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SUPPORTING INFORMATION

Flexibility and Disorder in Modified-Linker MIL-53 Materials

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Table S1: Unit cell parameters of various modified Al-MIL-53 frameworks compared with the unmodified framework as determined by *in situ* powder XRD.

Functional Group	Hydrated	Dehydrated	Superhydrated	Methanol
-H	*a* = 19.513(2) Å *b* = 7.612(1) Å *c* = 6.576(1) Å *β* = 104.24(1) ° *V* = 946.8 Å^3 ***Cc***[a]	*a* = 6.6085(9) Å *b* = 16.675(3) Å *c* = 12.813(2) Å *V* = 1412.0 Å^3 ***Imma***[a]	*Not studied*	*Not studied* **-**
-NO$_2$	*a* = 19.687(10) Å *b* = 8.257(5) Å *c* = 6.635(3) Å *β* = 106.87(4) ° *V* = 1032.1(12) Å^3 [b]	*a* = 16.522(2) Å *b* = 12.974(2) Å *c* = 6.6285(8) Å *V* = 1420.9(4) Å^3 ***Imcm (170 °C)***	*a* = 16.240(2) Å *b* = 13.886(2) Å *c* = 6.7026(9) Å *V* = 1511.5(4) Å^3 *a* = 20.334(4) Å *b* = 8.344(1) Å *c* = 6.700(2) Å *β* = 107.87(1) ° *V* = 1082.0(4) Å^3 ***Imcm*** *(major phase)* ***+ C2/c***	*a* = 15.964(3) Å *b* = 13.812(2) Å *c* = 6.6561(9) Å *V* = 1467.6(3) Å^3 ***Imcm***
-Br	*a* = 19.567(14) Å *b* = 8.532(12) Å *c* = 6.616(5) Å *β* = 107.22(6) ° *V* = 1055.1(23) Å^3 [b]	*a* = 16.435(2) Å *b* = 13.057(1) Å *c* = 6.6198(5)Å *V* = 1420.6(1) Å^3 ***Imcm (210 °C)***	*a* = 16.082(6) Å *b* = 13.530(4) Å *c* = 6.619(2) Å *V* = 1471.0 (10) Å^3 ***Imcm***	*a* = 16.0824(7) Å *b* = 13.7878(8)Å *c* = 6.6593(4) Å *V* = 1476.7(1) Å^3 ***Imcm***
-CH$_3$	*a* = 19.700(17) Å *b* = 7.999(7) Å *c* = 6.603(5) Å *β* = 106.40(5) ° *V* = 998.1(19) Å^3 [b]	*a* = 16.567(2) Å *b* = 12.928(1) Å *c* = 6.6143(5) Å *V* = 1416.6(2) Å^3 ***Imcm (190 °C)***	*a* = 16.701(4) Å *b* = 12.979(3) Å *c* = 6.636(1) Å *V* = 1438.4(4) Å^3 ***Imcm*** *(major phase)* ***+ C2/c***	*a* = 16.503(1) Å *b* = 13.2173(8) Å *c* = 6.6488(5) Å *V* = 1450.2(1) Å^3 ***Imcm***

					a = 19.857(8) Å b = 8.0953(8) Å c = 6.643(2) Å β = 107.19(4) ° V = 1020.1(4) Å^3			
-(OH)$_2$	a = 19.762(4) Å b = 7.6320(16) Å c = 6.5786(14) Å β = 105.768(13) ° V = 954.9(5) Å^3	[b]	a = 20.654(3) Å b = 6.8765(9) Å c = 6.9034(8) Å β = 112.85(1) ° V = 903.6(2) Å^3	***C2/c***	a = 16.905(5) Å b = 12.487(2) Å c = 6.621(2) Å V = 1397.6(5) Å^3	***Imcm***	a = 16.855(2) Å b = 12.838(1) Å c = 6.6753(6) Å V = 1444.5(2) Å^3	***Imcm***
-COOH	a = 19.6055(17) Å b = 8.4476(22) Å c = 6.6520(6) Å β = 106.8(6) ° V = 1054.7(4) Å^3	***Cc***[c]	a = 16.052(3) Å b = 13.543(2) Å c = 6.598(1) Å V = 1434.2(2) Å^3	***Imcm (310 °C)***	a = 16.006(6) Å b = 13.734(4) Å c = 6.641(1) Å V = 1460.0(6) Å^3 a = 19.93(2) Å b = 8.503(2) Å c = 6.652(7) Å β = 109.9(2) ° V = 1059.6(9) Å^3	***Imcm (major phase) + C2/c***	a = 16.082(6)Å b = 13.530(4) Å c = 6.619(2) Å V = 1440(1) Å^3	***Imcm***
-Cl	a = 19.776(4) Å b = 7.9371(16) Å c = 6.6010(17) Å β = 106.589(13) ° V = 993.0(5) Å^3	[b]	a = 16.716(2) Å b = 12.899(2) Å c = 6.6376(6) Å V = 1431.3(3) Å^3	***Imcm (190 °C)***	a = 18.58(2) Å b = 12.002(7) Å c = 6.722(6) Å V = 1499(1) Å^3 a = 19.790(8) Å b = 7.9709(8) Å c = 6.587(1) Å β = 106.87(4) ° V = 994.4(3) Å^3	***C2/c (major phase) + Imcm***	a = 16.556(8)Å b = 12.938(7) Å c = 6.586(3) Å V = 1411(2) Å^3	***Imcm***

-NH_2	a = 19.722(7) Å^3 b = 7.692(3) Å^3 c = 6.578(4) Å^3 β = 105.1(3) ° V = 961.5(10) Å^3 ***C2/c***^{b}	*No change*	*No change*	*No change*

a: data from T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G.Férey, *Chem. Eur. J.*, 2004, **10,** 1373-1382.

b: data from S. Biswas, T. Ahnfeldt and N. Stock, *Inorg. Chem.*, 2011, **50,** 9518-9526.

c: data from: N. Reimer, B. Gil, B. Marszalek and N. Stock, *CrystEngComm*, 2012, **14,** 4119-4125

S1: Al-MIL-53-Cl

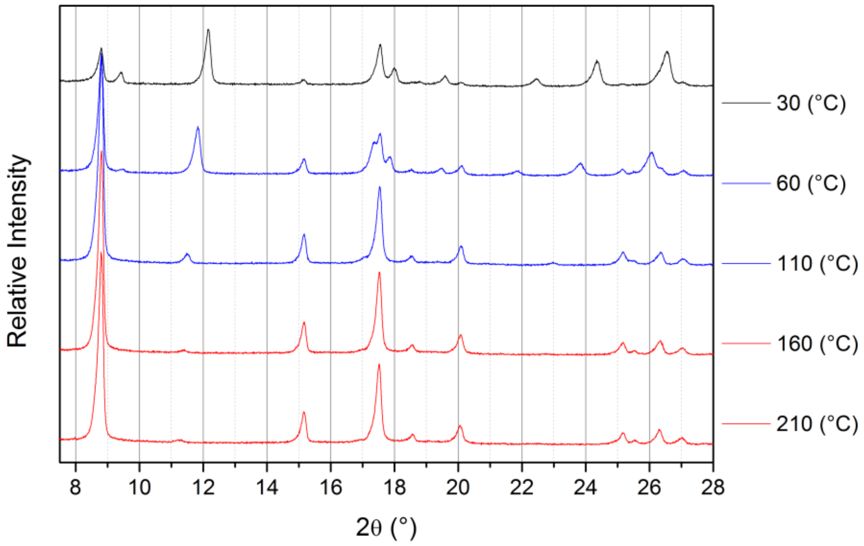


Figure S1.1: Behaviour of dehydrated Al-MIL-53-Cl upon cooling from 210°C to 30°C. Red = dehydrated phase, blue = mixed phase and black = hydrated phase.

S2: Al-MIL-53-NO_2

The monoclinic hydrated phase of the $–NO_2$ modified framework has a unit cell volume of 1032 Å^3 at room temperature. Figure S2.1 shows the thermal dehydration of the framework. It was observed that evolution from the hydrated phase to an expanded dehydrated phase, as is seen for unmodified Al-MIL-53, was complete at a temperature of 170 °C. Similarly the cooling of the sample back to 30 °C was recorded; the results show some hysteresis in the flexibility as the framework only begins to contract below 110 C, Figure S2.2. Longer data collection was performed while the sample was held at 210 °C. These data were used to perform a Le Bail profile fit which allows the unit cell parameters to be found. The starting point for the refinement was the unit cell of the dehydrated Cr-MIL-53, which has a unit cell volume of 1486.1 Å^3 and has the orthorhombic space group, *Imcm*.[1] This analysis, Figure b, confirms that the Al-MIL-53-NO_2 expands to the fully-open structure with a unit cell volume of 1420.9 Å^3.

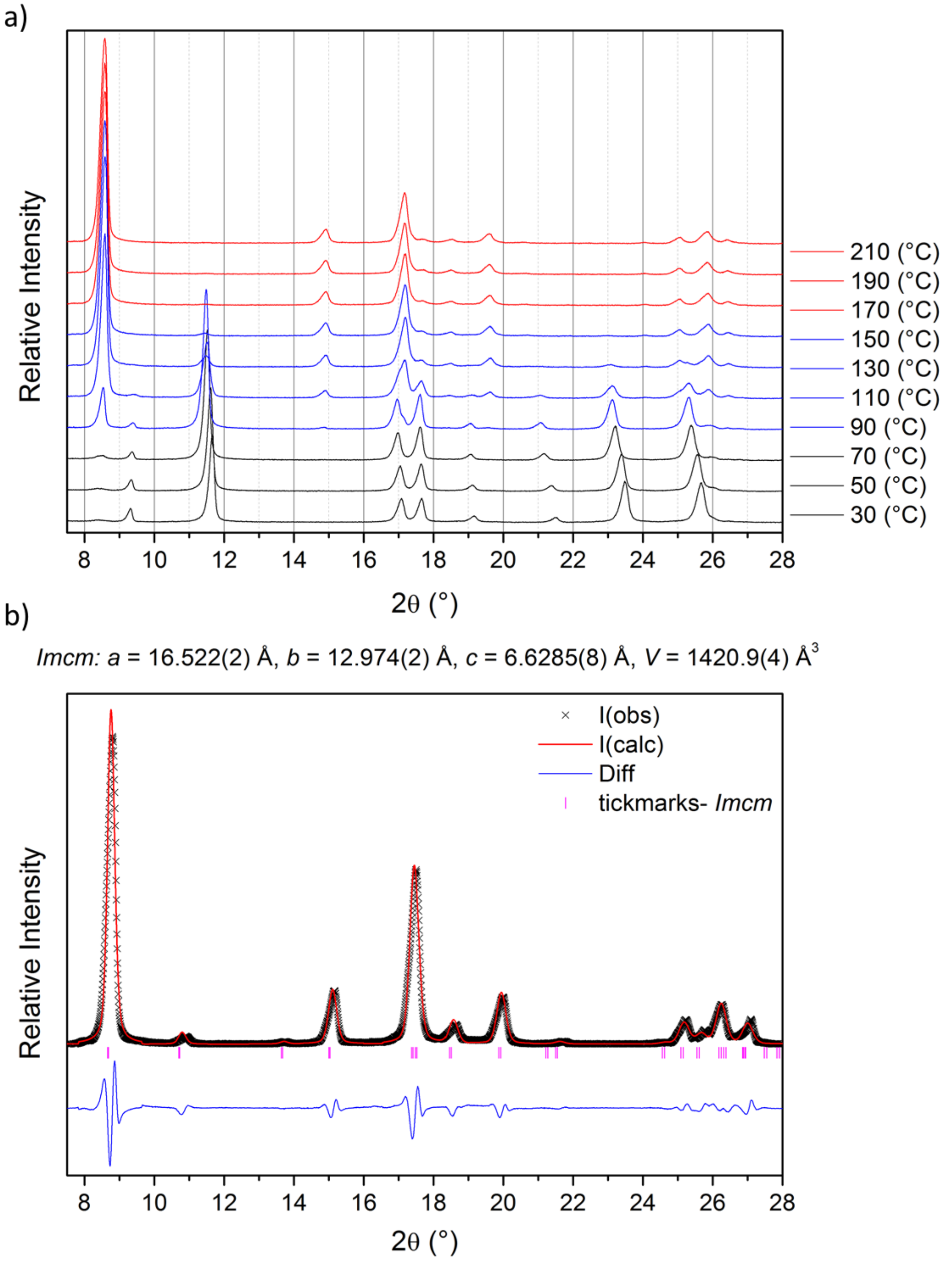


Figure S2.1: Dehydration of the -NO_2 modified Al-MIL-53 by heating to 210 °C. a) Individual XRD patterns showing the change in symmetry with increasing temperature (black = hydrated (*C*2/*c*), blue = mixed phase and red = dehydrated (*Imcm*)) and b) Le Bail profile fit for data recorded at 210 °C.

