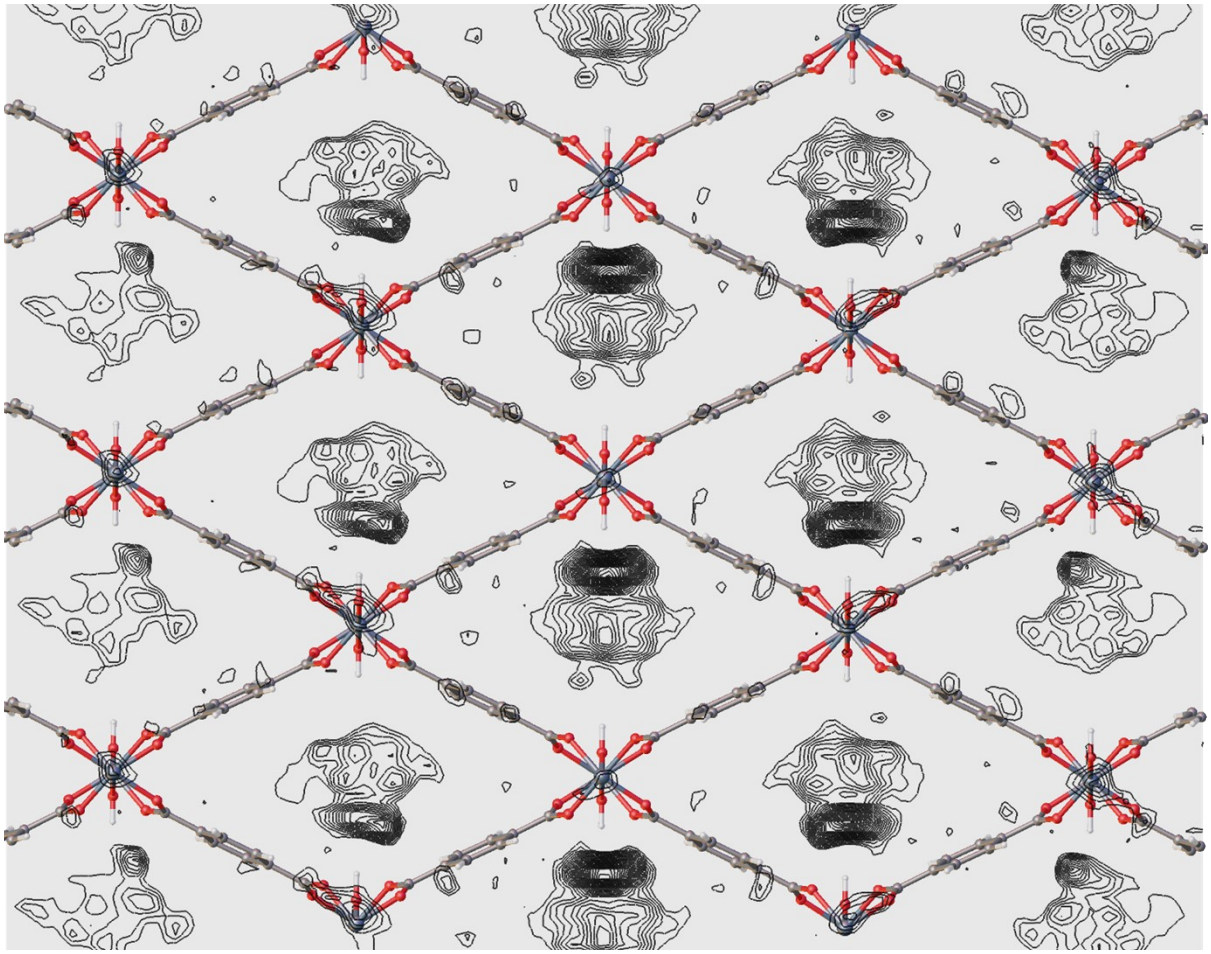

Figure S2: Residual electron density contour map for int-**1**·0.7DEF·0.08HF at 100 K created by ccdx in Olex2,[1] viewed along the pore direction.

