SUPPORTING INFORMATION

Mechanical Properties of a Gallium Fumarate Metal-Organic Framework: A Joint Experimental-Modelling Exploration

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1. Synthesis

All chemicals and solvents were purchased from commercial sources and were used without further purification.

2. Fourier-transform infrared (FTIR)

FTIR spectra were recorder on a Nicolet 6700 FTIR thermo scientific spectrometer in the 400-4000 cm^{-1} range.

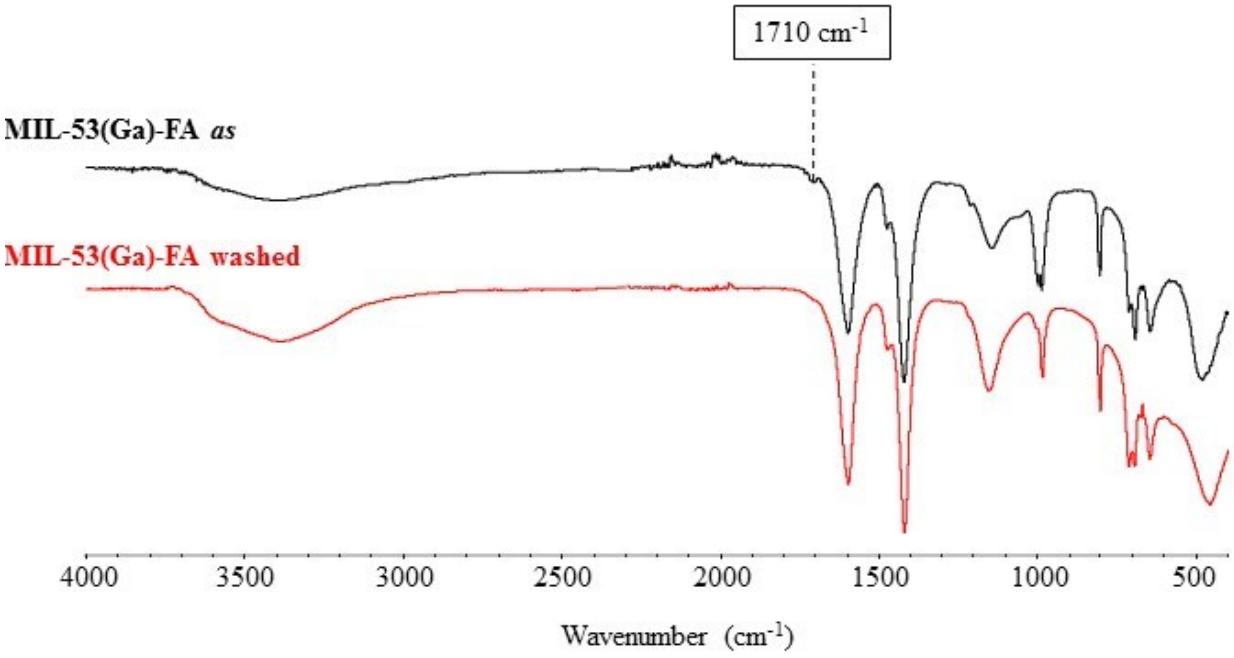

Figure S1. *Infra-red spectra of the as-synthesized and washed MIL53(Ga)-FA.*

3. Thermogravimetric analyses (TGA)

TGA was performed on a Perkin Elmer, STA 6000 apparatus under O_2 flow between room temperature and 600 °C in an aluminium crucible (heating speed 3 °C.min^{-1}) using 10 mg of product.

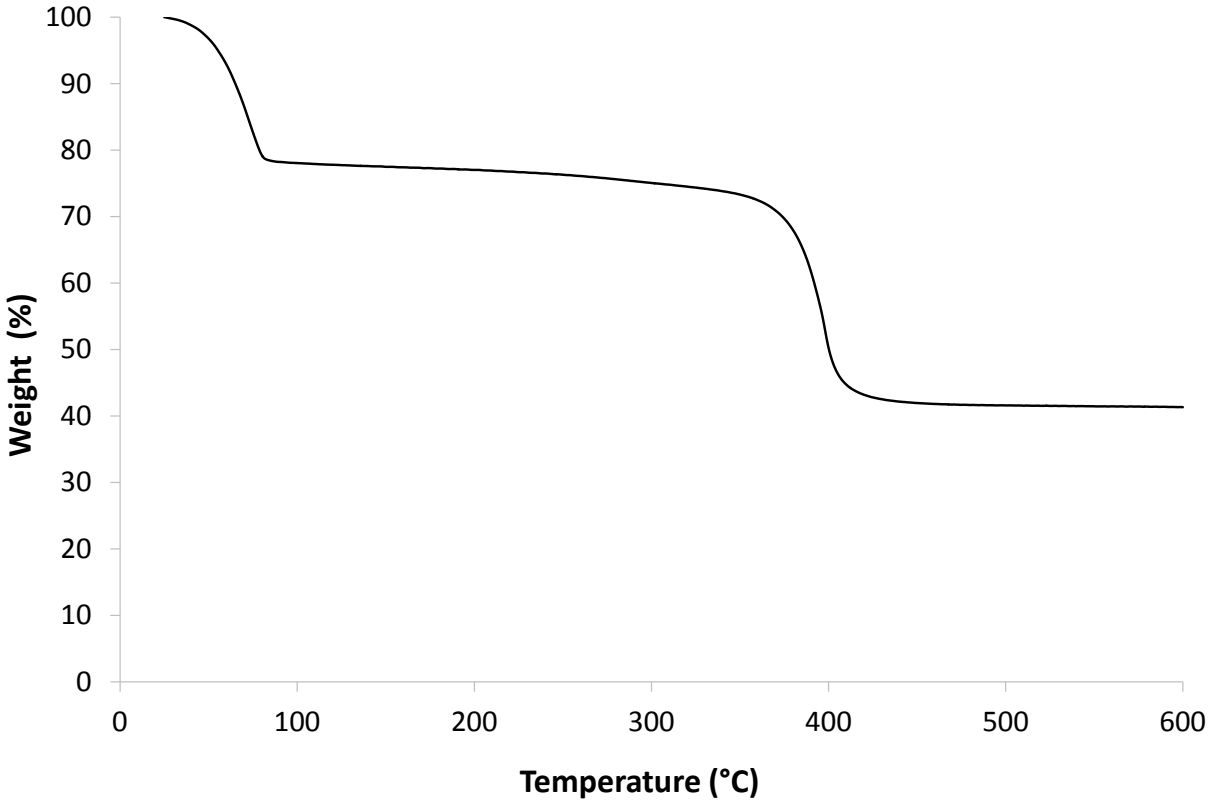

Figure S2. *Thermogravimetric curve of the MIL-53(Ga)-FA in the range 25°C-600°C.*

4. BET area

BET area experiments were performed at 77K on a Belsorp Mini apparatus using nitrogen as the probing gas, after a Belsorp Prep treatment overnight at 150 °C under primary vacuum (BEL Japan).

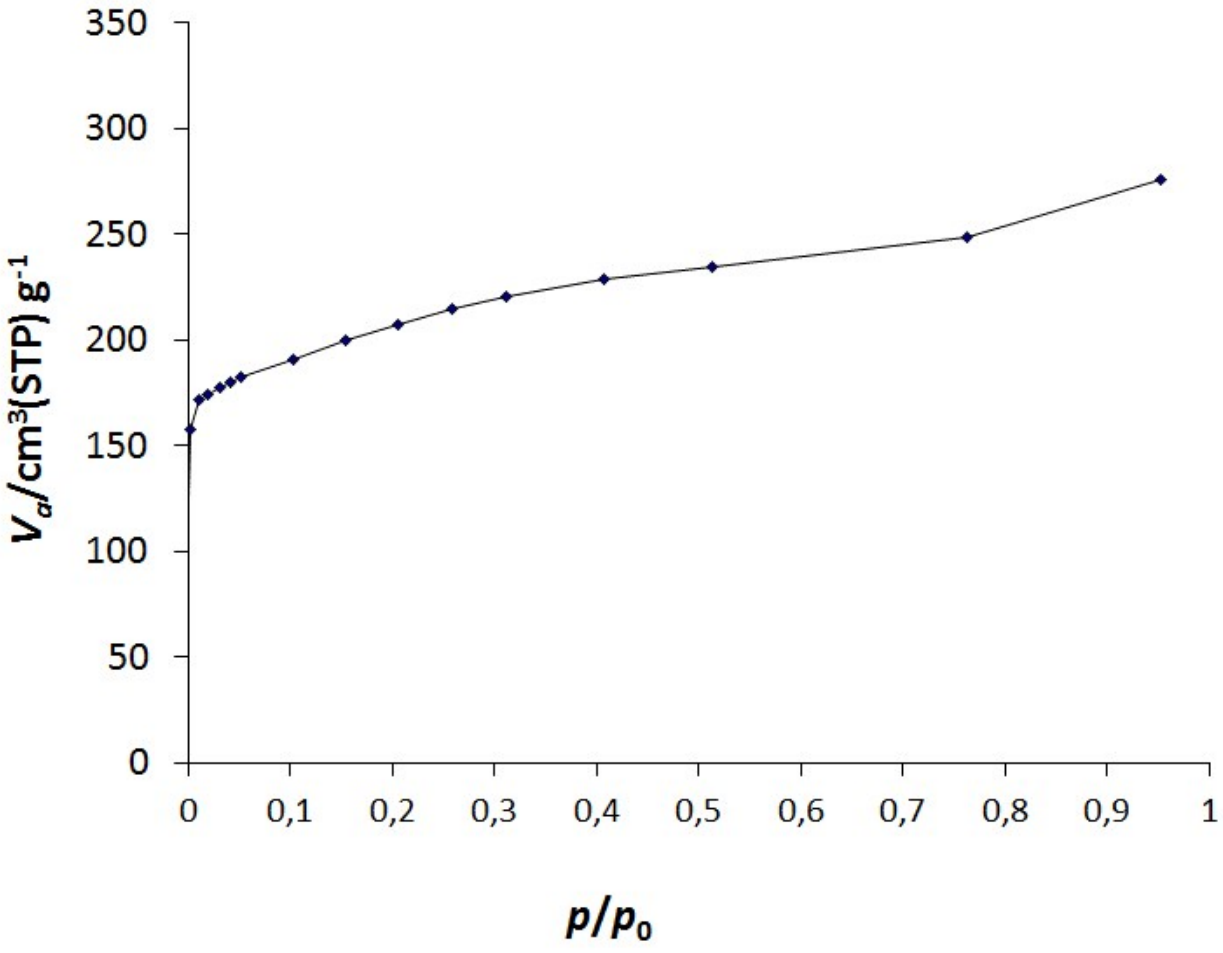

Figure S3. *N_2 adsorption Isotherm of MIL-53(Ga)-FA.*

5. Mercury Porosimetry

Considering the pore size of MOF materials (and pressure range explored by mercury intrusion (P≤420 MPa)), the non-wetting mercury cannot penetrate into the pores, hence the pressure increase induces an hydrosatic pressure on the crystallites. The volume of intruded mercury is then directly related to the volumetric strain corresponding to the compressibility of the material. The hydrostatic compression experiments were performed using a Hg porosimeter Micromeritics Autopore 9240 on outgassed (~6.5 Pa, 1 h) powdered MOF samples. The pressure applied can vary from 0.1 to 420 MPa. In the explored range of pressure, Washburn's law is applied with $P = \frac{-4\gamma cos\theta}{d}$, where γ is the mercury surface tension (0.485 N/m) and θ is the contact angle (130°). The pore diameters accessible for Hg would range in the interval [2×10^7–400 Å].