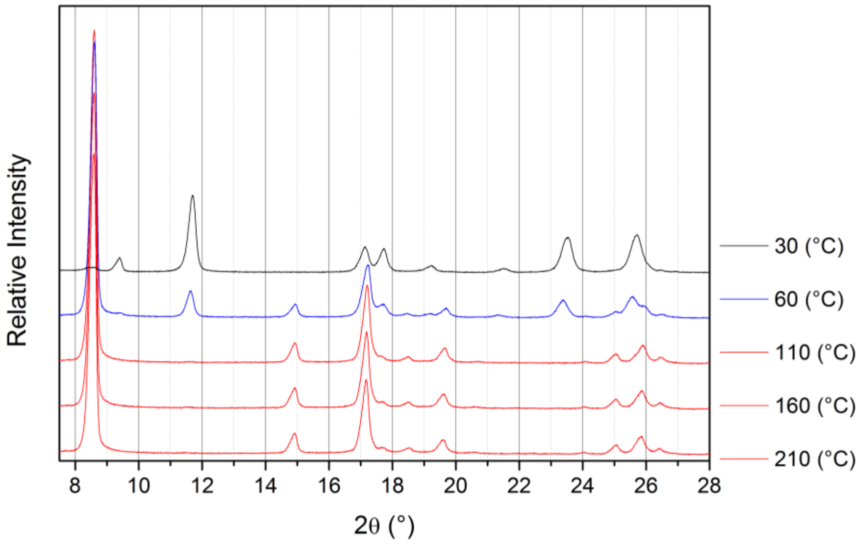


Figure S2.2: Behaviour of dehydrated Al-MIL-53-NO_2 upon cooling from 210°C to 30°C. Red = dehydrated phase, blue = mixed phase and black = hydrated phase.

Figure S2.3 shows that superhydration of the framework occurs using the method described previously (*i.e*. preparing a paste with the material) and this is evidenced by the initial pattern at 30 °C exhibiting the fully-open, *Imcm,* pattern. It was expected that the *Imcm* phase would only exist while the sample remained as a paste and that upon drying to a powder it would contract to the closed phase as was seen for Cr-MIL-53.[2] However, heat was required to remove the additional water molecules from the pores. The sample was heated to 100 °C and then returned to 30 °C, which showed that the process was fully reversible. Dehydration of the fully-open superhydrated phase occurs via the closed hydrated phase (seen at 60 °C), showing that the water is lost in two steps; the additional water being lost first. Then further heating showed that the framework started expanding to give the dehydrated phase as was seen previously for the dehydration experiment. Upon cooling to 30 °C the framework takes up water from the air and returns to the hydrated phase. Longer data collection was used to collect data at 30 °C before thermal treatment was applied. These data were used to perform a Le Bail profile fit; longer data collection was possible for this dataset as the framework retained water at 30 °C. Figure b shows that it was necessary to use a mixed-phase refinement as the expansion of the whole structure due to superhydration had not occurred; a minor amount of the hydrated phase was still present. The fully-open phase was refined using the *Imcm* space group as before, whereas the starting point of the refinement for the closed phase used hydrated Cr-MIL-53, which has a unit cell volume of 994 Å^3 and has the monoclinic space group, *C2/c*.[1] This analysis shows that this method was unable to superhydrate the material completely.

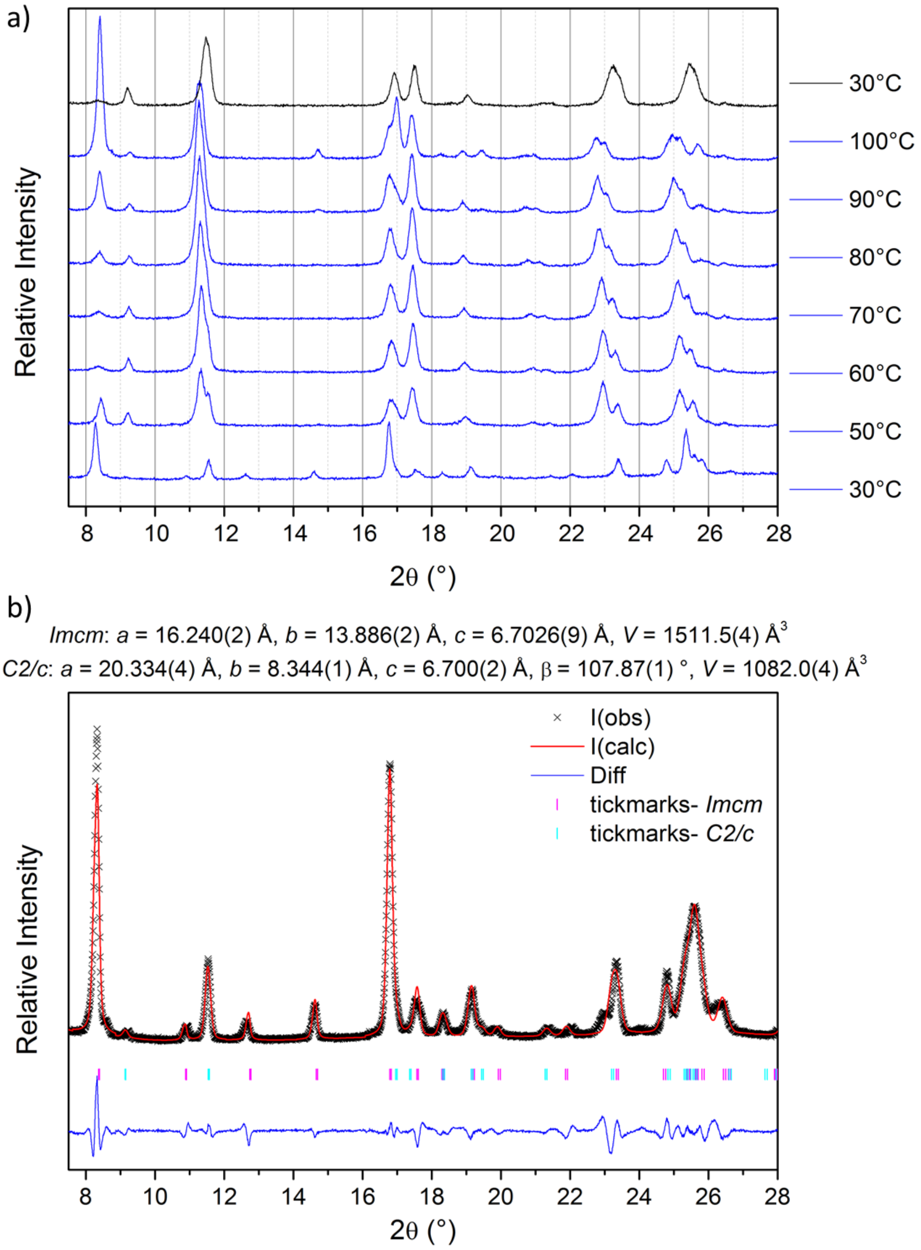


Figure S2.3: The removal of H_2O from the superhydrated phase of the -NO_2 modified Al-MIL-53. a) Individual XRD patterns show the removal of H_2O using temperature (blue = mixed phase and black = hydrated (C2/c)) and b) Le Bail profile fit for the partially superhydrated phase of NO_2 modified Al-MIL-53 recorded at room temperature.

The uptake of methanol by the –NO_2 modified Al-MIL-53 was followed using *in situ* XRD, Figure S2.4. The methanol vapour was introduced into the gas chamber on scan number 3 (point A) and was removed and replaced with N_2 on scan number 23 (point B). The contour plot highlights the change in framework symmetry during the experiment. After the addition of methanol vapour it can be seen that the framework expands from the hydrated phase to the fully-open phase but does not expand via a transient half-open phase as was seen for fluorinated Fe-MIL-53 in the presence of liquid methanol.[3] After the introduction of a N_2 gas flow the methanol is lost from the pores and the framework returns to a pore volume similar to the hydrated phase. Interestingly, water should not be present in the N_2 gas flow therefore it is suggested that the fully-open phase contains a mixture of methanol and water molecules as was observed for hydrated Fe-MIL-53 upon the adsorption of methanol.[4] Consequently, after the introduction of the pure N_2 gas flow the methanol molecules are desorbed from the framework but the water remains. This requires further investigation. To improve the signal-to-noise ratio in the pattern of the fully-open methanol phase of –NO_2 modified Al-MIL-53 a longer data collection was used. This dataset was used to perform a Le Bail profile fit showing that the framework fully-opens to give the orthorhombic, *Imcm*, structure with a refined unit cell volume of 1467.6 $Å^3$. This fully-open phase is larger than the fully-open phase recorded for the dehydrated material, 1420.9 Å. Greater expansion upon the adsorption of guest molecules, when compared to the dehydrated phase, was also seen for Cr-MIL-53;[5] providing further evidence for the inclusion of the guest molecules within the –NO_2 modified material.

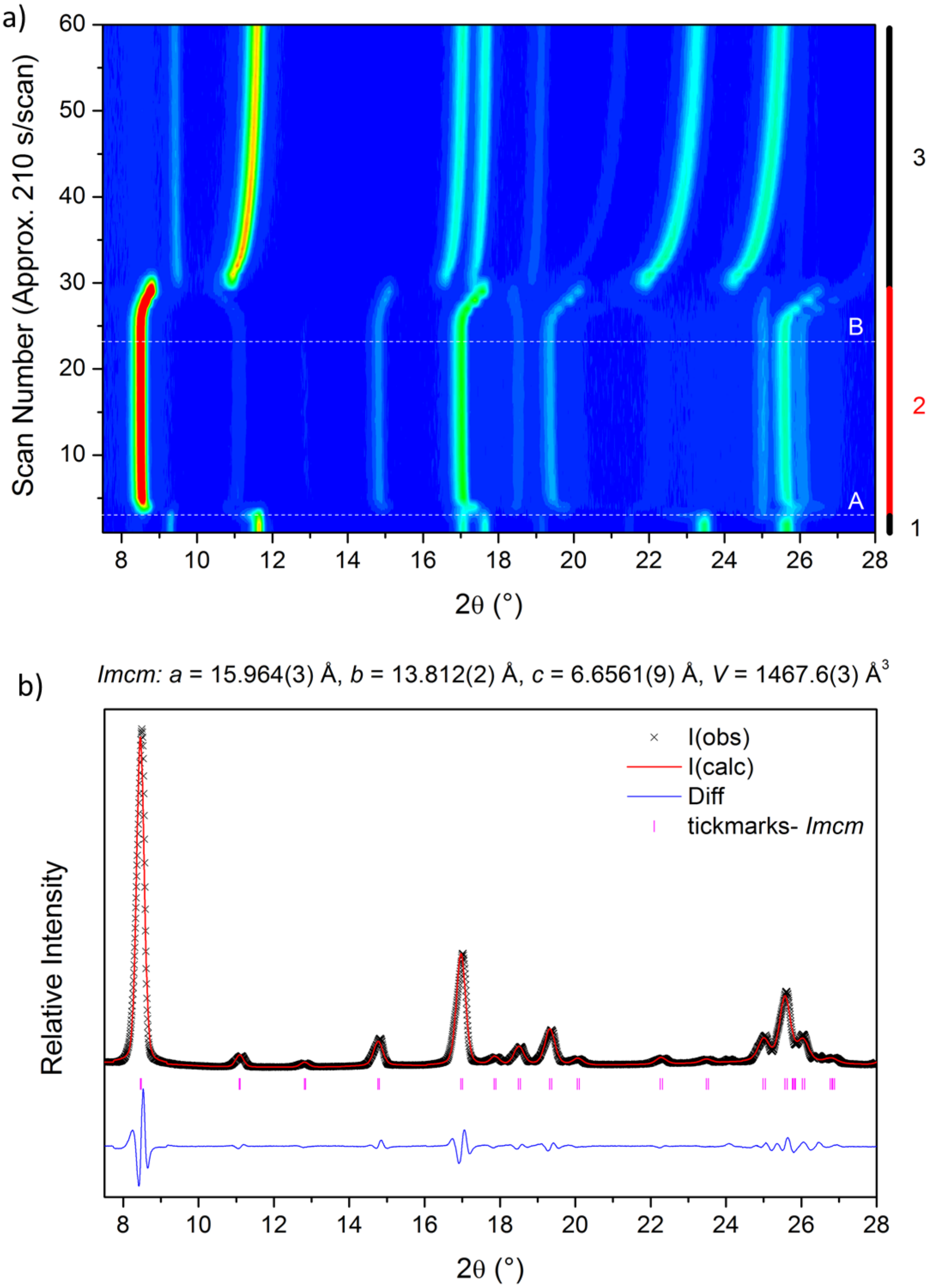


Figure S2.4: Behaviour of the -NO_2 modified Al-MIL-53 in response to methanol vapour. a) Contour plot, where A indicates the introduction of methanol vapour and B indicates when the gas flow was switched to pure N_2 (Phase 1/3 (black) = hydrated phase (*C*2/*c*), Phase 2 (red) = fully-open MeOH phase (*Imcm*)) and b) Le Bail profile fit for the fully-open methanol phase