Table S2: Summary of gallium and fluorine elemental analysis for int-**1**·0.7DEF·0.08HF.

Element	**Mass %**
Ga	22.36
F	1.72

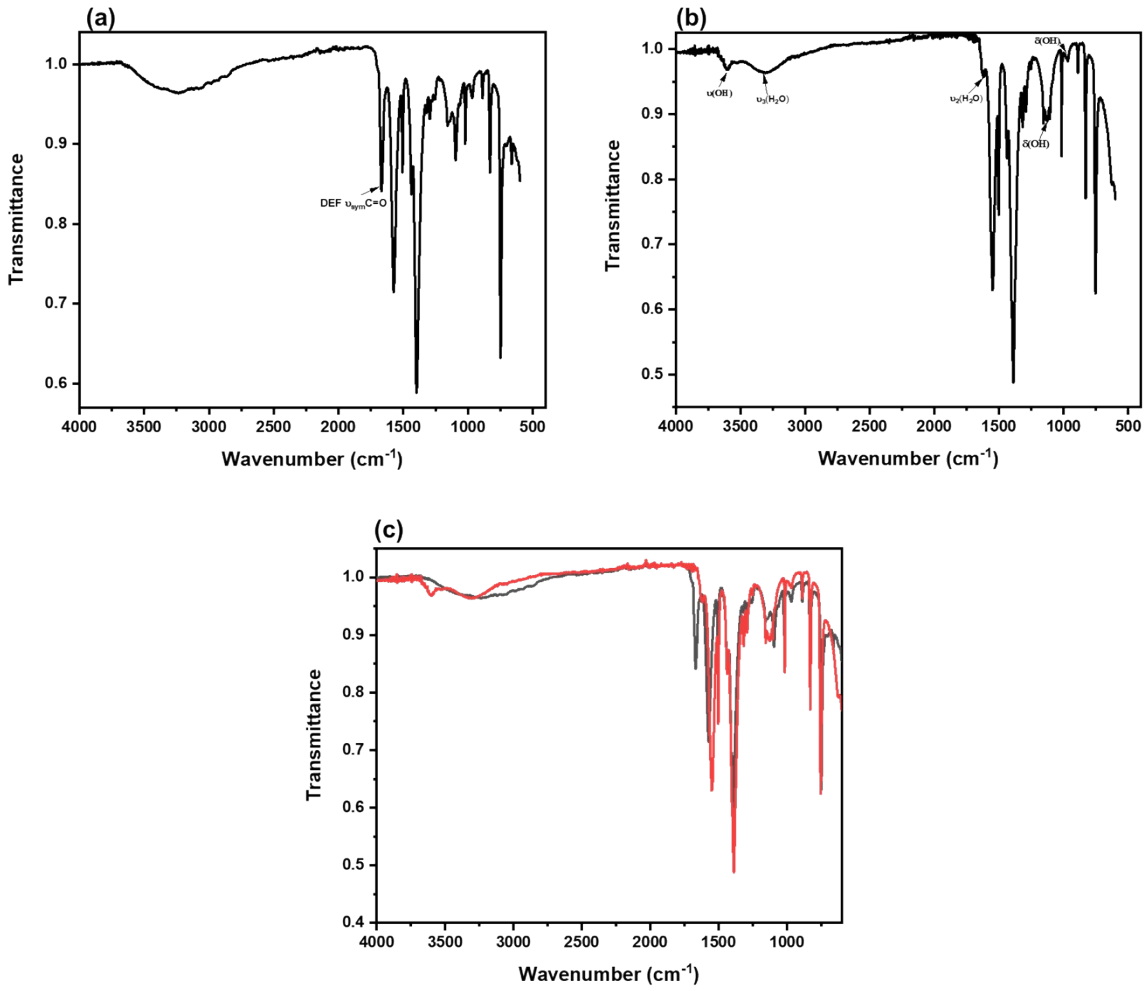

Figure S3: ATR IR spectra of int-**1**·0.7DEF·0.08HF (a), and int-**1**·H_2O (b) and an overlay of the two spectra (c). In (c) int-**1**·0.7DEF·0.08HF = black and int-**1**·H_2O = red.