6. Pressure profile at 0 K

In order to extract a pressure-volume profile from the computed energy profile at 0 K, a polynomial of order 10 was fitted to the computed (V, E) data points using a least-squares fit. Once the polynomial coefficients are known, a Taylor expansion of order 9 for the pressure profile can easily be derived by taking the negative derivative of the energy polynomial. Finally, by identifying the maximum and minimum of the pressure profile, the transition pressures for the large pore (lp) to the contracted pore (cp) form and contracted pore (cp) to the large pore (lp) form transitions respectively can be estimated. Given the specific fitting procedure, the transition pressures are prone to some uncertainty and some caution should be taken in interpreting the specific values. The results are shown in Figure S4.

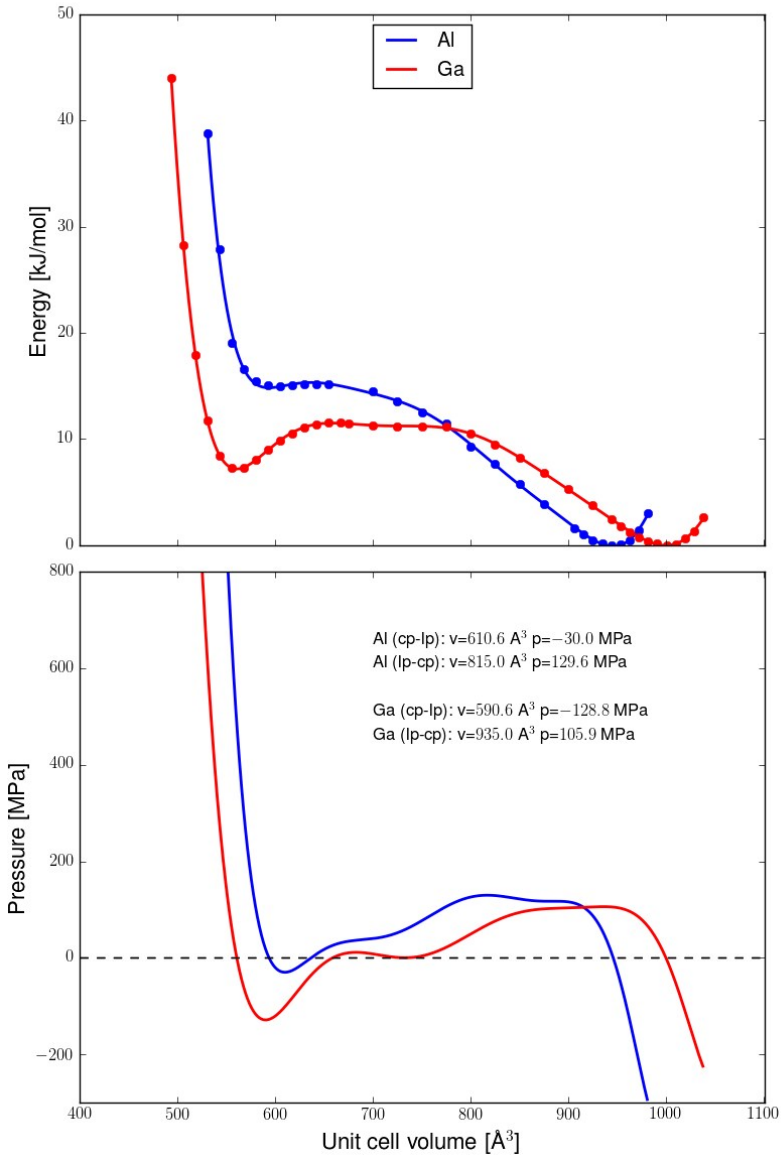

Figure S4*: (top) Energy profile (at 0 K) as function of unit cell volume and (bottom) the corresponding pressure profile for Al-fumarate (blue) and Ga-fumarate (red). The energy profile contains the results from constrained geometry optimizations at a chosen set of volumes (dots) as well as a fit of a polynomial series of order 10 to the energy data points (solid line). The pressure profile corresponds to the negative volume-derivative of the energy profile polynomial (solid line).*

7. Free energy calculation

To be able to assess whether or not the energy barrier between the contracted phase and large-pore phase at 0 K will remain present at 300 K, we estimated the free energy of the contracted phase and large-pore phase for both materials using normal mode analysis (NMA). Hence, the internal energy, entropy and free energy are given by:

$$E = E_{el} + \sum_{i=1}^{3N}\left(\frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}\right)$$

$$S = k_B\sum_{i=1}^{3N}\left(\frac{\beta\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} - ln\left(1 - e^{-\beta\hbar\omega_i}\right)\right)$$

$$F = E_{el} + \sum_{i=1}^{3N}\left(\frac{\hbar\omega_i}{2} + k_BT\cdot ln\left(1 - e^{-\beta\hbar\omega_i}\right)\right)$$

in which $\hbar$ is the reduced Planck constant, $\beta = \frac{1}{k_BT}$ with k_B the Boltzmann constant and T the temperature and ω_i represent the normal mode frequencies. The term E_{el} represents the electronic energy, i.e. corresponds to the 0 K energy shown in the energy profile, while the first and second term in the summation of E represents the zero-point energy (ZPE) and thermal energy (E_{th}) respectively. All these contributions are shown in Table S1.

Table S1 : *Electronic energy at 0 K, zero-point energy, thermal energy, entropy and free energy difference between large-pore and contracted-pore forms (lp-cp) at 300 K for the Al- and Ga-fumarate materials. All contributions are given in kJ/mol per unit cell.*

	Al-fumarate	**Ga-fumarate**
ΔE_{el}	15.0	7.2
ΔZPE	1.3	2.4
ΔE_{th}	-2.0	-3.1
-TΔS	10.4	9.2
ΔF	24.8	15.7

In case of Al-fumarate, the free energy increases from 15.0 kJ/mol at 0 K to 24.8 kJ/mol at 300 K. In other words, due to the temperature increase, the contracted pore form is destabilized by 9.8 kJ/mol with respect to the large pore form. If we compare this number with the energy barrier of less than 1 kJ/mol in the energy profile at 0 K, we expect that the energy barrier will disappear at 300 K. For Ga-fumarate, the free energy increases from 7.2 kJ/mol at 0 K to 15.7 kJ/mol at 300 K, indicating the contracted pore form is destabilized with 8.5 kJ/mol with respect to the large pore version. Comparing this number with the barrier of almost 5 kJ/mol in the energy profile at 0 K, we expect this barrier to remain present at 300 K. Finally, we also computed the contributions as a function of temperature, the results are shown in Figure S5.

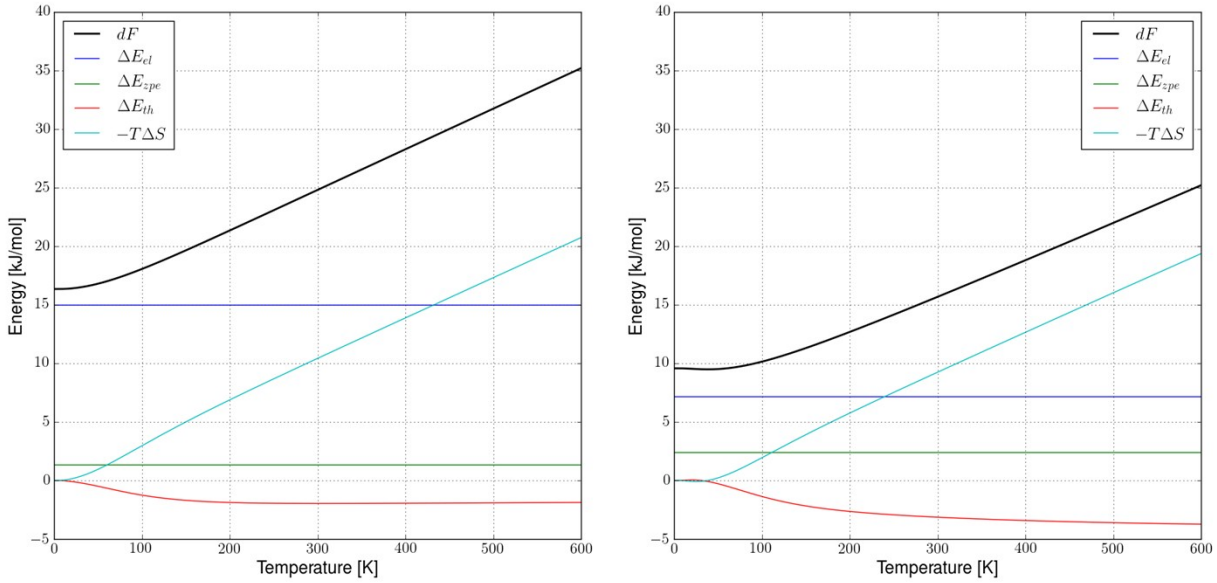

Figure S5: *Difference in free energy (and its decomposition) between the contracted and large pore phase for (left) Al-fumarate and (right) Ga-fumarate as a function of temperature according to the normal mode approximation.*

8. Equation-of-state fits for large-pore (LP) and contracted-pore (CP) forms of Al- and Ga-fumarate

The results of the Vinet equation-of-state fits for both materials in the large-pore and contracted phase are displayed in Figures S6 (MIL-53(Ga)-FA lp-form), S7 (MIL-53(Ga)-FA cp-form), S8 (MIL-53(Al)-FA lp-form) and S9 (MIL-53(Al)-FA c^p-form). The fitted parameters (the equilibrium volume V_0, the bulk modulus B_0 and the derivative of the bulk modulus B_1) are indicated in the figures.