S3. Al-MIL-53-Br

The monoclinic hydrated phase of –Br modified Al-MIL-53 has a unit cell volume of 1055 Å^3. The thermal dehydration of the sample is shown in Figure S3.1. A gradual shift of the hydrated Bragg peaks towards high angle can be seen before the growth of the fully-open phase is first visible above 130 °C. However, complete evolution to the fully-open framework was not seen at 210 °C using this *in situ* method. Longer data collection was performed as the sample was held at 210 °C; as the material was held at this temperature complete evolution to the fully-open phase was achieved. The Le Bail refinement, Figure S3.1b, shows that the framework expands to the orthorhombic, *Imcm*, phase to give a unit cell volume of 1420 Å^3. Powder XRD patterns on cooling are shown in Figure S3.2.

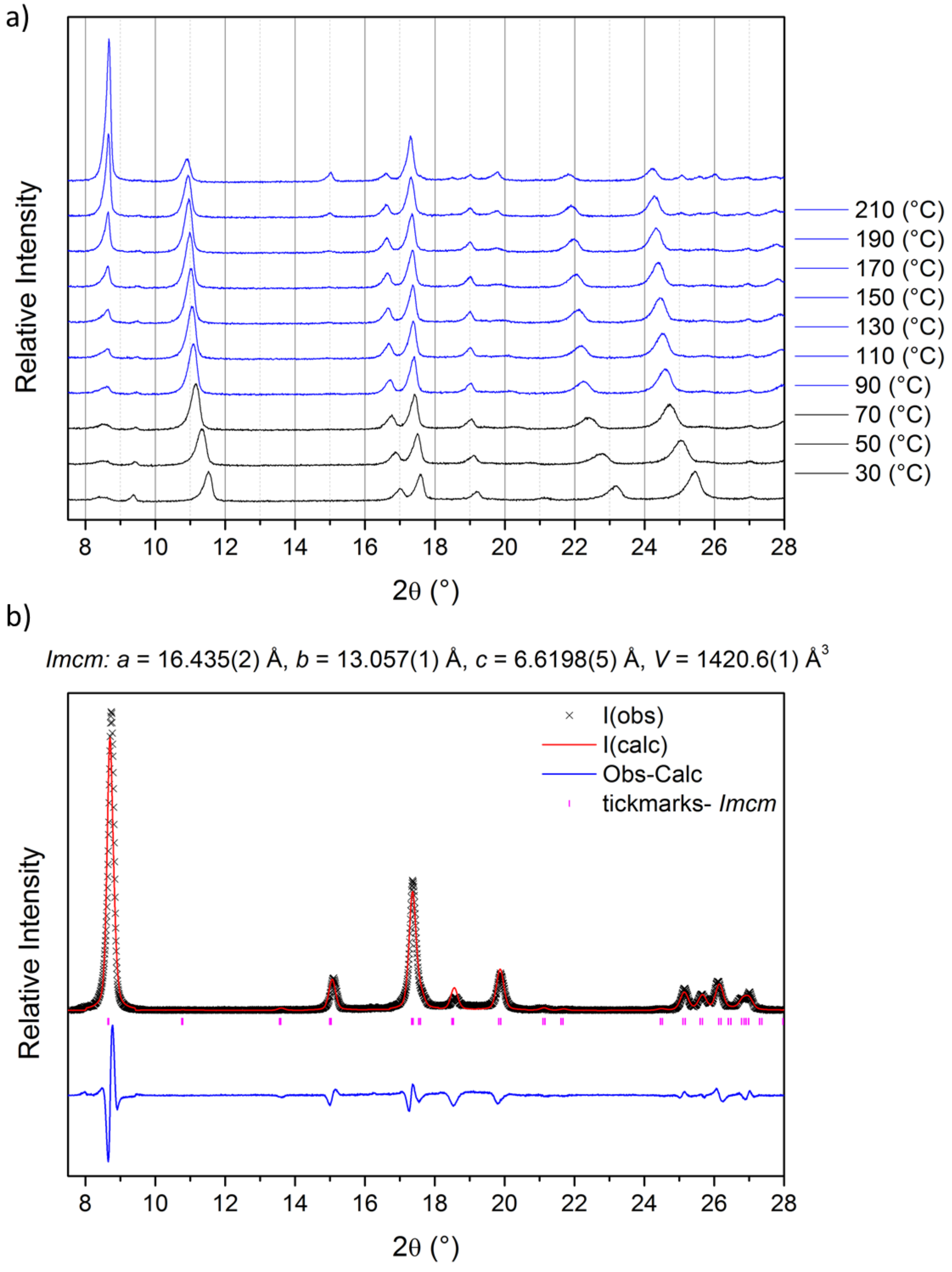


Figure S3.1: Thermal dehydration of the –Br modified Al-MIL-53. a) Individual XRD patterns showing the response of the framework to increasing temperature (black = hydrated (*C*2/*c*), blue = mixed phase and red = dehydrated (*Imcm*))and b) Le Bail profile fit for the phase recorded at 210 °C.

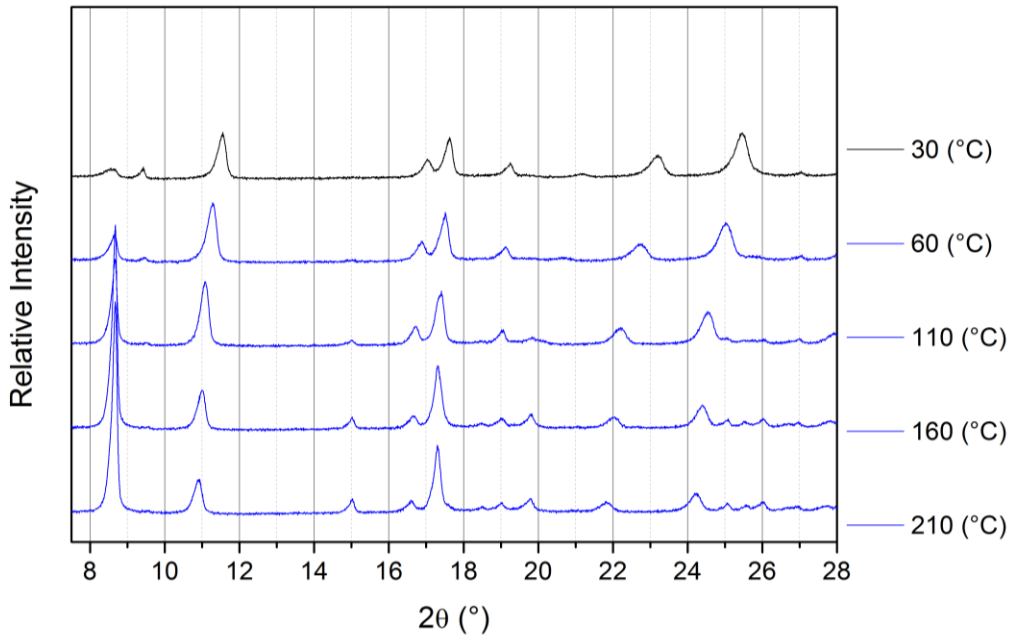


Figure S3.2: Behaviour of dehydrated Al-MIL-53-Br upon cooling from 210°C to 30°C. Blue = mixed phase and black = hydrated phase.

Superhydration of the framework was investigated and it was observed that although the framework initially takes up water in the powder/water suspension the interaction is not very strong and it is easily lost from the framework. The contour plot, Figure S3.3, shows the contraction of the framework upon the loss of water without the need for any external stimuli *e.g*. heat. The sample was maintained at 30 °C throughout this experiment and no gas flow was used. Due to the difficulties experienced in making the paste remain level in the sample holder, especially after contraction upon drying, the Bragg peaks have very low intensities. Therefore the individual XRD patterns have a low signal-to-noise ratio but it is still possible to identify the strongest Bragg reflections that indicate the presence of each phase. A Le Bail profile fit was performed on the first pattern recorded for the contour plot. The low signal-to-noise ratio increased the errors of the refinement but it can be clearly seen that the superhydrated phase has the fully-open, *Imcm*, structure (Figure S3.3b).

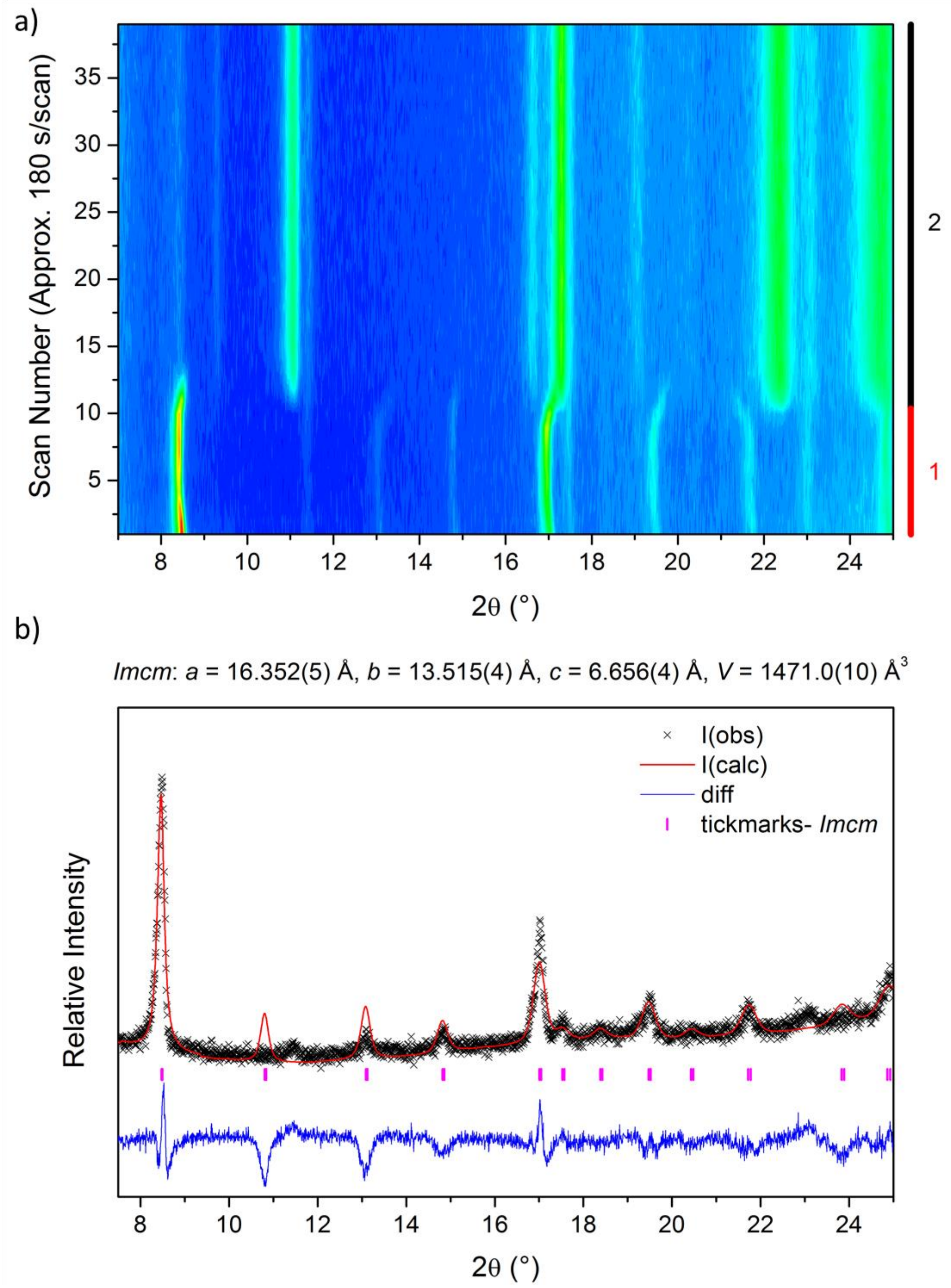


Figure S3.3: The removal of H_2O from the superhydrated phase of the -Br modified Al-MIL-53. a) Contour plot showing the gradual loss of the excess water at 30 °C (Phase 1 (red) = superhydrated phase (*Imcm*) and Phase 2 (black) = hydrated phase (*C*2/*c*)) and b) Le Bail profile fit of the first scan of the contour plot when the material is superhydrated.