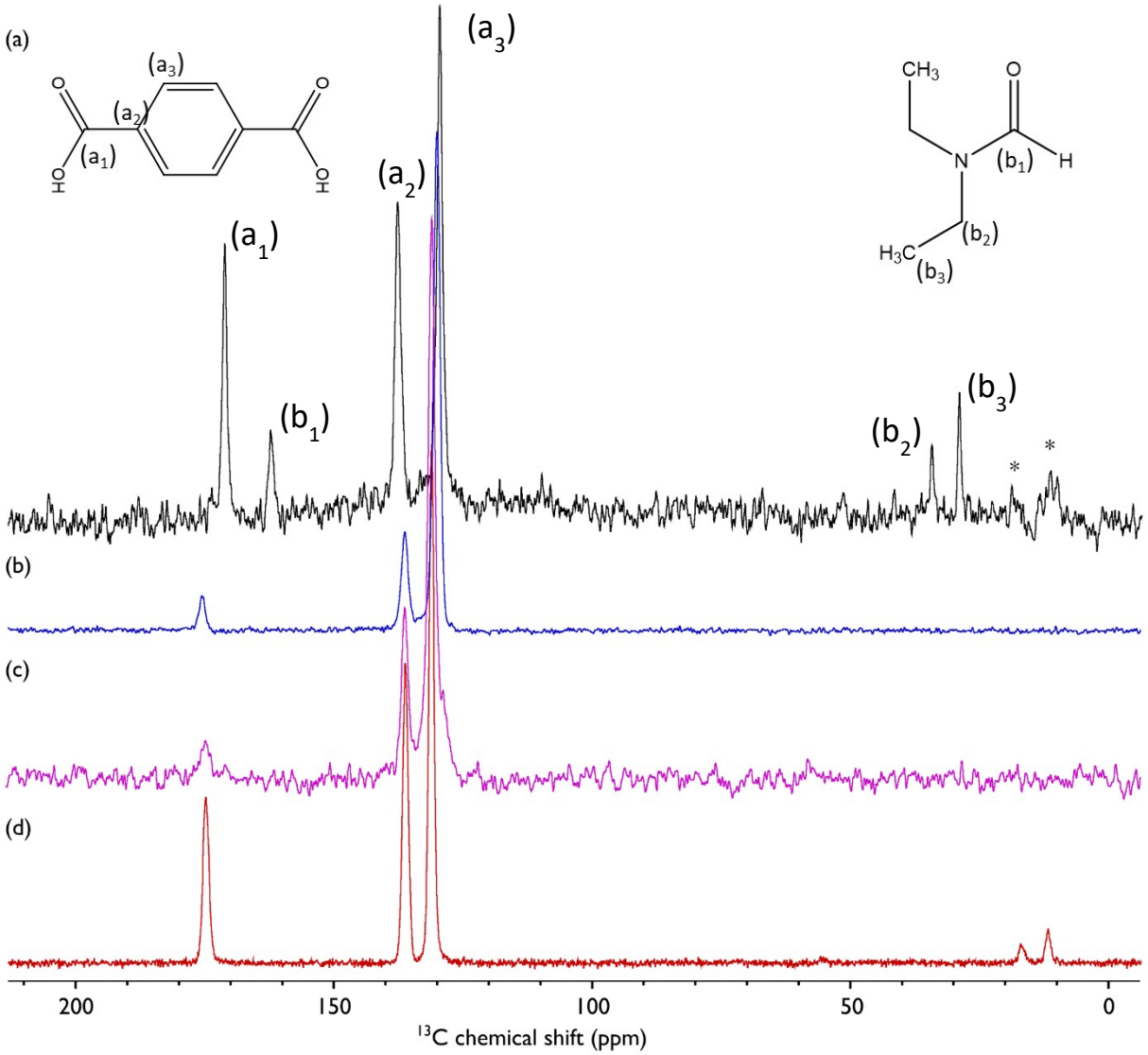

Figure S4: {^{1}H-}^{13}C CP MAS NMR spectrum of (a) int-**1**·0.7DEF·0.08HF (black; δ ppm: a_1 = 171 ppm, a_2= 138 ppm, a_3 = 129 ppm, b_1 = 162 ppm, b_2 = 34 ppm, b_3 = 29 ppm) (b) int-**1**·H_2O (blue: a_1 = 175 ppm, a_2= 136 ppm, a_3 = 130 ppm), np-**1**/lp-**1** (magenta: a_1 = 175 ppm, a_2= 136 ppm, a_3 = 131 (np-**1**) & shoulder = 129 ppm (lp-**1**)) and (d) np-**1** (red: a_1 = 175 ppm, a_2= 136 ppm, a_3 = 131 ppm). (a,d) were recorded at 9.4 T using a MAS frequency of 12 kHz whereas (b,c) were recorded at 16.4 T using a MAS frequency of 50 kHz. Spinning sidebands are denoted with * and appear in (a) and (d).

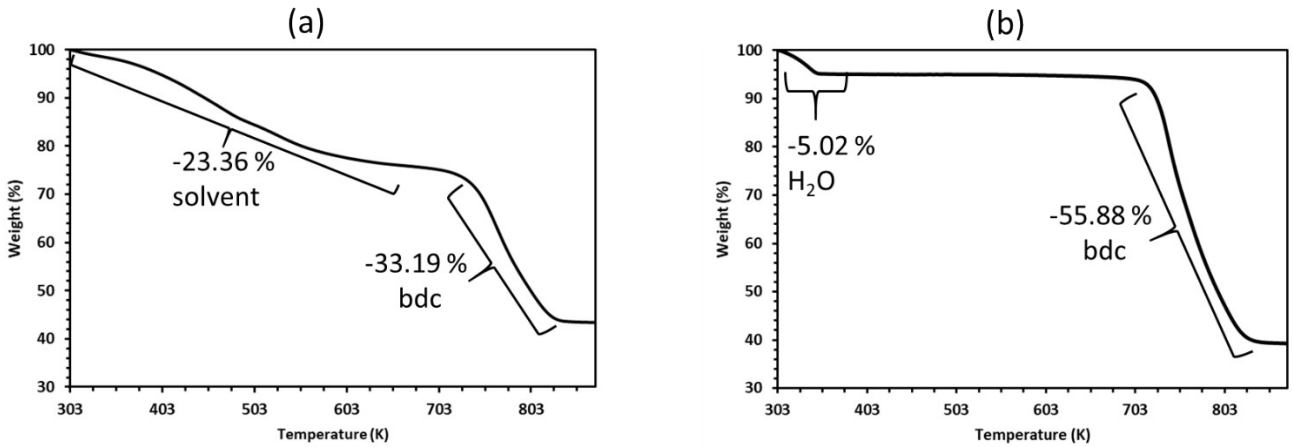

Figure S5: TGA plots under N_2(g) for int-**1**·0.7DEF·0.08HF (a) and int-**1**·H_2O (b).

Table S3: Summary of crystal data and structure refinement for int-**1**·H_2O.

Empirical formula	$C_8H_{6.8}F_{0.2}GaO_{5.8}$
Formula weight	268.80
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	6.6570(15)
b/Å	7.436(2)
c/Å	19.182(4)
α/°	90
β/°	96.15(2)
γ/°	90
Volume/Å^3	944.1(4)
Z	4
ρ_{calc}g/cm^3	1.894
μ/mm^{-1}	4.142
F(000)	536.0
Crystal size/mm^3	0.109 × 0.035 × 0.011
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.274 to 90.884
Index ranges	-6 ≤ h ≤ 6, -6 ≤ k ≤ 6, -17 ≤ l ≤ 17
Reflections collected	946
Independent reflections	946 [R_{int} = 0.1225, R_{sigma} = 0.0284]
Data/restraints/parameters	946/0/38
Goodness-of-fit on F^2	1.202
Final R indexes [I>=2σ (I)]	R_1 = 0.0785, wR_2 = 0.1749
Final R indexes [all data]	R_1 = 0.0869, wR_2 = 0.1814
Largest diff. peak/hole / e Å^{-3}	0.60/-0.53