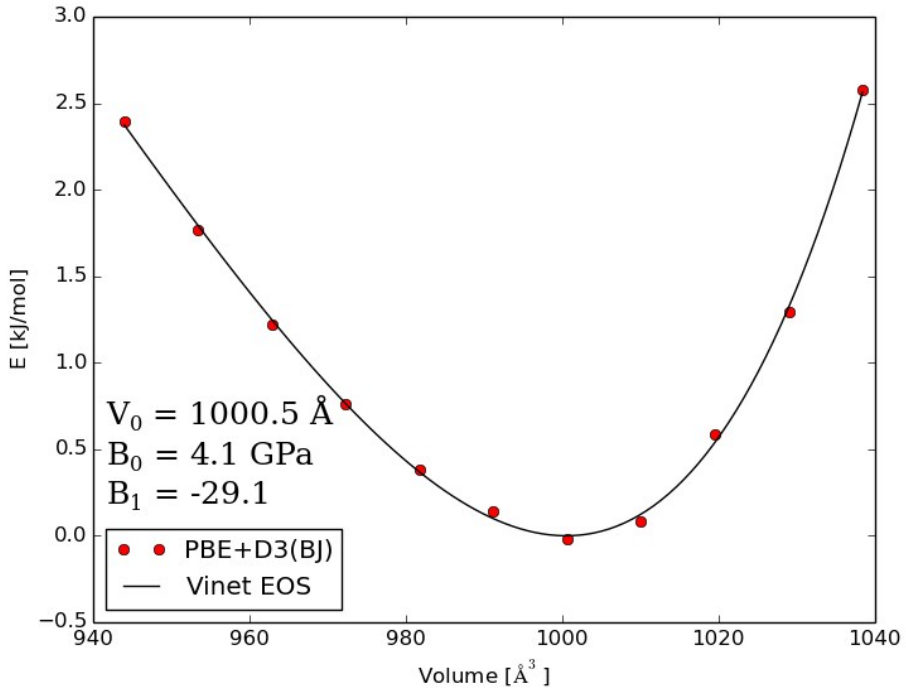

Figure S6: *Results of MIL-53(Ga)-FA in the large pore phase*

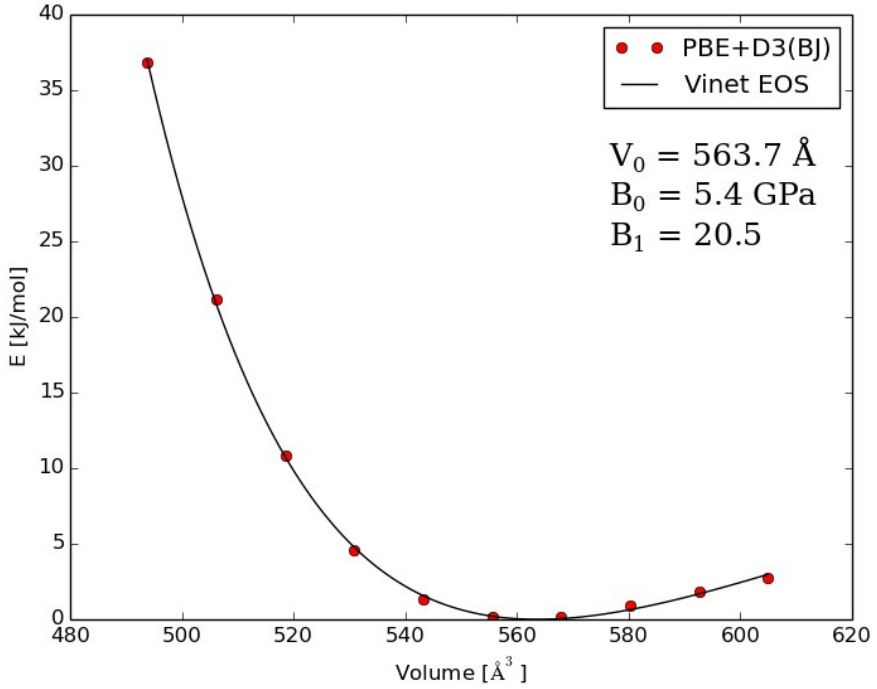

Figure S7: *Results of MIL-53(Ga)-FA in the contracted pore phase.*

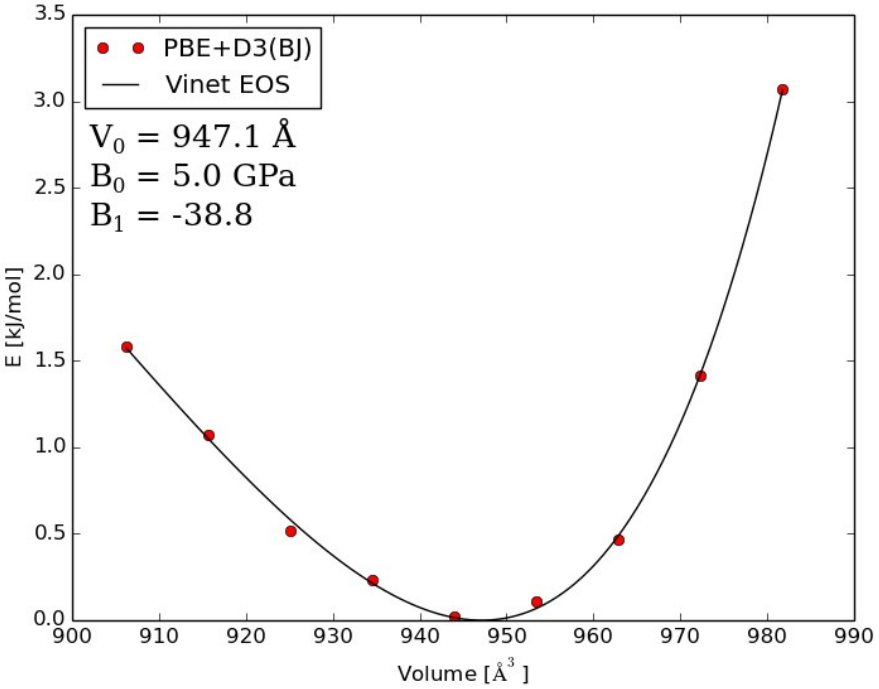

Figure S8: *Results of MIL-53(Al)-FA in the large pore phase.*

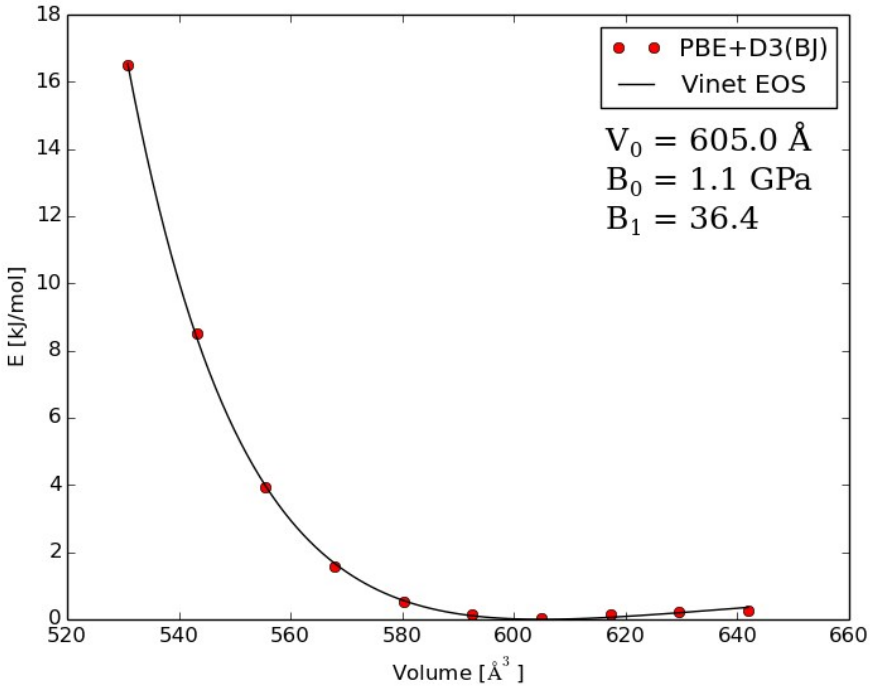

Figure S9: *Results of MIL-53(Al)-FA in the contracted pore phase.*

9. Tensorial analysis of the elastic constants

We calculated the full elastic constant tensor of both materials in the contracted and large-pore phase with the extended Hessian approach.[1] The tensorial analysis was done with ELATE.[2]

The directional Young modulus for MIL-53(Al)-FA and MIL-53(Ga)-FA are displayed in Figure S10. The strongest direction in both materials is along the organic linker. However, it can be noted that the metal ion also has a large influence (88 GPa (Al) vs. 63 GPa (Ga)). The AlOH chain (82 GPa) is harder to deform than the GaOH chain (54 GPa). Breathing occurs along the weakest direction, which is similar for both materials (7-8 GPa).