The sample was exposed to a flow of methanol vapour and then a stationary environment was used while a long data collection was performed. This pattern, which has a good signal-to-noise ratio, was used for a Le Bail profile fit. Figure S3.4 shows that the –Br modified framework fully-opens in response to methanol vapour. The refined unit cell volume was determined to be 1476.7 Å^3, which is larger than the calculated volume for the dehydrated phase of this framework, 1420.6 Å^3.

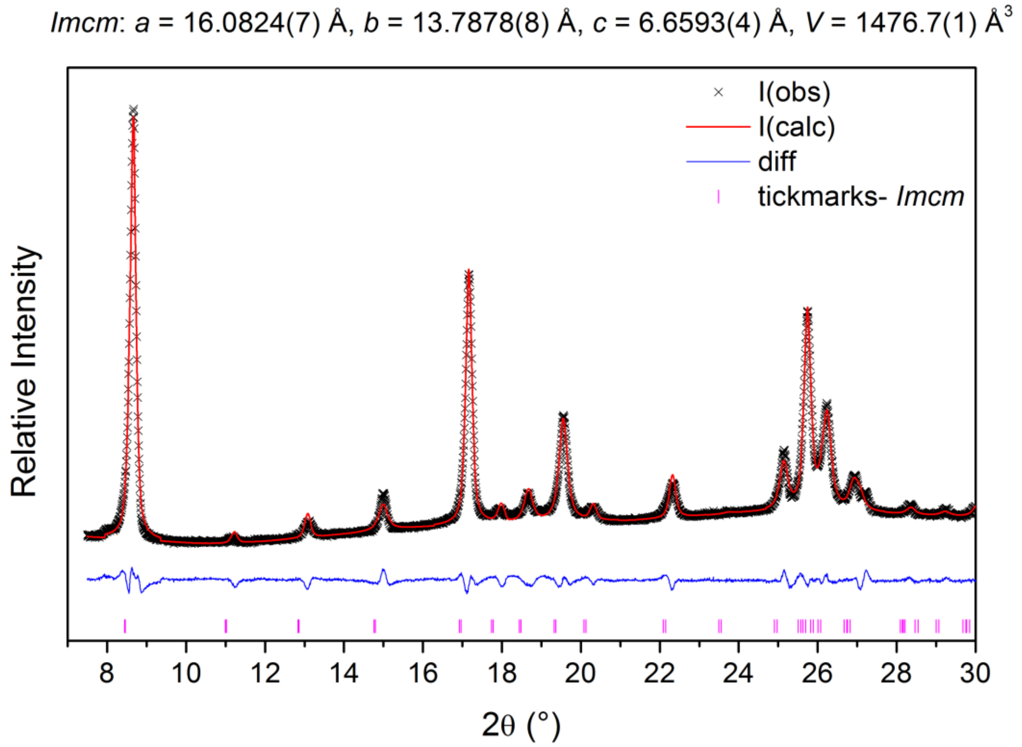


Figure S3.4: Le Bail profile fit for the fully-open methanol phase of Al-MIL-53-Br.

S4 Al-MIL-53-CH_3

The monoclinic hydrated phase of the –CH_3 modified Al-MIL-53 framework has a unit cell volume of 998 Å^3. The thermal dehydration of the framework is shown in Figure S4.1, which shows that the framework reaches complete expansion at 190 °C. Upon cooling back to room temperature the framework remains fully-open until the temperature drops below 110 °C. A long data collection was recorded while the sample was held at 210 °C to improve the pattern used for the profile parameter refinement. The Le Bail profile parameter fit confirms that the framework is fully-expanded at high temperatures, Figure S4.1b. The refinement gives a unit cell volume of 1416.6 Å^3. Powder XRD on cooling are shown in Figure S4.2.

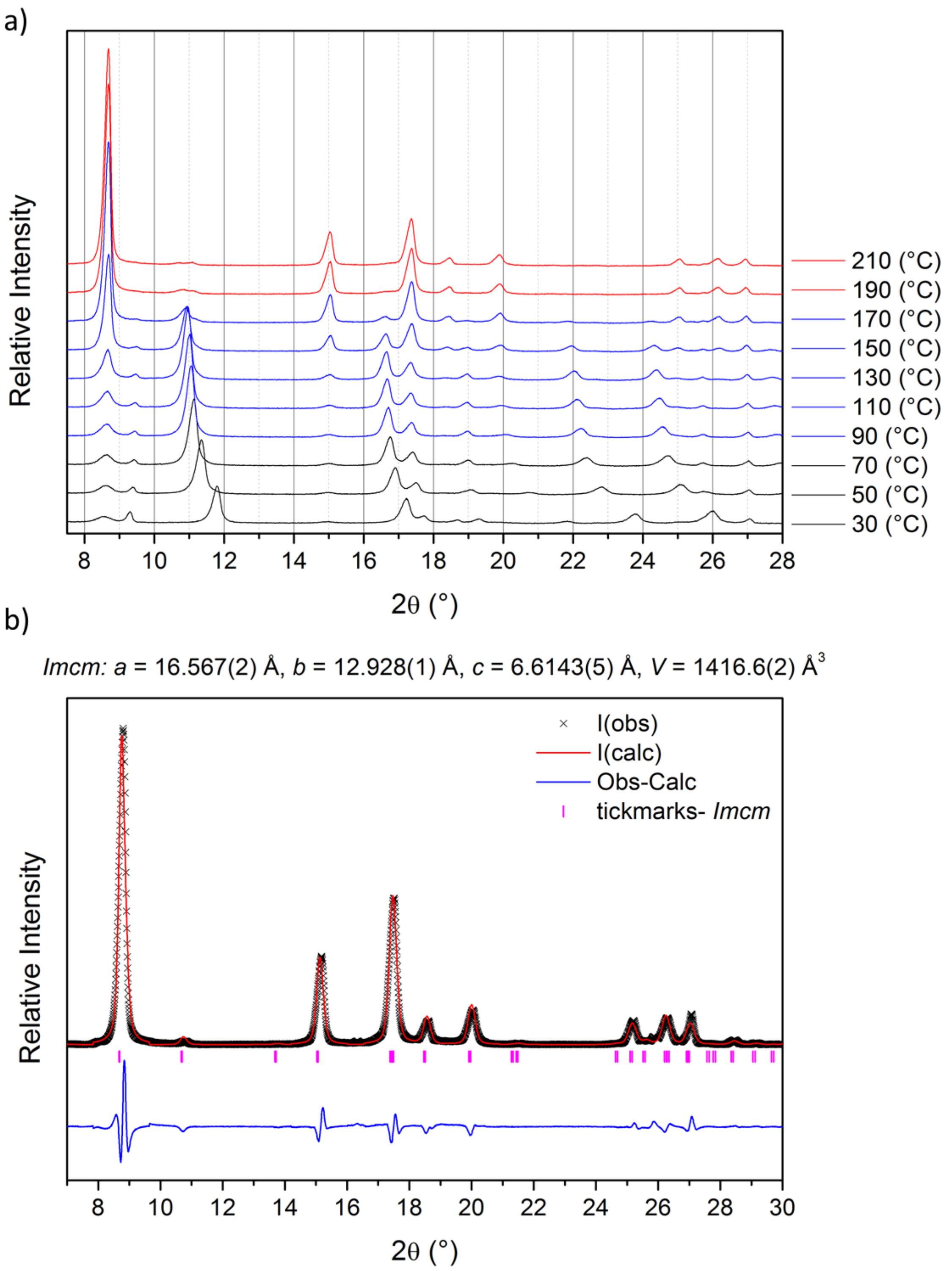


Figure S4.1: Thermal dehydration of the –CH_3 modified Al-MIL-53. a) Individual XRD patterns showing the change in symmetry with increasing temperature (black = hydrated phase (*C*2/*c*), blue = mixed phase and red = dehydrated phase (*Imcm*)) and b) Le Bail profile fit for data recorded at 210 °C.

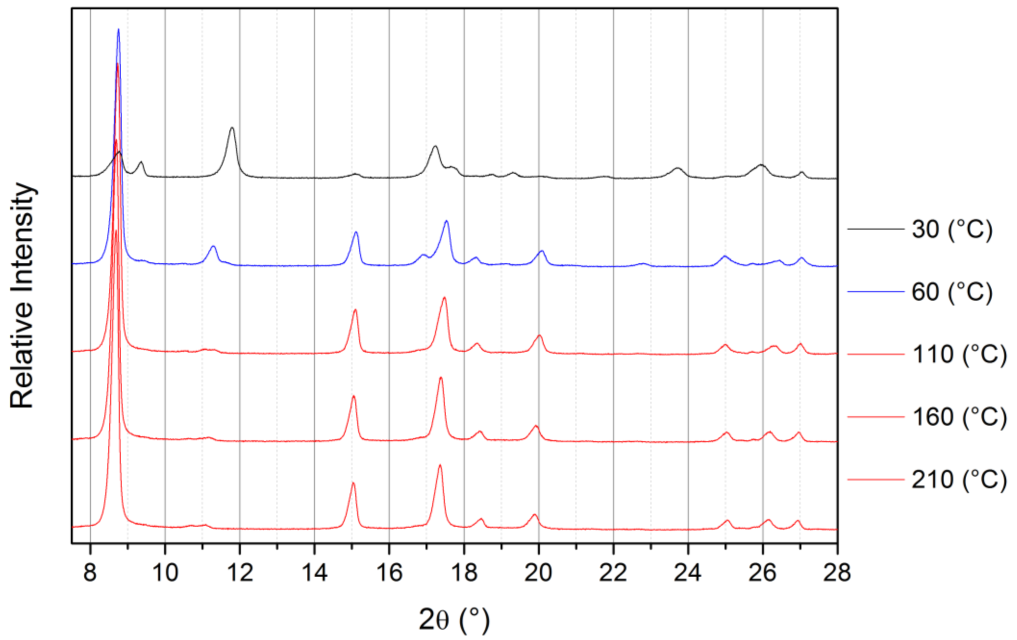


Figure S4.2: Behaviour of dehydrated Al-MIL-53-CH_3 upon cooling from 210°C to 30°C. Red = dehydrated phase, blue = mixed phase and black = hydrated phase.

Superhydration of the framework was attempted as for the previous samples. The initial individual XRD pattern shows that, under the same conditions as were used for the other samples, this framework does not superhydrate to give the fully-open phase. The appearance of the (110) peak (~ 8°) of the fully-open phase indicates that some of the material opened, but the interaction was not sufficient to open the entire sample. A Le Bail profile fit (Figure S4.3) was performed on the first pattern recorded during this experiment, which confirms the hydrated phase has partially expanded to the, *Imcm*, structure.