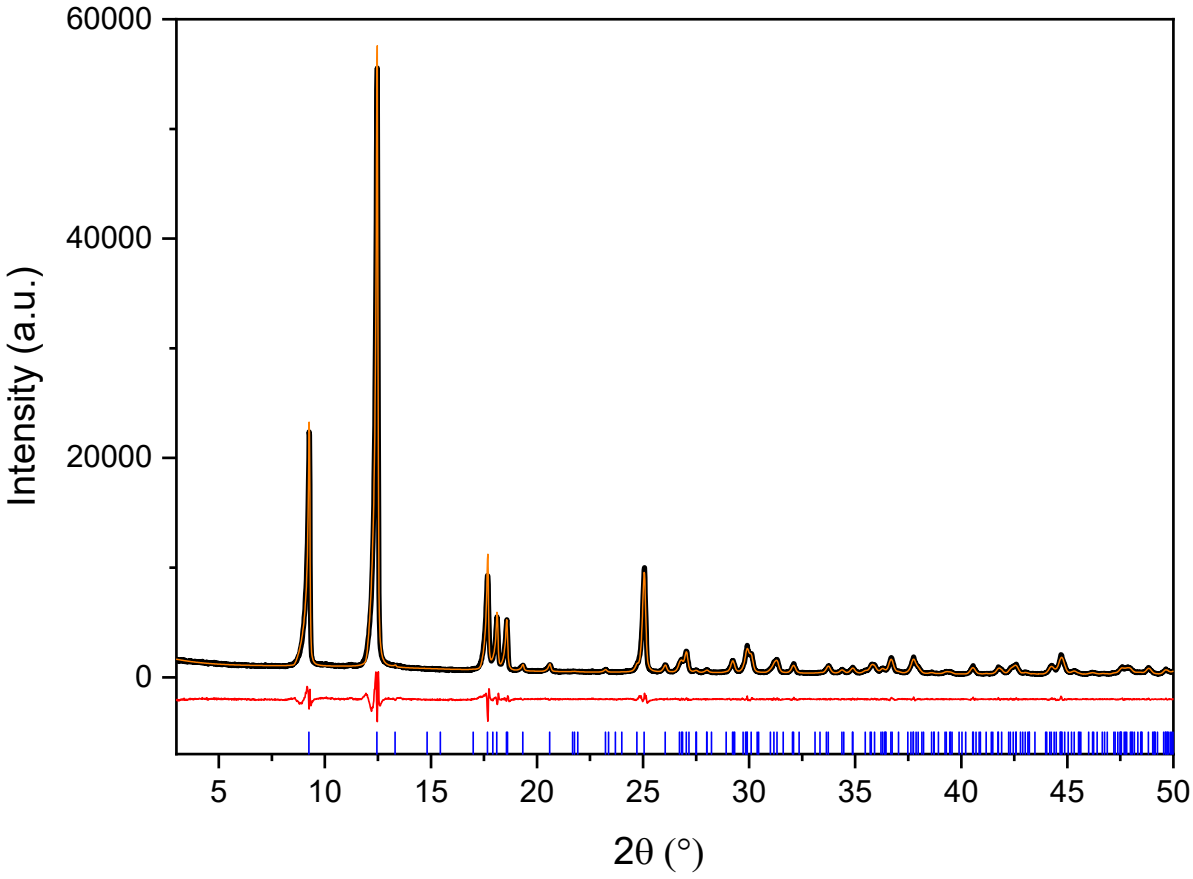

Figure S6: Pawley fit for monophasic int-**1**·H_2O (experimental pattern also shown in Figure 7(1)). Final refined unit cell parameters: I2/a, a = 6.680(5) Å, b =7.652(4) Å, c= 19.205(2) Å, β= 95.82(2)°, R_{wp} = 7.40%, R_{exp} = 2.72%. Experimental pattern in black, calculated pattern in orange, difference plot in red and hkl marks in blue.

Table S4: Summary of elemental analysis results for int-**1**·H_2O compared to the expected values based on an overall formula of $[GaF_{0.2}(OH)_{0.80}(bdc)]\cdot H_2O$.