Important is that the anisotropy factors do not give insight in the relative flexibility of the fumarate materials, although it can be seen that the MIL-53(Ga)-FA is in general weaker, i.e. a lower directional Young modulus, along the metal-oxide chain, the organic linker and slightly weaker along the breathing direction. However, both fumarate materials are less flexible than their BDC analogues, and this is also found with the anisotropy factors.[3,4]

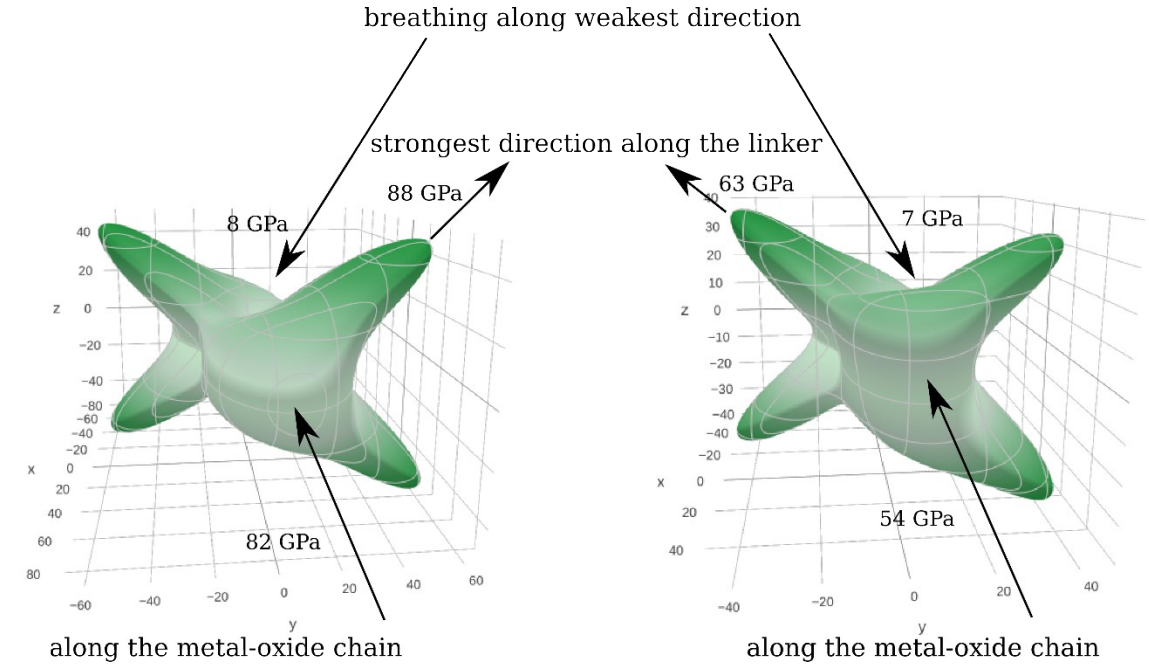

Figure S10: *The directional Young modulus for MIL-53(Al)-FA (left) and MIL-53(Ga)-FA (right). The figure was made with ELATE.*[13]

Table S2: *The elastic constant tensor of MIL-53(Al)-FA large pore phase (lp).*

	C_{xx} [GPa]	C_{yy} [GPa]	C_{zz} [GPa]	C_{xy} [GPa]	C_{yz} [GPa]	C_{zx} [GPa]
C_{xx} [GPa]	92.51	29.23	17.17	-0.49	1.16	9.56
C_{yy} [GPa]		88.19	46.14	-0.42	1.12	17.58
C_{zz} [GPa]			32.52	-0.38	0.85	9.73
C_{xy} [GPa]				25.31	14.88	-0.17
C_{yz} [GPa]					26.50	0.04
C_{zx} [GPa]						20.40

Table S3: *The elastic constant tensor of MIL-53(Ga)-FA large pore phase (lp).*

	C_{xx} [GPa]	C_{yy} [GPa]	C_{zz} [GPa]	C_{xy} [GPa]	C_{yz} [GPa]	C_{zx} [GPa]
C_{xx} [GPa]	55.09	7.30	4.68	1.61	3.07	3.53
C_{yy} [GPa]		52.75	28.65	1.76	5.13	9.91
C_{zz} [GPa]			23.45	-1.16	3.33	6.03
C_{xy} [GPa]				20.99	10.26	-1.22
C_{yz} [GPa]					33.43	-2.43
C_{zx} [GPa]						12.93

Table S4: *The elastic constant tensor of MIL-53(Al)-FA contracted phase (cp).*

	C_{xx} [GPa]	C_{yy} [GPa]	C_{zz} [GPa]	C_{xy} [GPa]	C_{yz} [GPa]	C_{zx} [GPa]
C_{xx} [GPa]	123.44	17.09	8.26	0.42	0.04	-20.68
C_{yy} [GPa]		66.18	3.96	-0.35	-0.16	2.09
C_{zz} [GPa]			17.65	0.01	-0.01	-6.13
C_{xy} [GPa]				6.70	1.23	0.06
C_{yz} [GPa]					11.17	-0.06
C_{zx} [GPa]						14.13

Table S5: *The elastic constant tensor of MIL-53(Ga)-FA contracted phase (cp).*

	C_{xx} [GPa]	C_{yy} [GPa]	C_{zz} [GPa]	C_{xy} [GPa]	C_{yz} [GPa]	C_{zx} [GPa]
C_{xx} [GPa]	96.66	37.50	14.92	21.33	-2.04	-21.59
C_{yy} [GPa]		177.10	16.75	44.81	6.79	-3.50
C_{zz} [GPa]			25.73	3.43	-0.20	-6.18
C_{xy} [GPa]				42.84	-2.09	3.31
C_{yz} [GPa]					10.70	3.24
C_{zx} [GPa]						16.59

Table S6: *Minimal and maximal values of Young modulus, linear compressibility, shear modulus and Poisson ratio. The anisotropy A_X is defined as X_{max}/X_{min}.*

	E_{min}	E_{max}	A_E	β_{min}	β_{max}	G_{min}	G_{max}	A_G	ν_{min}	ν_{max}
MIL-53(Al)-FA lp	8.3	86.8	10.4	-19.7	56.4	3.5	40.8	11.8	-0.74	1.58
MIL-53(Al)-FA cp	14.5	124.6	8.6	-12.0	64.7	6.4	38.1	6.0	-0.38	0.92
MIL-53(Ga)-FA lp	7.5	62.7	8.4	-15.9	61.6	3.0	37.7	12.7	-0.88	1.34
MIL-53(Ga)-FA cp	12.9	186.6	14.5	-12.3	-50.0	6.6	49.8	7.6	-0.78	1.32

Table S7: *The eigenvalues of the elastic constant tensor.*

	λ_1 [GPa]	λ_2 [GPa]	λ_3 [GPa]	λ_4 [GPa]	λ_5 [GPa]	λ_6 [GPa]
MIL-53(Al)-FA lp	6.4	11.0	16.2	40.8	68.1	142.9
MIL-53(Al)-FA cp	6.4	7.4	11.5	19.2	62.5	132.2
MIL-53(Ga)-FA lp	5.6	10.0	15.5	38.7	51.3	77.5
MIL-53(Ga)-FA cp	5.9	12.2	21.1	32.0	88.5	209.9

10. Comparison of internal coordinates of the large pore and contracted pore forms of MIL-53(Al)-FA and MIL-53(Ga)-FA

	MIL-53(Al)-FA (dehydrated)	MIL-53(Al)-FA (contracted)	MIL-53(Ga)-FA (dehydrated)	MIL-53(Ga)-FA (contracted)
Bonds				
H_HY.O_HY	0.968 ± 0.000	0.969 ± 0.000	0.972 ± 0.000	0.977 ± 0.000
C_CA.O_CA	1.273 ± 0.002	1.273 ± 0.001	1.274 ± 0.002	1.276 ± 0.002
C_FU.H_FU	1.091 ± 0.000	1.090 ± 0.000	1.090 ± 0.000	1.089 ± 0.002
M.O_CA	1.924 ± 0.015	1.923 ± 0.012	2.021 ± 0.025	2.022 ± 0.037
C_CA.C_FU	1.484 ± 0.000	1.482 ± 0.002	1.486 ± 0.001	1.483 ± 0.004
C_FU.C_FU	1.340 ± 0.000	1.340 ± 0.000	1.340 ± 0.000	1.338 ± 0.000
M.O_HY	1.859 ± 0.001	1.867 ± 0.005	1.935 ± 0.002	1.954 ± 0.018
Bends				
O_HY.M.O_HY	177.7 ± 0.0	180.0 ± 0.0	176.6 ± 0.1	180.0 ± 0.0
C_FU.C_CA.O_CA	116.9 ± 1.1	117.2 ± 2.1	116.6 ± 1.3	117.2 ± 2.8
M.O_HY.M	128.2 ± 0.0	128.4 ± 0.0	122.4 ± 0.1	121.4 ± 0.0
C_FU.C_FU.H_FU	120.8 ± 0.2	120.7 ± 0.0	120.8 ± 0.3	120.6 ± 0.0
O_CA.C_CA.O_CA	126.2 ± 0.1	125.6 ± 0.4	126.9 ± 0.1	125.5 ± 0.9
O_CA.M.O_HY	90.0 ± 1.9	90.0 ± 0.9	90.0 ± 3.3	90.0 ± 1.1
C_CA.C_FU.C_FU	122.5 ± 0.0	122.4 ± 0.2	122.6 ± 0.3	122.9 ± 0.1
O_CA.M.O_CA	119.6 ± 41.9	120.0 ± 42.5	119.4 ± 41.7	120.0 ± 42.7
M.O_CA.C_CA	132.9 ± 0.5	129.5 ± 2.5	131.1 ± 2.1	124.0 ± 2.2
C_CA.C_FU.H_FU	116.7 ± 0.2	116.5 ± 0.1	116.6 ± 0.3	116.3 ± 0.0
M.O_HY.H_HY	113.4 ± 0.1	115.7 ± 0.7	110.7 ± 0.8	113.8 ± 1.3
Diheds				
M.O_CA.C_CA.C_FU	172.5 ± 0.8	142.4 ± 15.1	168.0 ± 6.2	136.5 ± 22.7
C_FU.C_FU.C_CA.O_CA	90.1 ± 86.0	88.7 ± 78.0	90.0 ± 86.3	89.0 ± 81.1
C_CA.C_FU.C_FU.C_CA	180.0 ± 0.0	172.0 ± 0.0	180.0 ± 0.0	180.0 ± 0.0
H_FU.C_FU.C_CA.O_CA	89.9 ± 86.9	91.3 ± 83.2	90.0 ± 86.9	90.8 ± 85.3
C_CA.C_FU.C_FU.H_FU	0.9 ± 0.2	5.5 ± 3.7	0.8 ± 0.3	4.7 ± 2.1

Table: Bond lengths (in Angstrom), bending angles (deg) and dihedral angles (deg) of MIL-53(Al,Ga) with fumerate linker.

Table S8 : *Internal coordinates of the DFT optimized structures.*

11. X-ray powder diffraction

X-ray powder diffraction was performed on a PANalytical X'PERT II diffractometer using a monochromatic Cu-$K_{\alpha 1}$ source (λ=1.5406 Å) contained in sealed glass capillaries with operating voltage of 40 kV and a beam current of 40 mA. The patterns were collected for 2θ from 5° to 100°.