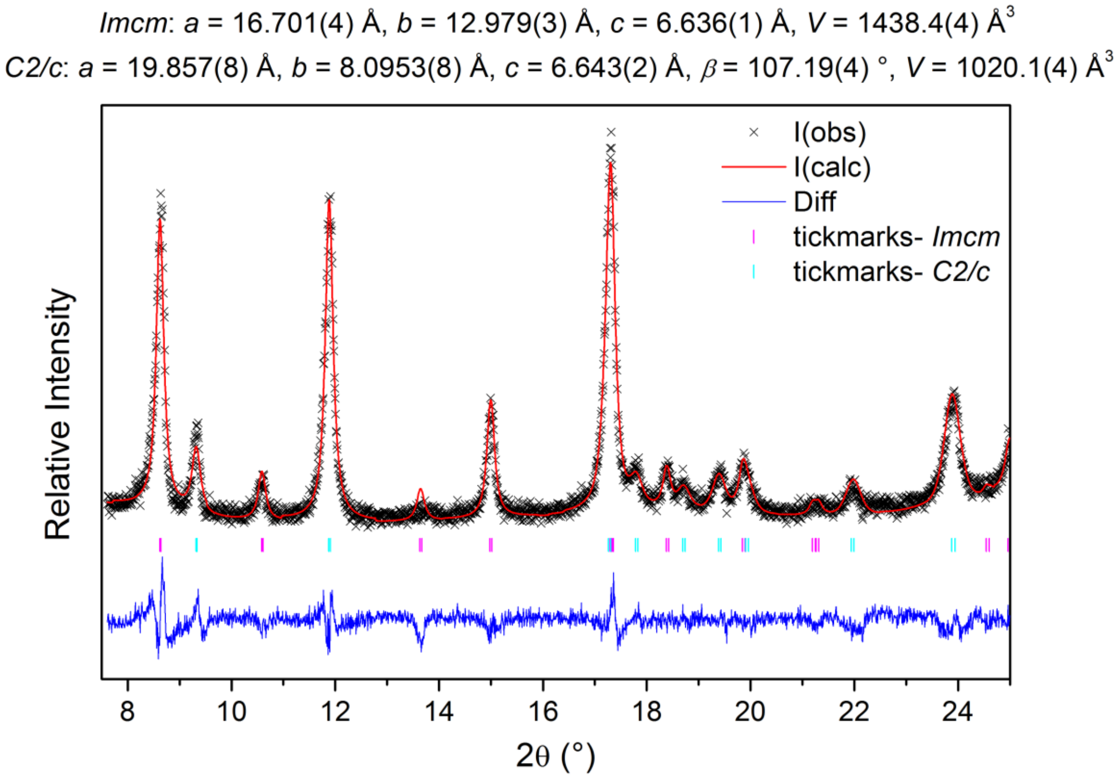


Figure S4.3: Le Bail profile fit for the partially superhydrated –CH_3 modified Al-MIL-53.

The contour plot, Figure S4.4, shows that the hydrated phase undergoes a slight expansion upon the addition of methanol vapour before switching to the fully-open phase. When the methanol vapour is turned off and replaced by N_2 gas (point B) the framework exhibits a small contraction, which is indicative of the removal of the guest to give the dehydrated phase, 1416.6 Å^3. The growth of some Bragg peaks, in equivalent 2*θ* positions to those seen before complete expansion, are observed suggesting that some of the material has contracted slightly upon the removal of the guest. Figure S4.4b shows the Le Bail profile parameter fit for the fully-open methanol phase; the framework expands to a unit cell volume of 1450.2 Å^3. Long data collection and a stationary methanol environment were used to collect these data.

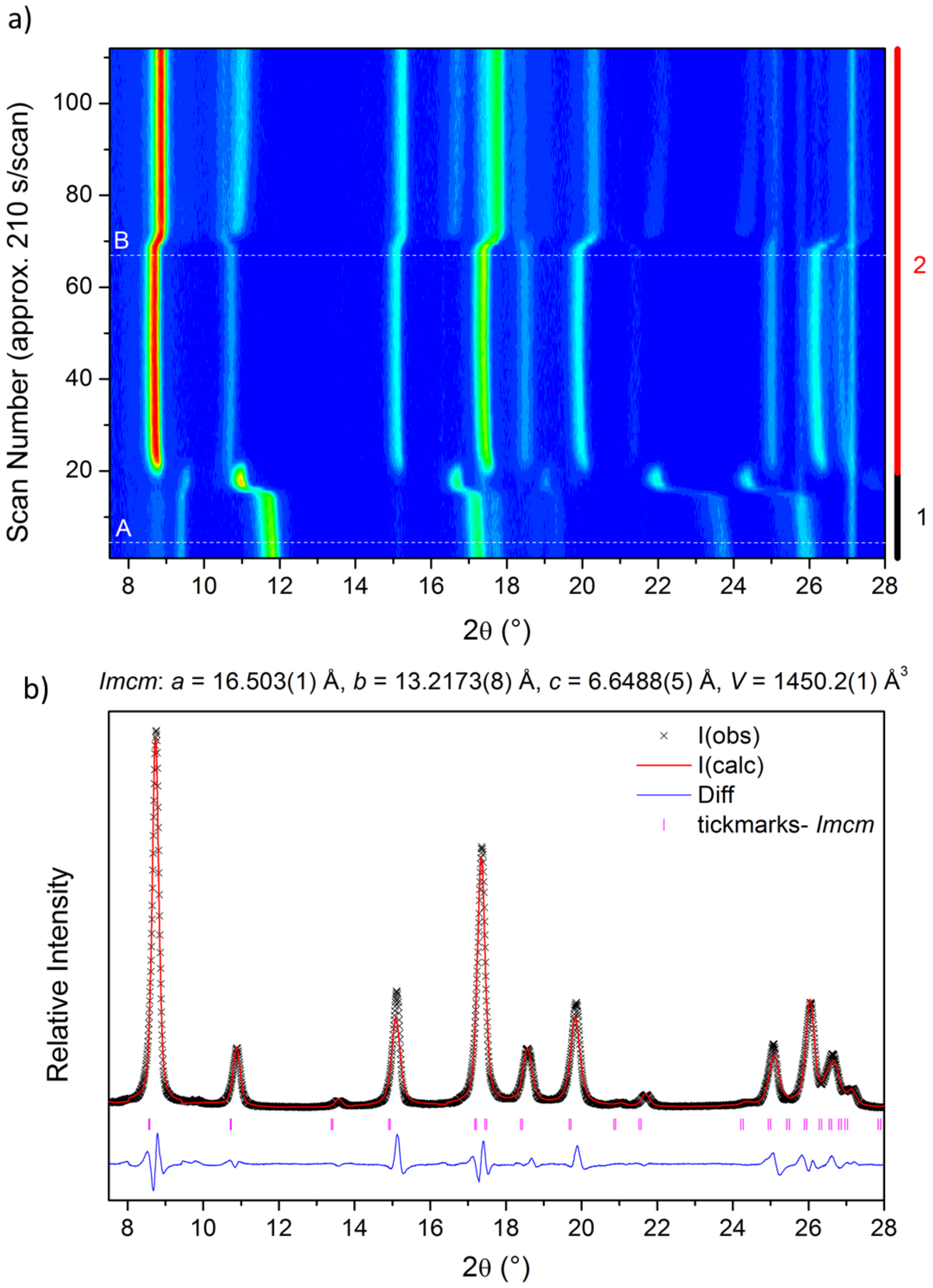
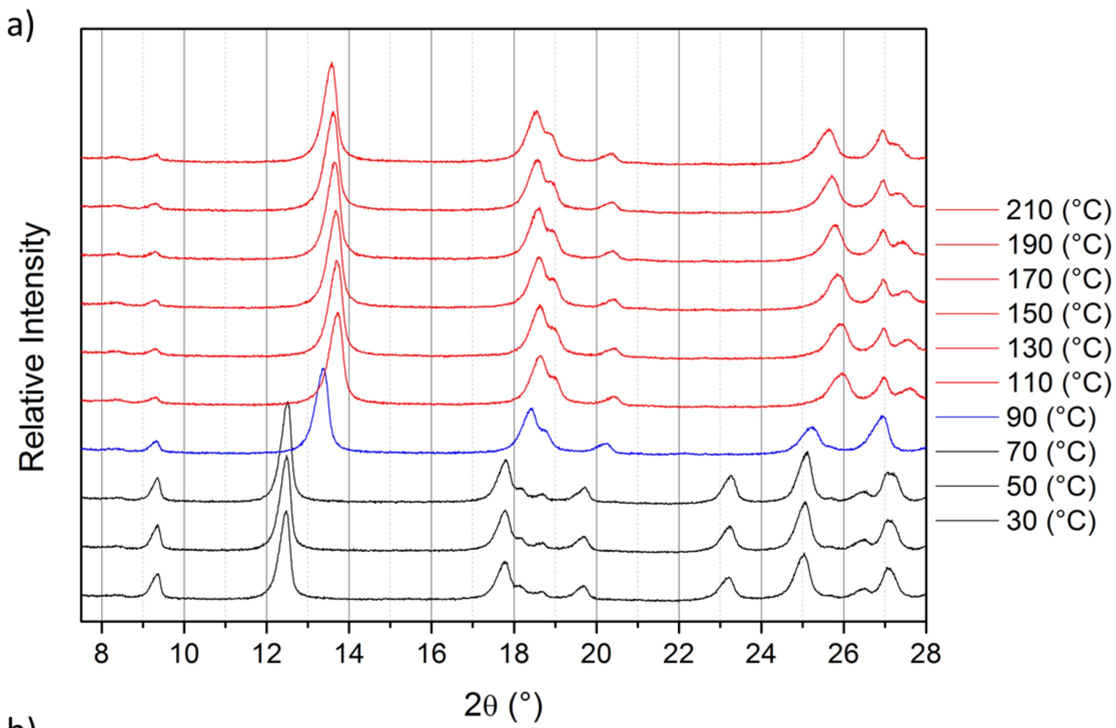
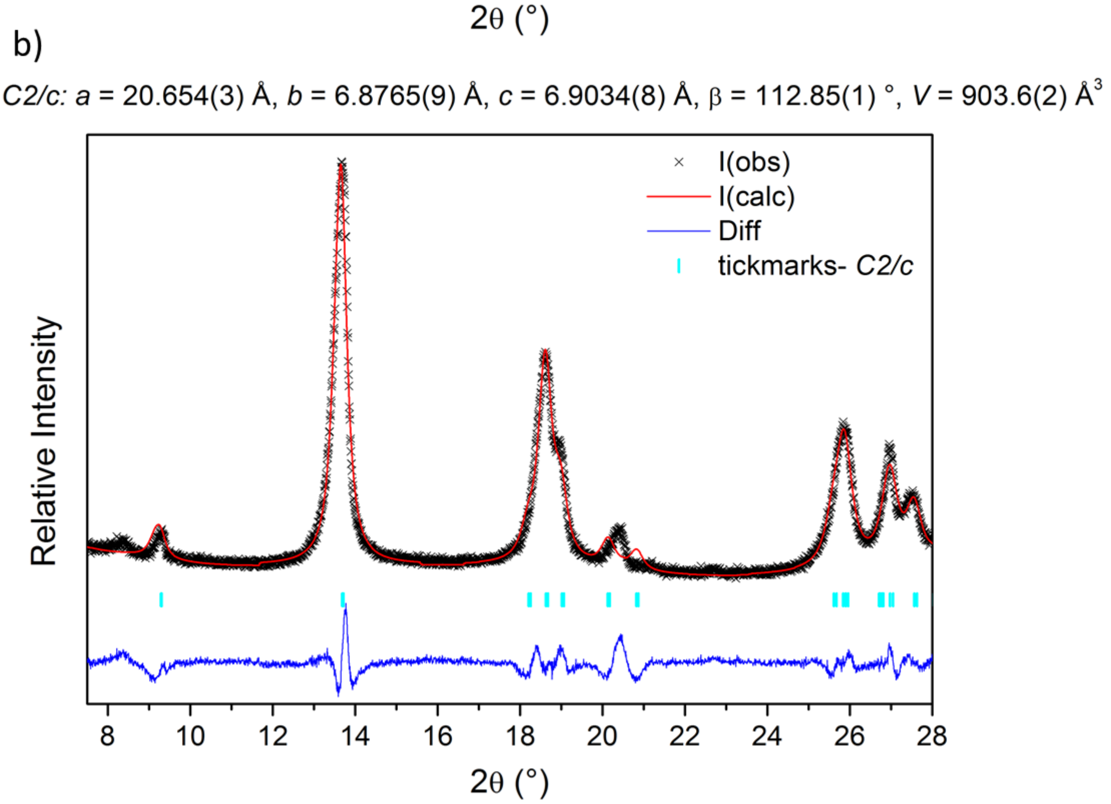


Figure S4.4: Behaviour of –CH_3 modified Al-MIL-53 in response to methanol vapour. a) Contour plot showing methanol adsorption (Phase 1 (black) = hydrated phase (*Cc*) and Phase 2 (red) = fully-open phase (*Imcm*)) and b) Le Bail profile fit for the fully-open methanol phase.