Element	Observed mass %	Expected mass %
Ga	25.01	25.74
F	1.37	1.41
N	0	0
C	35.67	35.36
H	2.46	2.51

Table S5: Summary of unit cell parameters for the variable temperature in-situ SCXRD study on int-**1**·H_2O over the temperature range of 100-500 K. Data were collected in either 100 K or 50 K steps.

Number	**T (K)**	**Space group**	**a (Å)**	**b (Å)**	**c (Å)**	**β (°)**	**Unit cell volume ($Å^3$)**
1	100	*I2/a*	6.6442(18)	7.418(3)	19.187(8)	96.23(3)	940.1(6)
2	200	*I2/a*	6.6428(14)	7.488(2)	19.091(5)	96.03(2)	944.3(4)
3	300	*I2/a*	6.723(4)	7.116(10)	19.358(12)	95.58(6)	921.6(15)
4	400	*I2/a*	6.6442(14)	7.062(4)	19.111(4)	95.245(19)	893.0(5)
5	500	*Imma*	16.529(2)	6.6846(11)	13.175(3)	90	1455.6(5)
6	450	*Imma*	16.508(2)	6.6680(9)	13.144(2)	90	1446.8(4)
7	400	*Imma*	16.551(3)	6.6737(14)	13.142(4)	90	1451.7(6)
8	350	*Imma*	16.546(3)	6.6728(15)	13.111(4)	90	1447.5(6)
9	300	*Imma*	16.568(3)	6.6658(15)	13.089(4)	90	1445.5(6)
10	250	*Imma*	16.567(4)	6.6552(15)	13.039(4)	90	1437.7(6)
11	200	*Imma*	16.600(4)	6.654(2)	12.971(5)	90	1432.8(8)
12	150	*Imma*	16.423(6)	6.653(3)	13.242(7)	90	1446.7(11)

13	100	*Imma*	16.189(5)	6.669(2)	13.557(6)	90	1463.6(9)
14	150	*Imma*	16.411(5)	6.650(2)	13.226(5)	90	1443.5(8)
15	200	*Imma*	16.620(6)	6.649(2)	12.944(6)	90	1430.3(10)
16	250	*Imma*	16.571(7)	6.642(3)	13.017(8)	90	1432.7(12)
17	300	*Imma*	16.566(7)	6.657(3)	13.015(8)	90	1435.2(13)
18	350	*Imma*	16.549(7)	6.639(3)	13.051(7)	90	1433.8(11)
19	400	*Imma*	16.526(3)	6.6462(17)	13.061(4)	90	1434.6(6)
20	450	*Imma*	16.518(3)	6.6565(14)	13.064(4)	90	1436.5(6)
21	500	*Imma*	16.528(3)	6.6596(14)	13.093(4)	90	1441.2(6)

Table S6: Summary of crystal data and structure refinement for np-**1** at 400 K

Empirical formula	$C_8H_{4.8}F_{0.2}GaO_{4.8}$
Formula weight	251.24
Temperature/K	400.0(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	6.6442(14)
b/Å	7.062(4)
c/Å	19.111(4)
α/°	90
β/°	95.245(19)
γ/°	90
Volume/Å^3	893.0(5)
Z	4
ρ_{calc}g/cm^3	1.869
μ/mm^{-1}	4.242
F(000)	496.0
Crystal size/mm^3	0.059 × 0.017 × 0.004
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.294 to 94.776
Index ranges	-3 ≤ h ≤ 6, -6 ≤ k ≤ 6, -14 ≤ l ≤ 18
Reflections collected	635
Independent reflections	394 [R_{int} = 0.0415, R_{sigma} = 0.0955]
Data/restraints/parameters	394/0/43
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	R_1 = 0.0955, wR_2 = 0.2229
Final R indexes [all data]	R_1 = 0.1309, wR_2 = 0.2447
Largest diff. peak/hole / e Å^{-3}	0.96/-0.52

Table S7: Summary of crystal data and structure refinement for lp-**1**.