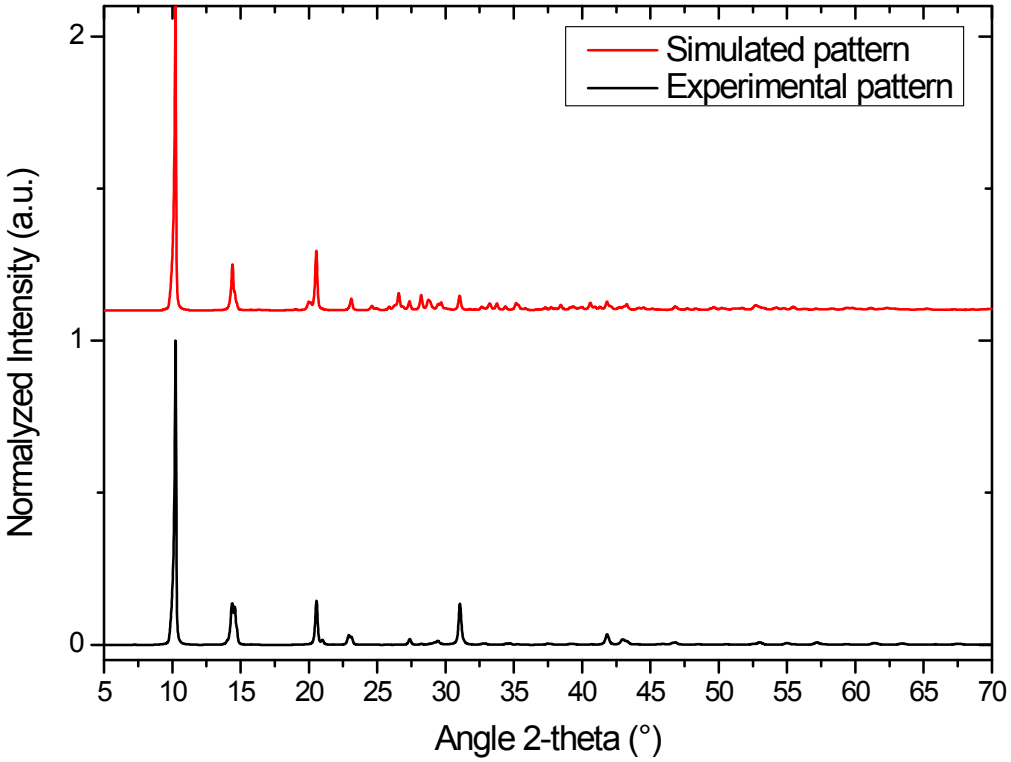

Figure S11. *Comparison between the experimental PXRD pattern obtained for hydrated MIL-53(Ga)-FA (black) and the PXRD pattern calculated from the predicted structure model for the dehydrated phase(red).*

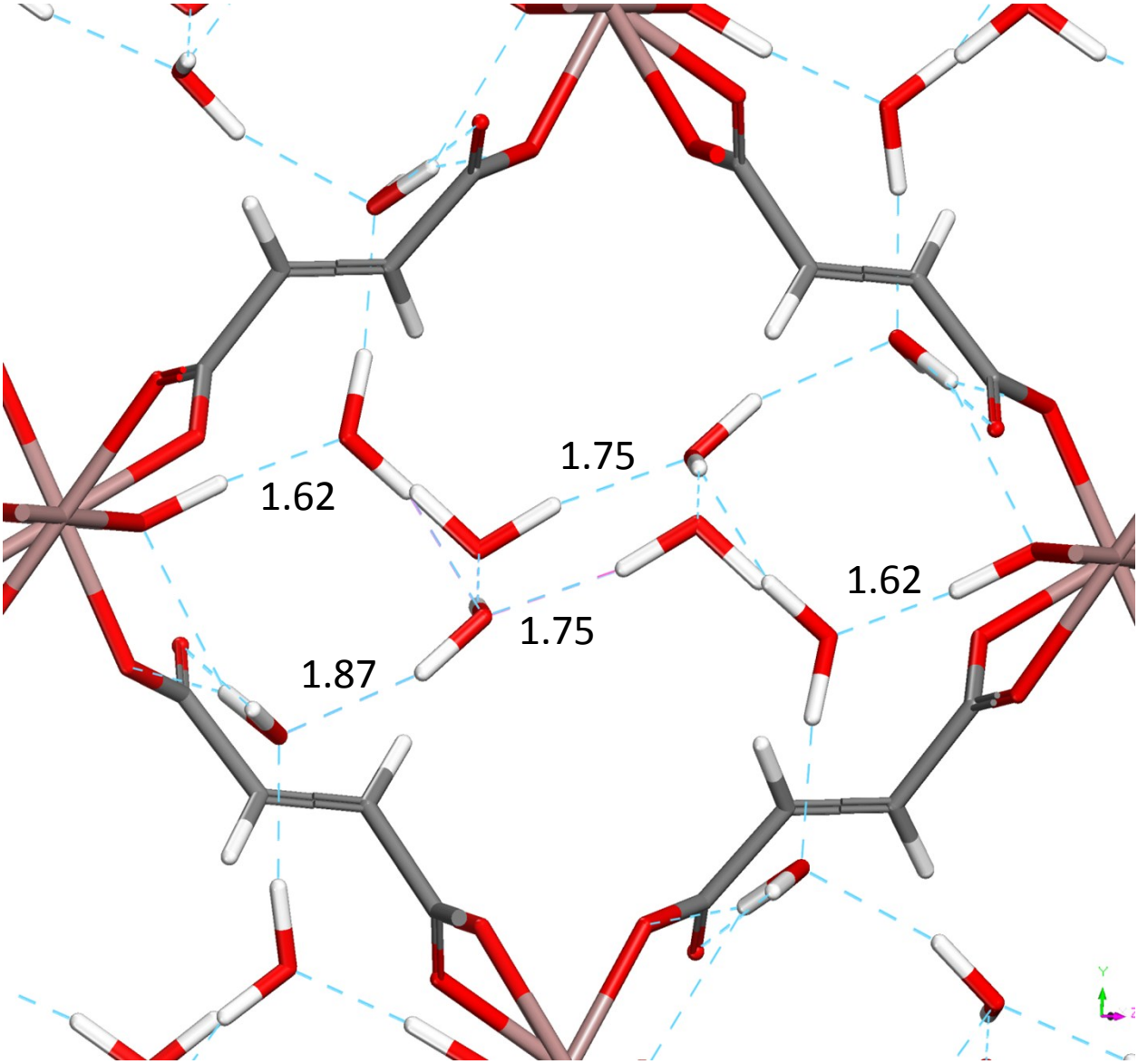

Figure S12. *Interaction between adsorbed water and MIL-53(Ga)-FA framework.*

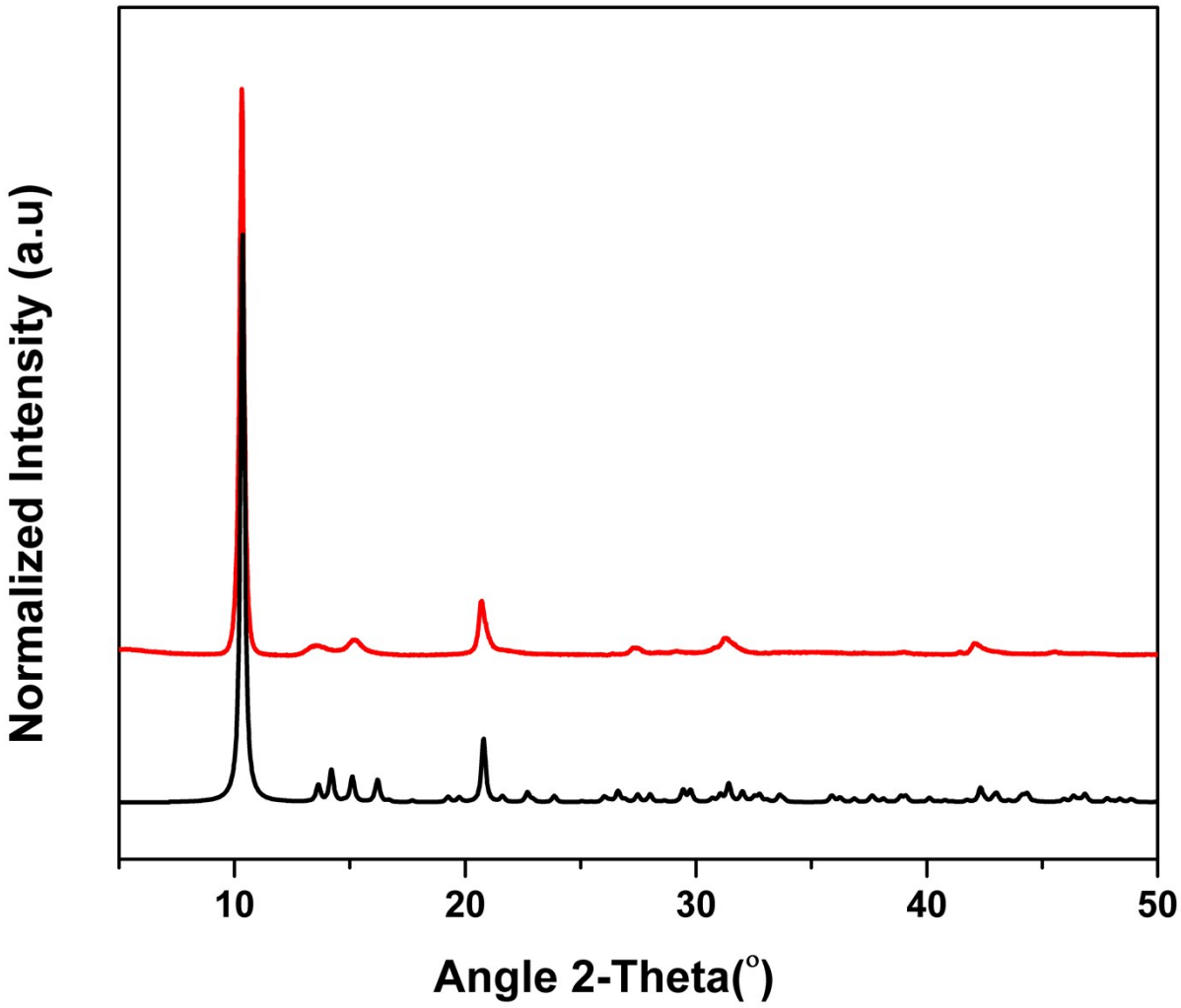

Figure S13. *Comparison between the experimental PXRD pattern obtained for dehydrated MIL-53(Ga)-FA (red) and the PXRD pattern calculated from the predicted structure model for the dehydrated phase(black).*