S5: Al-MIL-53-$(OH)_2$

The hydrated, monoclinic phase of the -$(OH)_2$ modified Al-MIL-53 has a unit cell volume of 955 Å^3. The thermal dehydration is shown in Figure S5.1. The framework does not expand as was seen for the previous frameworks. The peaks shift to a higher value of 2θ indicating that the structure has contracted. A possible reason for this contrast in behaviour is that the –OH functional groups which have been added to the terephthalate rings are able to hydrogen bond with neighbouring groups resulting in the framework being "locked" in a contracted phase. These interactions would be strengthened as a result of the removal of water as the functional groups could come closer together. Figure S5.1b shows the Le Bail profile fit for the data recorded *in situ* at 210 °C. The monoclinic, *C2/c,* dehydrated phase of Fe-MIL-53, 904.4 Å^3, was used as a starting point for the refinement as a contraction upon dehydration is also seen for this material. This analysis confirms that the framework contracts upon dehydration and shows the assumption that it contracts in a similar way to Fe-MIL-53 to be reasonable. The unit cell volume was refined to be 903.6 Å^3. Powder XRD on cooling are shown in Figure S5.2.





C2/c: *a* = 20.654(3) Å, *b* = 6.8765(9) Å, *c* = 6.9034(8) Å, β = 112.85(1) °, *V* = 903.6(2) Å^3

Figure S5.1: Thermal dehydration of the –$(OH)_2$ modified Al-MIL-53. a) Individual XRD patterns showing the change in unit cell parameters with increasing temperature (Black = hydrated phase (*C*2/*c*), blue = mixed phase and red = dehydrated phase (*C*2/*c*)) and b) Le Bail profile fit for data recorded at 210 °C.

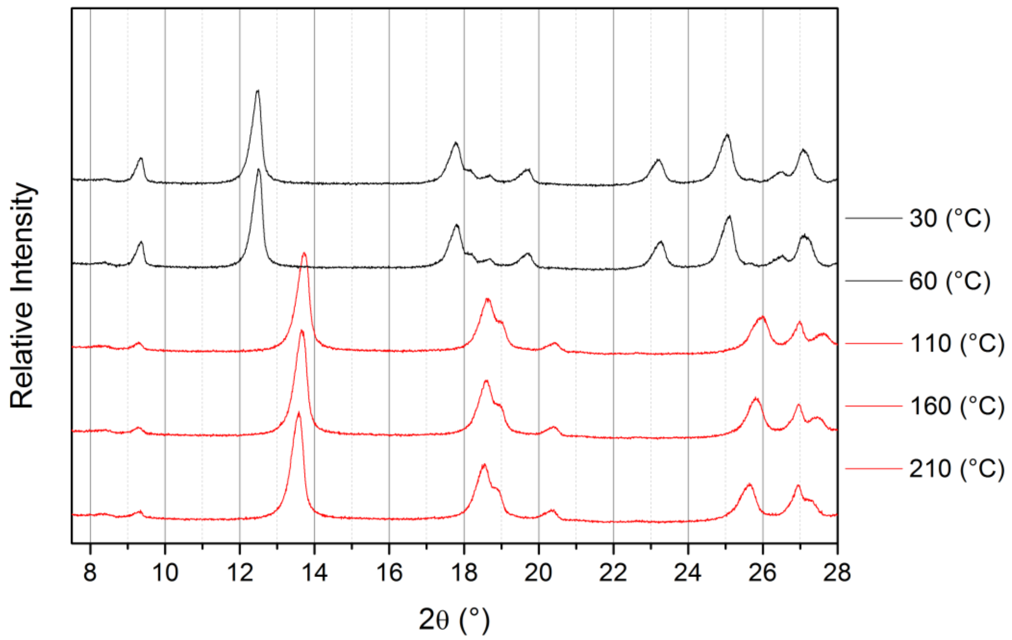


Figure S5.2*:* Behaviour of dehydrated Al-MIL-53-$(OH)_2$ upon cooling from 210°C to 30°C. Red = dehydrated phase, blue = mixed phase and black = hydrated phase.

The superhydration experiment for the –$(OH)_2$ modified Al-MIL-53 shows that the pores of the framework are able to accommodate extra water at room temperature as the framework expands to the fully-open phase (Figure S5.3). It was also found that the interaction between the excess water and the framework was stronger than the interaction seen between the –Br modified Al-MIL-53 and excess water. After leaving at 30 °C for several hours, which was enough to remove the excess water from the –Br modified framework, only a minor contraction of the dihydroxy modified framework was seen. The sample was left overnight under the same conditions but no further contraction was seen when the sample was tested the following day. The *in situ* data collection was resumed with a flow of dry nitrogen which forced the excess water molecules out of the framework to give the hydrated phase. As the sample was not removed from the diffractometer between experiments it was possible to join the two datasets together; labelled as point (A) in the contour plot. The first scan from the contour plot was used to perform a Le Bail profile fit for this dataset, Figure b. This analysis confirms that the framework fully-opens in the presence of excess water to give the orthorhombic structure with a refined unit cell volume of 1397.6 Å^3. This is smaller than the unit cell volume found for the other superhydrated modified materials. One possible explanation for the smaller unit cell volume is that hydrogen bonding between the additional –OH groups on the linkers and the H_2O guest molecules can occur; resulting in a smaller unit cell volume.

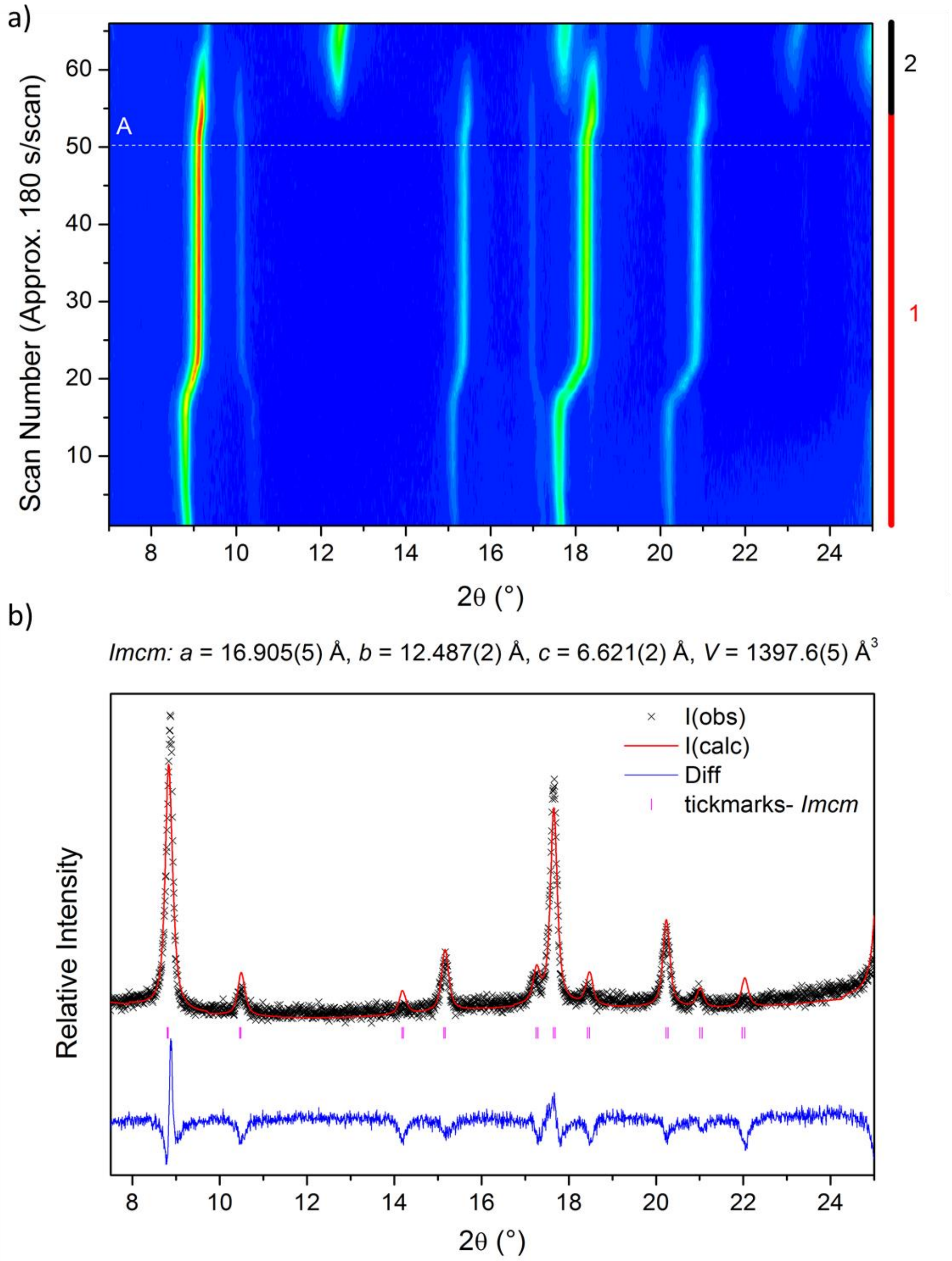


Figure S5.3: Removal of excess H_2O from the superhydrated –$(OH)_2$ modified Al-MIL-53. a) contour plot showing the removal of the excess water using a flow of dry nitrogen gas (Phase 1 (red) = superhydrated phase (*Imcm*) and Phase 2 (black) = hydrated phase(*C*2/*c*)) and b) Le Bail profile fit for the superhydrated phase; data were recorded at room temperature.

The methanol sorption experiment shows that the framework also expands in response to methanol vapour. The interaction between methanol and this framework is strong enough that residual methanol vapour inside the sample chamber was sufficient to open the framework fully before data collection had begun. A flow of methanol vapour was passed over the sample to ensure it had opened fully before being replaced by a flow of pure N_2 gas (point B). The contour plot in Figure S5.4a shows that there is a gradual contraction of the fully-open phase before it exhibits a change in symmetry upon closing to a unit cell volume similar to the half-open phase seen for Fe-MIL-53. After more than three hours under a flow of N_2 gas, contraction to the dehydrated phase was not seen. A Le Bail profile fit (Figure S5.4b) was performed for both phases seen in the contour plot. A longer data collection, in a stationary methanol environment, was used to record the data used for the refinement of the fully-open phase whereas the data collected *in situ* was used for the half-open phase refinement. The unit cell parameters of the half-open Fe-MIL-53[lutidine] phase were used as the starting point for the refinement of the half-open phase. These analyses show that the framework expands to the fully-open, *Imcm*, phase with a unit cell volume of 1444.5 $Å^3$ and contracts via a half-open, *C2/c*, phase with a unit cell volume of 1110.5 $Å^3$.

Previous methanol adsorption experiments for Fe-MIL-53 showed that the framework could contain two equivalents of methanol in the fully-open phase and one equivalent of methanol in the half-open phase. The contraction of the Al-MIL-53-$(OH)_2$ framework to a volume similar to this half-open phase could be a consequence of the methanol being removed from the framework in two steps.