Empirical formula	$C_8H_{4.8}F_{0.2}GaO_{4.8}$
Formula weight	251.24
Temperature/K	99.97(17)
Crystal system	orthorhombic
Space group	Imma
a/Å	16.189(5)
b/Å	6.669(2)
c/Å	13.557(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1463.6(9)
Z	4
ρ_{calc}g/cm^3	1.140
μ/mm^{-1}	2.588
F(000)	496.0
Crystal size/mm^3	0.059 × 0.017 × 0.004
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.508 to 92.366
Index ranges	-14 ≤ h ≤ 15, -5 ≤ k ≤ 6, -12 ≤ l ≤ 10
Reflections collected	1257
Independent reflections	373 [R_{int} = 0.0652, R_{sigma} = 0.0706]
Data/restraints/parameters	373/33/37
Goodness-of-fit on F^2	1.184
Final R indexes [I>=2σ (I)]	R_1 = 0.0734, wR_2 = 0.1744
Final R indexes [all data]	R_1 = 0.0927, wR_2 = 0.1841
Largest diff. peak/hole / e Å^{-3}	0.54/-0.92

Table S8: Summary of the calculated number of N_2 molecules per gallium in lp-**1** based on SQUEEZE[2] calculations.

Sequence number	Temperature (K)	N_2 (g) per Ga^{3+}
5	500	0
6	450	0
7	400	0
8	350	0.32
9	300	0.26
10	250	0.68
11	200	1
12	150	2.35
13	100	4
14	150	2.538
15	200	1
16	250	1
17	300	0.8
18	350	0.43
19	400	0.64
20	450	0.45
21	500	0.28

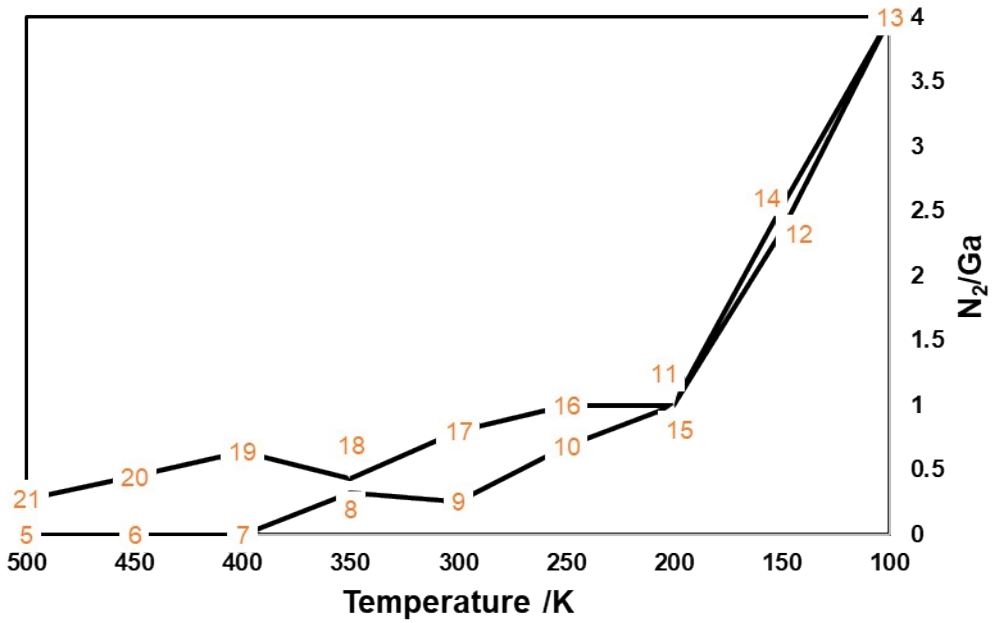

Figure S7: Number of N_2(g) molecules per gallium in lp-**1** as a function of temperature as determined using SQUEEZE.[2]

Table S9: Summary of unit cell parameters from the variable temperature *in-situ* SCXRD study over the temperature range of 300-400 K. Data were collected in either 100 or 25 K steps.