12. Crystallographic data

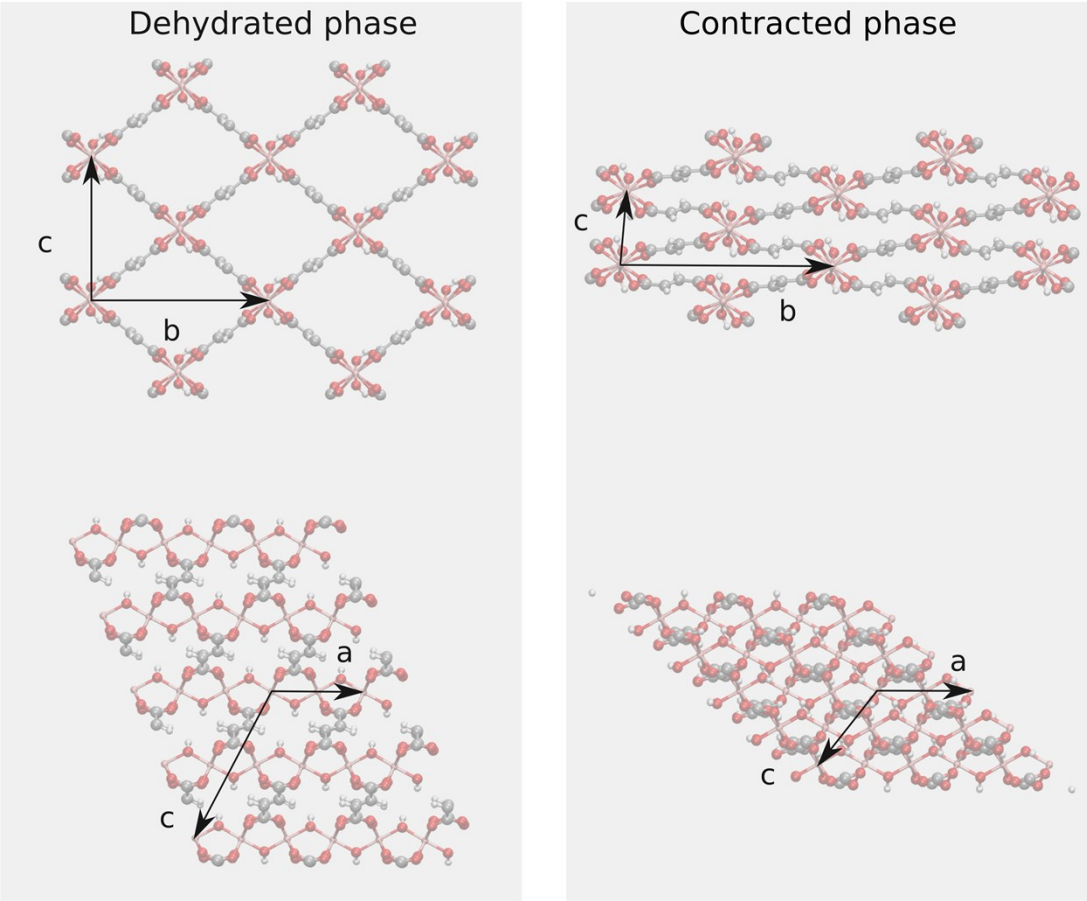

Figure S14. *Definition of the unit cell parameters in MIL-53-FA.*

12.1. Hydrated form

```
_pd_phase_name                          'MIL-53(Ga)-FA hydrated form'
_cell_length_a                         7.15900
_cell_length_b                         12.28300
_cell_length_c                         14.46100
_cell_angle_alpha                       90
_cell_angle_beta                        122.87000
_cell_angle_gamma                       90
_symmetry_space_group_name_H-M          'P 1'
_symmetry_Int_Tables_number             1
```

```
loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  O1    1.0   0.680225   0.496743   0.425201   Biso  1.000000 O
  O2    1.0   0.319775   0.503256   0.574798   Biso  1.000000 O
  O3    1.0   0.319776   0.996743   0.074799   Biso  1.000000 O
  O4    1.0   0.680225   0.003256   0.925202   Biso  1.000000 O
  O5    1.0   0.997248   0.616017   0.617720   Biso  1.000000 O
  O6    1.0   0.002752   0.383982   0.382280   Biso  1.000000 O
  O7    1.0   0.002751   0.116017   0.882280   Biso  1.000000 O
  O8    1.0   0.997248   0.883983   0.117719   Biso  1.000000 O
  O9    1.0   0.636136   0.638338   0.568558   Biso  1.000000 O
  O10   1.0   0.363865   0.361661   0.431442   Biso  1.000000 O
  O11   1.0   0.363864   0.138338   0.931442   Biso  1.000000 O
  O12   1.0   0.636135   0.861661   0.068558   Biso  1.000000 O
  O13   1.0   0.257355   0.919517   0.874901   Biso  1.000000 O
  O14   1.0   0.742646   0.080482   0.125101   Biso  1.000000 O
  O15   1.0   0.742645   0.419517   0.625100   Biso  1.000000 O
  O16   1.0   0.257354   0.580482   0.374900   Biso  1.000000 O
  O17   1.0   0.999368   0.868605   0.913557   Biso  1.000000 O
  O18   1.0   0.000630   0.131394   0.086442   Biso  1.000000 O
  O19   1.0   0.000632   0.368606   0.586443   Biso  1.000000 O
  O20   1.0   0.999370   0.631394   0.413558   Biso  1.000000 O
  O21   1.0   0.096774   0.516984   0.896893   Biso  1.000000 O
  O22   1.0   0.903226   0.483017   0.103107   Biso  1.000000 O
  O23   1.0   0.903226   0.016984   0.603107   Biso  1.000000 O
  O24   1.0   0.096775   0.983017   0.396893   Biso  1.000000 O
  O25   1.0   0.257741   0.421624   0.095803   Biso  1.000000 O
  O26   1.0   0.742260   0.578377   0.904197   Biso  1.000000 O
  O27   1.0   0.742259   0.921624   0.404197   Biso  1.000000 O
  O28   1.0   0.257740   0.078377   0.595803   Biso  1.000000 O
  O29   1.0   0.571704   0.197561   0.785579   Biso  1.000000 O
  O30   1.0   0.428296   0.802440   0.214421   Biso  1.000000 O
  O31   1.0   0.428296   0.697561   0.714421   Biso  1.000000 O
  O32   1.0   0.571705   0.302440   0.285579   Biso  1.000000 O
  O33   1.0   0.467722   0.414817   0.767847   Biso  1.000000 O
```

O34	1.0	0.532278	0.585184	0.232152	Biso	1.000000 O
O35	1.0	0.532279	0.914817	0.732153	Biso	1.000000 O
O36	1.0	0.467722	0.085184	0.267848	Biso	1.000000 O
C1	1.0	0.844256	0.662479	0.622750	Biso	1.000000 C
C2	1.0	0.155745	0.337521	0.377250	Biso	1.000000 C
C3	1.0	0.155744	0.162478	0.877250	Biso	1.000000 C
C4	1.0	0.844256	0.837521	0.122750	Biso	1.000000 C
C5	1.0	0.891580	0.753934	0.698708	Biso	1.000000 C
C6	1.0	0.108421	0.246067	0.301291	Biso	1.000000 C
C7	1.0	0.108420	0.253934	0.801291	Biso	1.000000 C
C8	1.0	0.891580	0.746067	0.198709	Biso	1.000000 C
C9	1.0	0.073508	0.759664	0.800130	Biso	1.000000 C
C10	1.0	0.926493	0.240336	0.199870	Biso	1.000000 C
C11	1.0	0.926492	0.259664	0.699870	Biso	1.000000 C
C12	1.0	0.073508	0.740336	0.300130	Biso	1.000000 C
C13	1.0	0.111076	0.855959	0.870349	Biso	1.000000 C
C14	1.0	0.888923	0.144040	0.129651	Biso	1.000000 C
C15	1.0	0.888924	0.355959	0.629651	Biso	1.000000 C
C16	1.0	0.111077	0.644040	0.370349	Biso	1.000000 C
H1	1.0	0.755578	0.811885	0.672081	Biso	1.000000 H
H2	1.0	0.244424	0.188116	0.327918	Biso	1.000000 H
H3	1.0	0.244423	0.311885	0.827918	Biso	1.000000 H
H4	1.0	0.755577	0.688116	0.172082	Biso	1.000000 H
H5	1.0	0.208175	0.700190	0.832424	Biso	1.000000 H
H6	1.0	0.791825	0.299810	0.167575	Biso	1.000000 H
H7	1.0	0.791826	0.200190	0.667576	Biso	1.000000 H
H8	1.0	0.208176	0.799810	0.332425	Biso	1.000000 H
H9	1.0	0.173408	0.472399	0.965235	Biso	1.000000 H
H10	1.0	0.826595	0.527601	0.034766	Biso	1.000000 H
H11	1.0	0.826593	0.972399	0.534765	Biso	1.000000 H
H12	1.0	0.173406	0.027601	0.465235	Biso	1.000000 H
H13	1.0	0.034939	0.465358	0.836296	Biso	1.000000 H
H14	1.0	0.965061	0.534643	0.163705	Biso	1.000000 H
H15	1.0	0.965061	0.965358	0.663704	Biso	1.000000 H
H16	1.0	0.034941	0.034643	0.336296	Biso	1.000000 H
H17	1.0	0.357031	0.367449	0.151590	Biso	1.000000 H
H18	1.0	0.642970	0.632552	0.848410	Biso	1.000000 H
H19	1.0	0.642969	0.867449	0.348410	Biso	1.000000 H
H20	1.0	0.357031	0.132551	0.651590	Biso	1.000000 H
H21	1.0	0.126809	0.431719	0.102327	Biso	1.000000 H
H22	1.0	0.873192	0.568281	0.897673	Biso	1.000000 H
H23	1.0	0.873192	0.931719	0.397673	Biso	1.000000 H
H24	1.0	0.126809	0.068280	0.602327	Biso	1.000000 H
H25	1.0	0.725055	0.174303	0.811414	Biso	1.000000 H
H26	1.0	0.274945	0.825697	0.188586	Biso	1.000000 H
H27	1.0	0.274946	0.674303	0.688587	Biso	1.000000 H