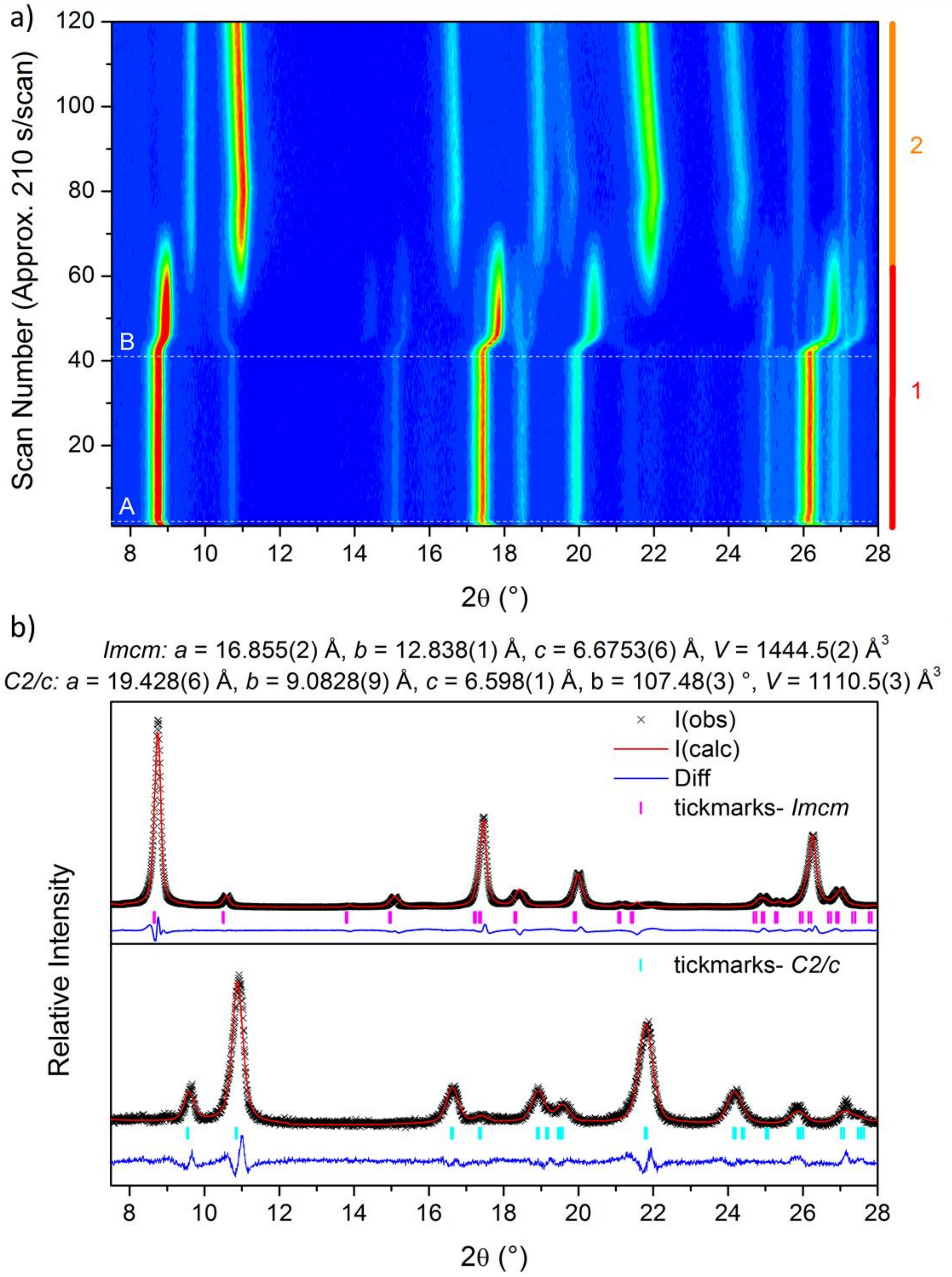


Figure S5.4: Behaviour of –$(OH)_2$ modified Al-MIL-53 in response to methanol vapour. a) Contour plot showing methanol desorption (Phase 1 (red) = fully-open methanol phase (*Imcm*) and Phase 2 (orange) = half-open methanol phase (*C*2/*c*)) and b) Le Bail profile fit for the fully-open methanol phase (top) and the half-open phase (bottom).

S6: Al-MIL-53-CO_2H

The hydrated, monoclinic phase for the -CO_2H modified Al-MIL-53 has a unit cell volume of 1055 Å^3. The thermal dehydration experiments show that the framework expands to the fully-open phase. Complete conversion to this phase does not occur until it is heated above 300 °C (Figure S6.1). The Le Bail profile fit for dehydrated -CO_2H modified Al-MIL-53 is shown in Figure S6.1b; the data collected *in situ* was used for this refinement. This analysis shows that the framework fully-opens to give the *Imcm* structure upon removal of the guest water molecules. The refined unit cell volume was found to be 1434.2 Å^3. Data on cooling are shown in Figure S6.2.

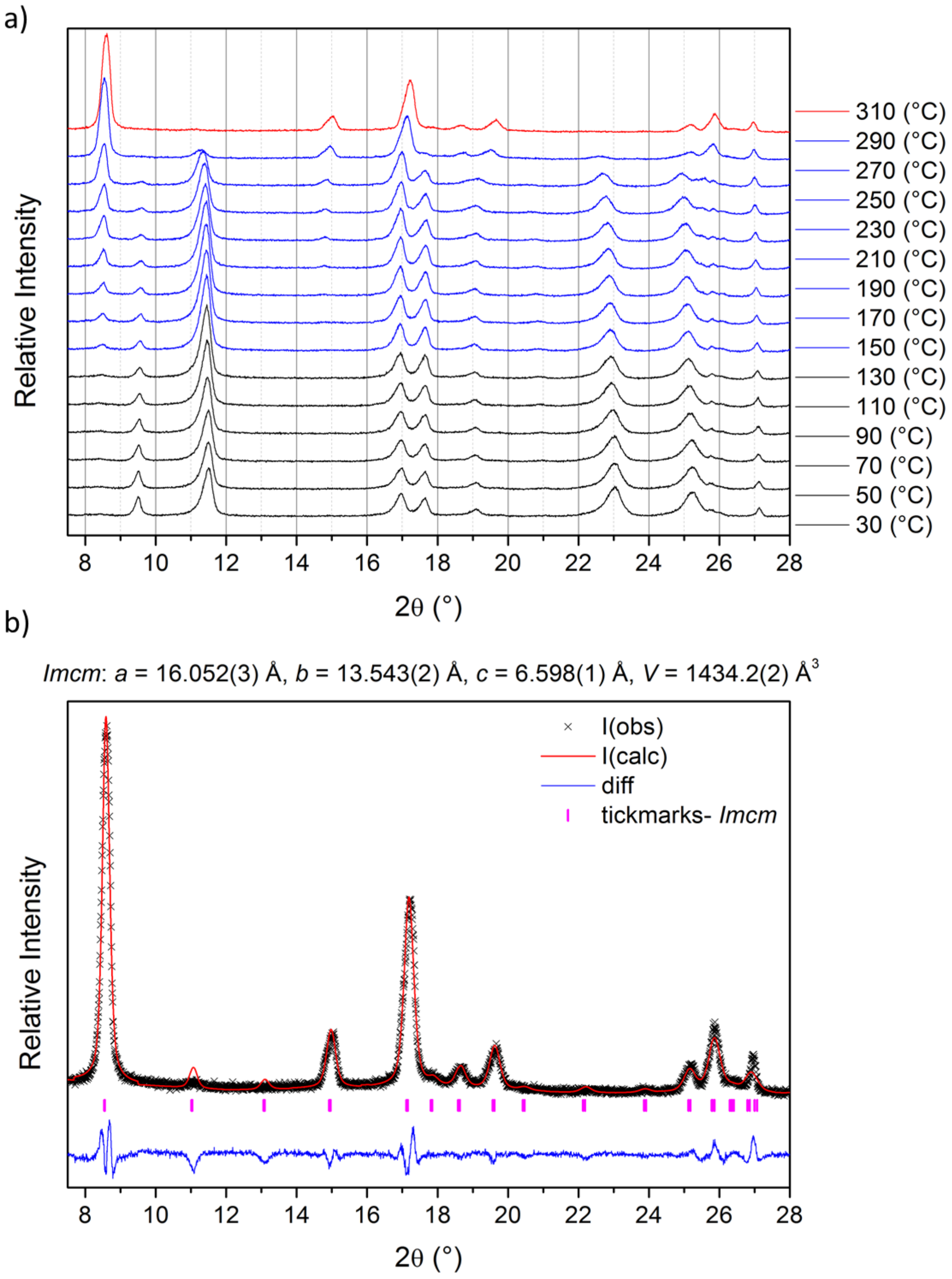


Figure S6.1: Thermal dehydration of the -CO_2H modified Al-MIL-53. a) Individual XRD patterns showing a change in symmetry with increasing temperature (black = hydrated (*C*2/*c*), blue = mixed phase and red = dehydrated (*Imcm*)) and b) Le Bail profile fit for data recorded at 310 °C.

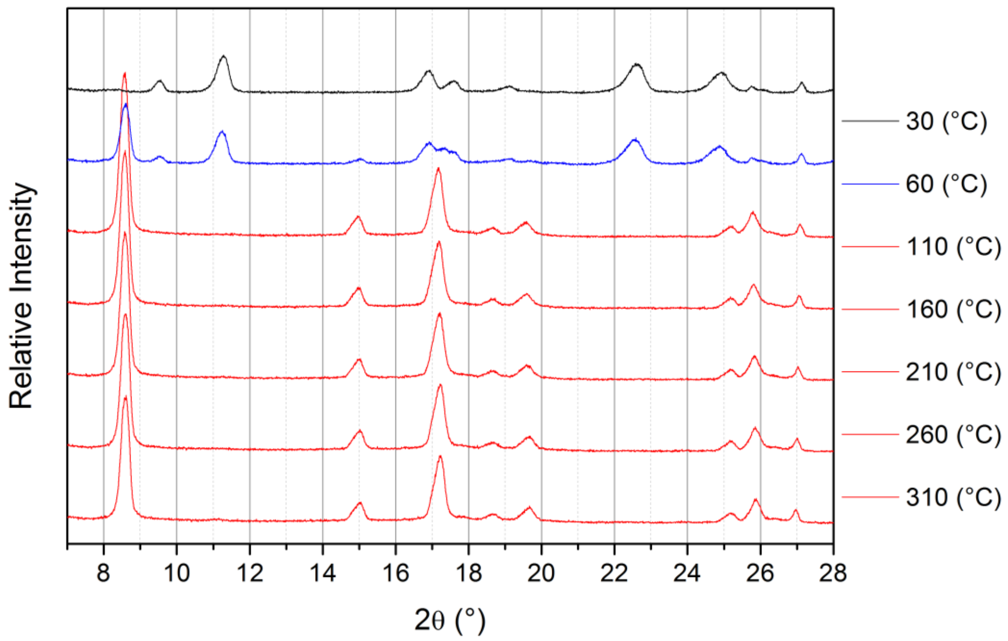


Figure S6.2: Behaviour of dehydrated Al-MIL-53-CO_2H upon cooling from 210°C to 30°C. Red = dehydrated phase, blue = mixed phase and black = hydrated phase.

The superhydration experiment shows that the framework partially expands in the presence of excess water, however there is still evidence in the individual XRD pattern (Figure S6.3b) for some residual hydrated phase (peak at ~ 11.5 °). The contour plot gives evidence that the excess water is not bound strongly within the framework as it is lost after approximately 30 minutes when held at 30 °C. Upon losing the excess water molecules the fully-open phase shows a gradual contraction before contracting fully to give the hydrated phase (Figure S6.3a). Figure S6.3b shows the Le Bail profile fit for the superhydrated -CO_2H modified Al-MIL-53. Data with a better signal-to-noise ratio could not be collected due to the rapid nature with which the framework loses the excess water. A mixed phase refinement was performed, as the whole framework had not expanded to give the fully-open *Imcm* structure; part of the framework still had the hydrated structure.