T (K)	**Space group**	**a (Å)**	**b (Å)**	**c (Å)**	**β (°)**	**Unit cell volume (Å^3)**
300–air hydrated	I2/a	6.694(5)	7.558(12)	19.257(15)	95.77(9)	969.2(18)
300–N_2 dehydrated	I2/a	6.677(4)	6.955(12)	19.368(11)	95.83(6)	894.8(17)
400	I2/a	6.730(3)	7.141(8)	19.363(10)	95.43(5)	926.4(12)
425	I2/a	6.707(4)	7.203(9)	19.350(13)	95.43(6)	930.6(14)
450	I2/a	6.724(3)	7.263(7)	19.341(11)	95.17(5)	940.7(12)
475	I2/a	6.707(5)	7.298(12)	19.327(15)	95.13(7)	942.2(18)
500	I2/a	6.716(3)	7.367(10)	19.316(15)	94.74(6)	952.4(15)

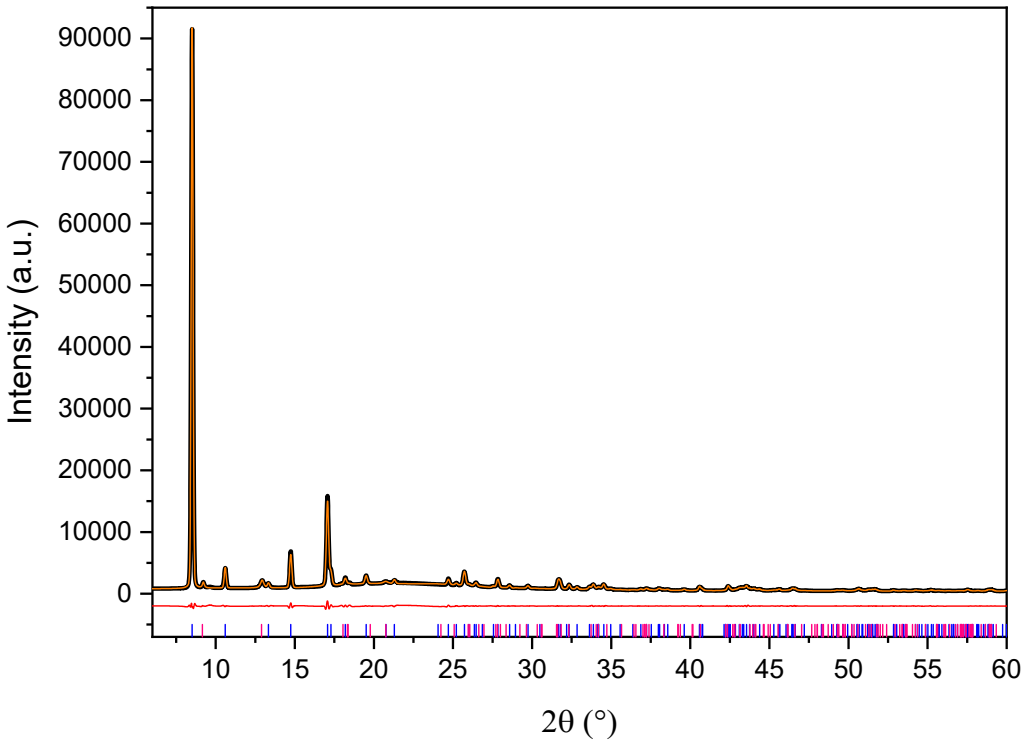

Figure S8: Pawley fit for lp-**1** at 500 K (experimental pattern also shown in Figure 7(2)) showing the presence of a small proportion of np-**1**. Final refined unit cell parameters: lp-**1**: *Imma,* a= 16.67(1) Å, b =6.732(4) Å, c=13.268(8) Å, V = 1489(2) Å^3; np-**1**: *I2/a*, a = 6.69(2) Å, b = 7.321(5)Å, c= 19.23(2) Å, β= 94.7(4)° V =939(2) Å^3; R_{wp} = 3.28 %, R_{exp} = 0.052 %. Experimental pattern in black, calculated pattern in orange, difference plot in red and hkl marks in blue and pink for lp and np phases respectively.

References

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

2 A. L. Spek, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 9–18.