H28	1.0	0.725055	0.325697	0.311414	Biso	1.000000	H
H29	1.0	0.545158	0.159541	0.837092	Biso	1.000000	H
H30	1.0	0.454843	0.840460	0.162909	Biso	1.000000	H
H31	1.0	0.454842	0.659541	0.662908	Biso	1.000000	H
H32	1.0	0.545157	0.340459	0.337091	Biso	1.000000	H
H33	1.0	0.526480	0.339644	0.780601	Biso	1.000000	H
H34	1.0	0.473520	0.660356	0.219399	Biso	1.000000	H
H35	1.0	0.473520	0.839644	0.719400	Biso	1.000000	H
H36	1.0	0.526480	0.160356	0.280602	Biso	1.000000	H
H37	1.0	0.581279	0.463004	0.826378	Biso	1.000000	H
H38	1.0	0.418721	0.536997	0.173621	Biso	1.000000	H
H39	1.0	0.418722	0.963003	0.673621	Biso	1.000000	H
H40	1.0	0.581279	0.036997	0.326378	Biso	1.000000	H
H41	1.0	0.610239	0.536425	0.351823	Biso	1.000000	H
H42	1.0	0.389762	0.463574	0.648176	Biso	1.000000	H
H43	1.0	0.389762	0.036425	0.148177	Biso	1.000000	H
H44	1.0	0.610239	0.963574	0.851824	Biso	1.000000	H
Ga1	1.0	0.500000	0.500000	0.500000	Biso	1.000000	Ga
Ga2	1.0	0.500001	0.000000	0.000000	Biso	1.000000	Ga
Ga3	1.0	0.000000	0.500000	0.500000	Biso	1.000000	Ga
Ga4	1.0	0.000000	1.000000	0.000000	Biso	1.000000	Ga

12.2. Dehydrated form

```
_pd_phase_name                  'MIL-53(Ga)-FA dehydrated form'
_cell_length_a                 6.78112
_cell_length_b                 13.54291
_cell_length_c                 14.09114
_cell_angle_alpha               90.32415
_cell_angle_beta               129.36914
_cell_angle_gamma                89.89798
_space_group_name_H-M_alt          'P 1'
_space_group_IT_number             1

loop_
_space_group_symop_operation_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
```

_atom_site_type_symbol

O1	1.0	0.865319	0.499244	0.085335	Biso	1.000000	O
O2	1.0	0.140099	0.498761	0.914398	Biso	1.000000	O
O3	1.0	0.140131	0.998845	0.414409	Biso	1.000000	O
O4	1.0	0.865363	0.999154	0.585350	Biso	1.000000	O
O5	1.0	0.780963	0.611939	0.891104	Biso	1.000000	O
O6	1.0	0.204745	0.378236	0.096352	Biso	1.000000	O
O7	1.0	0.264522	0.093432	0.629725	Biso	1.000000	O
O8	1.0	0.732745	0.900816	0.369960	Biso	1.000000	O
O9	1.0	0.419736	0.592606	0.869203	Biso	1.000000	O
O10	1.0	0.578277	0.401727	0.130992	Biso	1.000000	O
O11	1.0	0.570051	0.113618	0.609395	Biso	1.000000	O
O12	1.0	0.448253	0.876663	0.402941	Biso	1.000000	O
O13	1.0	0.578126	0.901627	0.630884	Biso	1.000000	O
O14	1.0	0.419955	0.092710	0.369345	Biso	1.000000	O
O15	1.0	0.448414	0.376585	0.903070	Biso	1.000000	O
O16	1.0	0.569815	0.613712	0.109232	Biso	1.000000	O
O17	1.0	0.204506	0.878127	0.596158	Biso	1.000000	O
O18	1.0	0.781235	0.112052	0.391293	Biso	1.000000	O
O19	1.0	0.732958	0.400681	0.870112	Biso	1.000000	O
O20	1.0	0.264272	0.593571	0.129560	Biso	1.000000	O
H1	1.0	0.724534	0.261299	0.750842	Biso	1.000000	H
H2	1.0	0.280409	0.731741	0.256449	Biso	1.000000	H
H3	1.0	0.235338	0.735870	0.719868	Biso	1.000000	H
H4	1.0	0.752064	0.256954	0.274032	Biso	1.000000	H
H5	1.0	0.724253	0.761444	0.250618	Biso	1.000000	H
H6	1.0	0.280653	0.231602	0.756648	Biso	1.000000	H
H7	1.0	0.235647	0.236008	0.220077	Biso	1.000000	H
H8	1.0	0.751760	0.756802	0.773826	Biso	1.000000	H
H9	1.0	0.062125	0.549906	0.852198	Biso	1.000000	H
H10	1.0	0.950652	0.550820	0.147723	Biso	1.000000	H
H11	1.0	0.950828	0.050662	0.647824	Biso	1.000000	H
H12	1.0	0.062264	0.050053	0.352288	Biso	1.000000	H
Ga1	1.0	0.504234	0.495400	0.002476	Biso	1.000000	Ga
Ga2	1.0	0.504269	0.995398	0.502491	Biso	1.000000	Ga
Ga3	1.0	0.997703	0.495521	0.997429	Biso	1.000000	Ga
Ga4	1.0	0.997719	0.995520	0.497429	Biso	1.000000	Ga
C1	1.0	0.554666	0.634699	0.846955	Biso	1.000000	C
C2	1.0	0.435021	0.357541	0.146528	Biso	1.000000	C
C3	1.0	0.454244	0.137645	0.650556	Biso	1.000000	C
C4	1.0	0.552601	0.854636	0.355798	Biso	1.000000	C
C5	1.0	0.431694	0.718923	0.760135	Biso	1.000000	C
C6	1.0	0.555089	0.273246	0.233096	Biso	1.000000	C
C7	1.0	0.556353	0.226795	0.730749	Biso	1.000000	C
C8	1.0	0.448380	0.765457	0.275677	Biso	1.000000	C
C9	1.0	0.554786	0.773102	0.732886	Biso	1.000000	C

C10	1.0	0.432006	0.219062	0.260348	Biso	1.000000 C
C11	1.0	0.448635	0.265313	0.775881	Biso	1.000000 C
C12	1.0	0.556078	0.726943	0.230533	Biso	1.000000 C
C13	1.0	0.434790	0.857422	0.646356	Biso	1.000000 C
C14	1.0	0.554937	0.134819	0.347138	Biso	1.000000 C
C15	1.0	0.552812	0.354517	0.855962	Biso	1.000000 C
C16	1.0	0.453988	0.637773	0.150372	Biso	1.000000 C

```
_pd_phase_name                    'MIL-53(Al)-FA dehydrated form'
_cell_length_a                   6.68823
_cell_length_b                   13.43689
_cell_length_c                   13.76002
_cell_angle_alpha                 90.00328
_cell_angle_beta                 130.01071
_cell_angle_gamma                  90.01398
_space_group_name_H-M_alt           'P 1'
_space_group_IT_number              1

loop_
_space_group_symop_operation_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  O1       1.0    0.851608     0.500312     0.076917    Biso  1.000000 O
  O2       1.0    0.148461     0.500277     0.923061    Biso  1.000000 O
  O3       1.0    0.148469     0.000294     0.423063    Biso  1.000000 O
  O4       1.0    0.851618     0.000294     0.576920    Biso  1.000000 O
  O5       1.0    0.763092     0.599952     0.881413    Biso  1.000000 O
  O6       1.0    0.231593     0.395156     0.114076    Biso  1.000000 O
  O7       1.0    0.238395     0.099393     0.619215    Biso  1.000000 O
  O8       1.0    0.766562     0.895788     0.385037    Biso  1.000000 O
  O9       1.0    0.421161     0.599809     0.879949    Biso  1.000000 O
  O10      1.0    0.572641     0.395288     0.115728    Biso  1.000000 O
  O11      1.0    0.578613     0.100494     0.619384    Biso  1.000000 O
  O12      1.0    0.427878     0.894532     0.385173    Biso  1.000000 O
  O13      1.0    0.572611     0.895272     0.615707    Biso  1.000000 O
  O14      1.0    0.421212     0.099827     0.379979    Biso  1.000000 O
  O15      1.0    0.427908     0.394516     0.885194    Biso  1.000000 O
  O16      1.0    0.578563     0.600511     0.119354    Biso  1.000000 O
  O17      1.0    0.231530     0.895124     0.614030    Biso  1.000000 O
  O18      1.0    0.763164     0.099985     0.381459    Biso  1.000000 O
  O19      1.0    0.766626     0.395755     0.885083    Biso  1.000000 O
  O20      1.0    0.238324     0.599426     0.119170    Biso  1.000000 O
  H1       1.0    0.749759     0.250683     0.765144    Biso  1.000000 H
  H2       1.0    0.255607     0.744984     0.239297    Biso  1.000000 H
  H3       1.0    0.249007     0.749810     0.733915    Biso  1.000000 H
```

H4	1.0	0.745458	0.245852	0.261658	Biso	1.000000 H
H5	1.0	0.749688	0.750715	0.265092	Biso	1.000000 H
H6	1.0	0.255670	0.244952	0.739342	Biso	1.000000 H
H7	1.0	0.249076	0.249841	0.233966	Biso	1.000000 H
H8	1.0	0.745395	0.745820	0.761613	Biso	1.000000 H
H9	1.0	0.040593	0.532942	0.841212	Biso	1.000000 H
H10	1.0	0.959768	0.532901	0.158836	Biso	1.000000 H
H11	1.0	0.959802	0.032861	0.658854	Biso	1.000000 H
H12	1.0	0.040627	0.032982	0.341230	Biso	1.000000 H
Al1	1.0	0.500071	0.497517	0.000040	Biso	1.000000 Al
Al2	1.0	0.500081	0.997517	0.500044	Biso	1.000000 Al
Al3	1.0	0.999956	0.497615	0.999950	Biso	1.000000 Al
Al4	1.0	0.999961	0.997616	0.499950	Biso	1.000000 Al
C1	1.0	0.549975	0.634478	0.848384	Biso	1.000000 C
C2	1.0	0.444115	0.360558	0.147127	Biso	1.000000 C
C3	1.0	0.450398	0.134597	0.651526	Biso	1.000000 C
C4	1.0	0.555430	0.860441	0.352953	Biso	1.000000 C
C5	1.0	0.436524	0.723525	0.765110	Biso	1.000000 C
C6	1.0	0.557538	0.271533	0.230408	Biso	1.000000 C
C7	1.0	0.563153	0.223802	0.734592	Biso	1.000000 C
C8	1.0	0.442602	0.771257	0.269875	Biso	1.000000 C
C9	1.0	0.557472	0.771500	0.730360	Biso	1.000000 C
C10	1.0	0.436593	0.223558	0.265160	Biso	1.000000 C
C11	1.0	0.442666	0.271225	0.769922	Biso	1.000000 C
C12	1.0	0.563084	0.723835	0.234542	Biso	1.000000 C
C13	1.0	0.444063	0.860531	0.647089	Biso	1.000000 C
C14	1.0	0.550039	0.134506	0.348426	Biso	1.000000 C
C15	1.0	0.555481	0.360413	0.852991	Biso	1.000000 C
C16	1.0	0.450335	0.634625	0.151484	Biso	1.000000 C