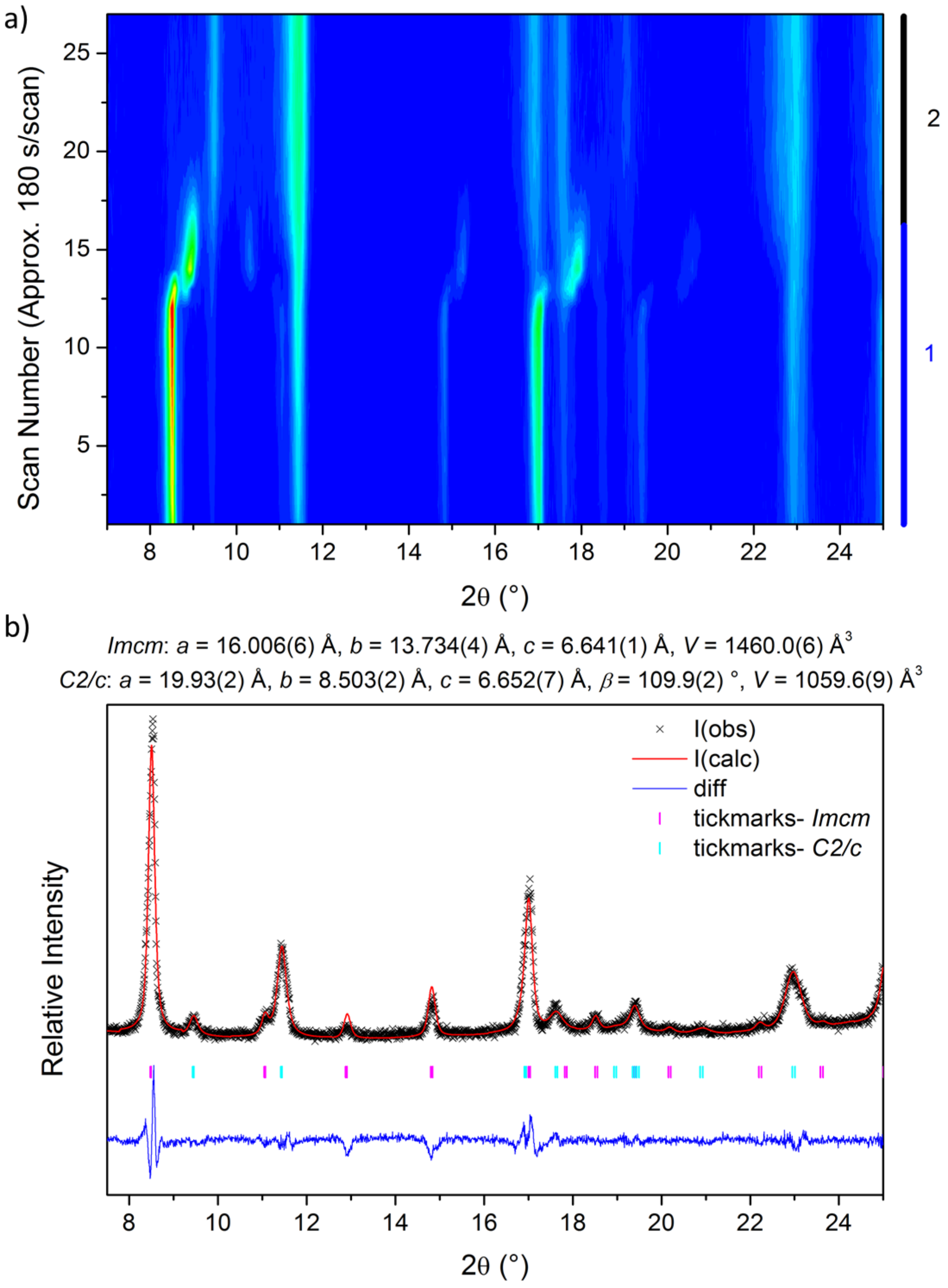


Figure S6.3: Removal of excess water from the superhydrated -CO_2H modified Al-MIL-53. a) Contour plot showing the contraction of the framework upon removal of water (Phase 1 (blue) = mixed phase and Phase 2 (black) = hydrated phase (*C*2/*c*)) and b) Le Bail profile fit for the partially superhydrated phase.

The methanol sorption experiment shows that the framework expands in response to methanol vapour (Figure S6.4). The methanol vapour was added to the sample chamber on scan 4 (point A) causing a one-step expansion of the framework to the fully-open phase. On scan 56 (point B) the methanol vapour was exchanged for pure nitrogen, after which the fully-open phase shows a gradual contraction before closing to a phase with a similar XRD pattern to the half-open methanol phase identified for the $–(OH)_2$ modified framework. The Le Bail profile fit for the fully-open methanol phase is shown in Figure S6.4b; the data collected *in situ* were used for this refinement. This analysis shows that the framework expands to the fully-open *Imcm* structure upon addition of methanol vapour. The refined unit cell volume was determined to be 1440 $Å^3$. A Le Bail profile fit of the half-open phase was not possible as it does not exist as a pure phase and the *in situ* data has a very low signal-to-noise ratio.

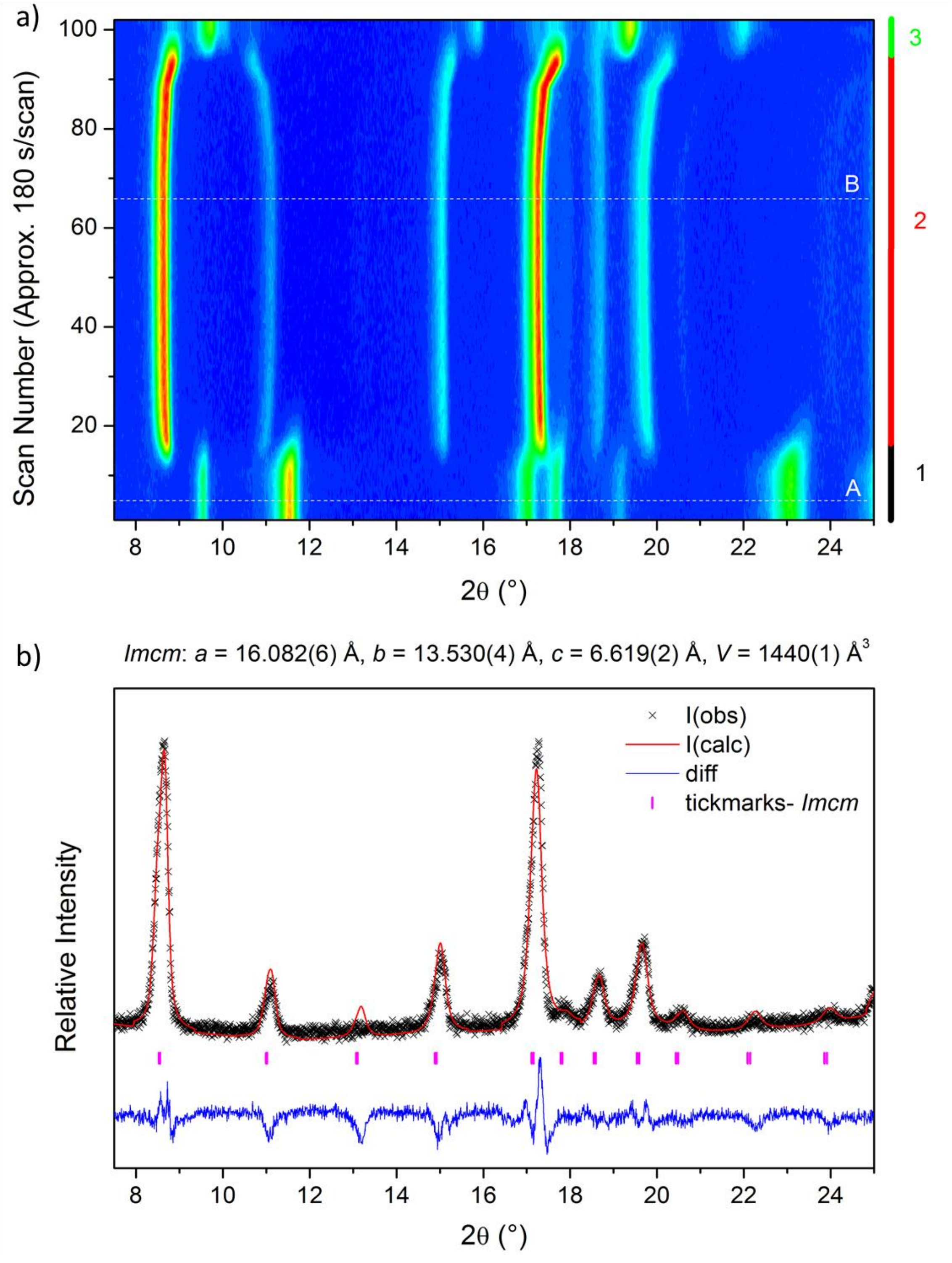

Imcm: *a* = 16.082(6) Å, *b* = 13.530(4) Å, *c* = 6.619(2) Å, *V* = 1440(1) Å^3

Figure S6.4: Behaviour of the -CO_2H modified Al-MIL-53 framework in response to methanol vapour. a) Contour plot showing the change in framework symmetry (Phase 1 (black) = hydrated phase (*C*2/*c*),Phase 2 (red) = fully-open methanol phase (*Imcm*) and Phase 3 (green) = mixed phase (fully-open and half-open)) and b) Le Bail profile fit for the fully-open methanol phase.

S7: Al-MIL-53-NH$_2$

The hydrated phase of –NH$_2$ modified Al-MIL-53 has a unit cell volume of 961 Å^3. The thermal dehydration of this material, shown in Figure S7.1, does not cause any significant changes in the framework unit cell parameters; there is no evidence that the structure breathes. This is in agreement with previously published XRD results.[6] The superhydration of the framework was also studied using the method outlined above but the experiment resulted in the conclusion that this framework was unable to breathe in response to these conditions.

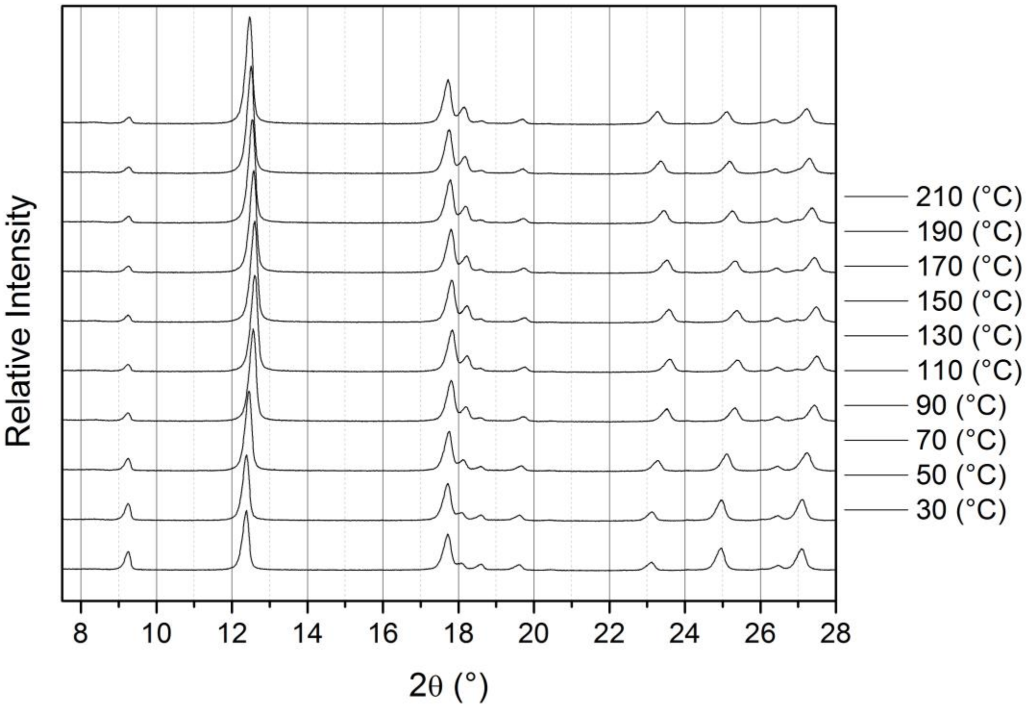


Figure S7.1: Thermal dehydration of the –NH$_2$ modified Al-MIL-53.

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