12.3. Contracted-pore form

```
_pd_phase_name                      'MIL-53(Ga)-FA contracted form'
_cell_length_a                     6.81509
_cell_length_b                     15.60451
_cell_length_c                     9.47470
_cell_angle_alpha                   97.02944
_cell_angle_beta                   145.69066
_cell_angle_gamma                    84.48072
_space_group_name_H-M_alt            'P 1'
_space_group_IT_number               1

loop_
_space_group_symop_operation_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  O1       1.0    0.957302     0.503142     0.182271    Biso  1.000000 O
  O2       1.0    0.040973     0.510621     0.826484    Biso  1.000000 O
  O3       1.0    0.040975     0.010623     0.326485    Biso  1.000000 O
  O4       1.0    0.957302     0.003140     0.682271    Biso  1.000000 O
  O5       1.0    0.593277     0.594230     0.764580    Biso  1.000000 O
  O6       1.0    0.404989     0.419529     0.244165    Biso  1.000000 O
  O7       1.0    0.294349     0.115904     0.713874    Biso  1.000000 O
  O8       1.0    0.703914     0.897861     0.294865    Biso  1.000000 O
  O9       1.0    0.401786     0.620504     0.879277    Biso  1.000000 O
  O10      1.0    0.596477     0.393249     0.129467    Biso  1.000000 O
  O11      1.0    0.710156     0.077340     0.797214    Biso  1.000000 O
  O12      1.0    0.288115     0.936421     0.211536    Biso  1.000000 O
  O13      1.0    0.596468     0.893247     0.629459    Biso  1.000000 O
  O14      1.0    0.401796     0.120505     0.379286    Biso  1.000000 O
  O15      1.0    0.288122     0.436418     0.711541    Biso  1.000000 O
  O16      1.0    0.710150     0.577342     0.297209    Biso  1.000000 O
  O17      1.0    0.404979     0.919526     0.744156    Biso  1.000000 O
  O18      1.0    0.593289     0.094233     0.264590    Biso  1.000000 O
  O19      1.0    0.703926     0.397859     0.794875    Biso  1.000000 O
  O20      1.0    0.294337     0.615906     0.213864    Biso  1.000000 O
  H1       1.0    0.834039     0.236493     0.866881    Biso  1.000000 H
```

H2	1.0	0.164214	0.777266	0.141839	Biso	1.000000 H
H3	1.0	0.361010	0.776250	0.825716	Biso	1.000000 H
H4	1.0	0.637242	0.237504	0.183026	Biso	1.000000 H
H5	1.0	0.834025	0.736495	0.366869	Biso	1.000000 H
H6	1.0	0.164228	0.277263	0.641851	Biso	1.000000 H
H7	1.0	0.361024	0.276252	0.325729	Biso	1.000000 H
H8	1.0	0.637228	0.737502	0.683013	Biso	1.000000 H
H9	1.0	0.862621	0.478122	0.662587	Biso	1.000000 H
H10	1.0	0.135663	0.535638	0.346173	Biso	1.000000 H
H11	1.0	0.135662	0.035637	0.846172	Biso	1.000000 H
H12	1.0	0.862622	0.978123	0.162588	Biso	1.000000 H
Ga1	1.0	0.499137	0.506877	0.004379	Biso	1.000000 Ga
Ga2	1.0	0.499137	0.006877	0.504379	Biso	1.000000 Ga
Ga3	1.0	0.999129	0.506879	0.004373	Biso	1.000000 Ga
Ga4	1.0	0.999131	0.006879	0.504374	Biso	1.000000 Ga
C1	1.0	0.485378	0.643476	0.808779	Biso	1.000000 C
C2	1.0	0.512881	0.370279	0.199965	Biso	1.000000 C
C3	1.0	0.532885	0.133596	0.770046	Biso	1.000000 C
C4	1.0	0.465374	0.880166	0.238689	Biso	1.000000 C
C5	1.0	0.453721	0.737876	0.784331	Biso	1.000000 C
C6	1.0	0.544535	0.275879	0.224412	Biso	1.000000 C
C7	1.0	0.606878	0.224693	0.795542	Biso	1.000000 C
C8	1.0	0.391373	0.789068	0.213178	Biso	1.000000 C
C9	1.0	0.544523	0.775877	0.724400	Biso	1.000000 C
C10	1.0	0.453735	0.237878	0.284344	Biso	1.000000 C
C11	1.0	0.391387	0.289066	0.713190	Biso	1.000000 C
C12	1.0	0.606865	0.724695	0.295530	Biso	1.000000 C
C13	1.0	0.512871	0.870277	0.699955	Biso	1.000000 C
C14	1.0	0.485390	0.143478	0.308790	Biso	1.000000 C
C15	1.0	0.465385	0.380164	0.738698	Biso	1.000000 C
C16	1.0	0.532875	0.633598	0.270037	Biso	1.000000 C

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_pd_phase_name                    'MIL-53(Al)-FA contracted form'
_cell_length_a                   6.72072
_cell_length_b                   15.05199
_cell_length_c                   10.49345
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_cell_angle_beta                 145.25237
_cell_angle_gamma                  90.02338
_space_group_name_H-M_alt          'P 1'
_space_group_IT_number             1

loop_
_space_group_symop_operation_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  O1      1.0   0.917161   0.522287   0.134660   Biso  1.000000 O
  O2      1.0   0.081158   0.491473   0.874123   Biso  1.000000 O
  O3      1.0   0.081062   0.022242   0.374029   Biso  1.000000 O
  O4      1.0   0.917152   0.991519   0.634676   Biso  1.000000 O
  O5      1.0   0.578306   0.573326   0.743017   Biso  1.000000 O
  O6      1.0   0.420004   0.440429   0.265759   Biso  1.000000 O
  O7      1.0   0.420247   0.073253   0.765743   Biso  1.000000 O
  O8      1.0   0.577962   0.940504   0.242958   Biso  1.000000 O
  O9      1.0   0.254242   0.577025   0.752520   Biso  1.000000 O
  O10     1.0   0.744083   0.436737   0.256267   Biso  1.000000 O
  O11     1.0   0.743774   0.077281   0.755831   Biso  1.000000 O
  O12     1.0   0.254442   0.936481   0.252874   Biso  1.000000 O
  O13     1.0   0.591239   0.897542   0.639782   Biso  1.000000 O
  O14     1.0   0.406974   0.116220   0.368926   Biso  1.000000 O
  O15     1.0   0.407472   0.397387   0.869583   Biso  1.000000 O
  O16     1.0   0.590838   0.616374   0.139195   Biso  1.000000 O
  O17     1.0   0.234337   0.894096   0.624291   Biso  1.000000 O
  O18     1.0   0.763864   0.119659   0.384407   Biso  1.000000 O
  O19     1.0   0.763452   0.394150   0.884328   Biso  1.000000 O
  O20     1.0   0.234861   0.619605   0.124453   Biso  1.000000 O
  H1      1.0   0.889800   0.236037   0.883520   Biso  1.000000 H
  H2      1.0   0.108440   0.777719   0.125209   Biso  1.000000 H
  H3      1.0   0.107826   0.735813   0.624776   Biso  1.000000 H
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H4	1.0	0.890457	0.277941	0.383977	Biso	1.000000 H
H5	1.0	0.669715	0.781970	0.209671	Biso	1.000000 H
H6	1.0	0.328555	0.231791	0.799085	Biso	1.000000 H
H7	1.0	0.328107	0.281807	0.298575	Biso	1.000000 H
H8	1.0	0.670149	0.731955	0.710154	Biso	1.000000 H
H9	1.0	0.888707	0.468276	0.722994	Biso	1.000000 H
H10	1.0	0.109625	0.545477	0.285796	Biso	1.000000 H
H11	1.0	0.109559	0.968328	0.785816	Biso	1.000000 H
H12	1.0	0.888656	0.045433	0.222890	Biso	1.000000 H
Al1	1.0	0.499160	0.506881	0.004392	Biso	1.000000 Al
Al2	1.0	0.499107	0.006880	0.504353	Biso	1.000000 Al
Al3	1.0	0.999157	0.506878	0.004390	Biso	1.000000 Al
Al4	1.0	0.999105	0.006879	0.504351	Biso	1.000000 Al
C1	1.0	0.377837	0.612128	0.716779	Biso	1.000000 C
C2	1.0	0.620474	0.401629	0.291995	Biso	1.000000 C
C3	1.0	0.620366	0.112216	0.791775	Biso	1.000000 C
C4	1.0	0.377852	0.901542	0.216935	Biso	1.000000 C
C5	1.0	0.296727	0.707607	0.657911	Biso	1.000000 C
C6	1.0	0.701559	0.306149	0.350842	Biso	1.000000 C
C7	1.0	0.701281	0.207694	0.850657	Biso	1.000000 C
C8	1.0	0.296960	0.806063	0.158074	Biso	1.000000 C
C9	1.0	0.479351	0.760070	0.675317	Biso	1.000000 C
C10	1.0	0.518903	0.253689	0.333413	Biso	1.000000 C
C11	1.0	0.518985	0.260017	0.833638	Biso	1.000000 C
C12	1.0	0.479284	0.753741	0.175116	Biso	1.000000 C
C13	1.0	0.430270	0.857764	0.644712	Biso	1.000000 C
C14	1.0	0.567950	0.155995	0.363998	Biso	1.000000 C
C15	1.0	0.568001	0.357716	0.864277	Biso	1.000000 C
C16	1.0	0.430298	0.656042	0.144496	Biso	1.000000 C

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