Impact of the metal centre (Al^{3+}, Fe^{3+}) on the post-synthetic lithiation of functionalized MIL-53s and electrochemical properties of the lithiated derivatives

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1. Powder X-ray diffraction

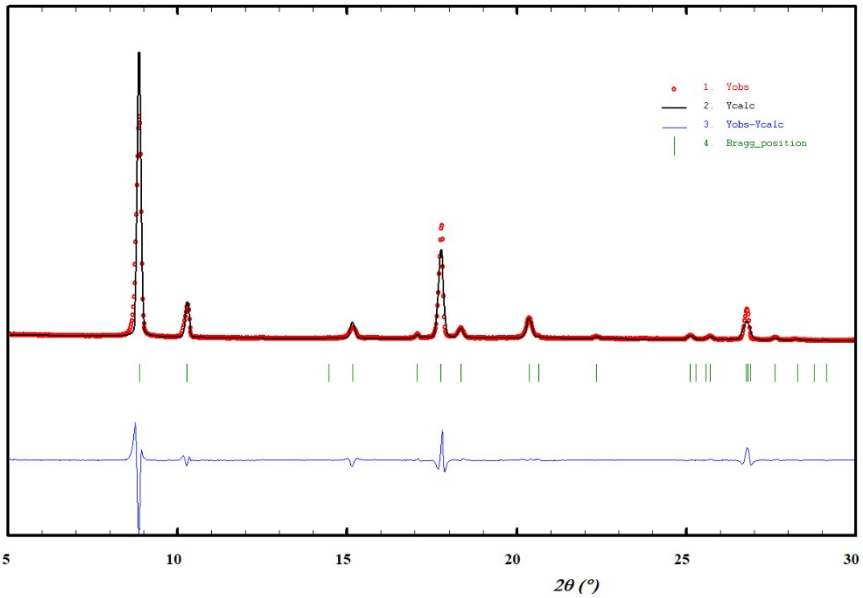


Figure S1. Le Bail fit of MIL-53(Al)-$(OH)_2$ as-prepared.

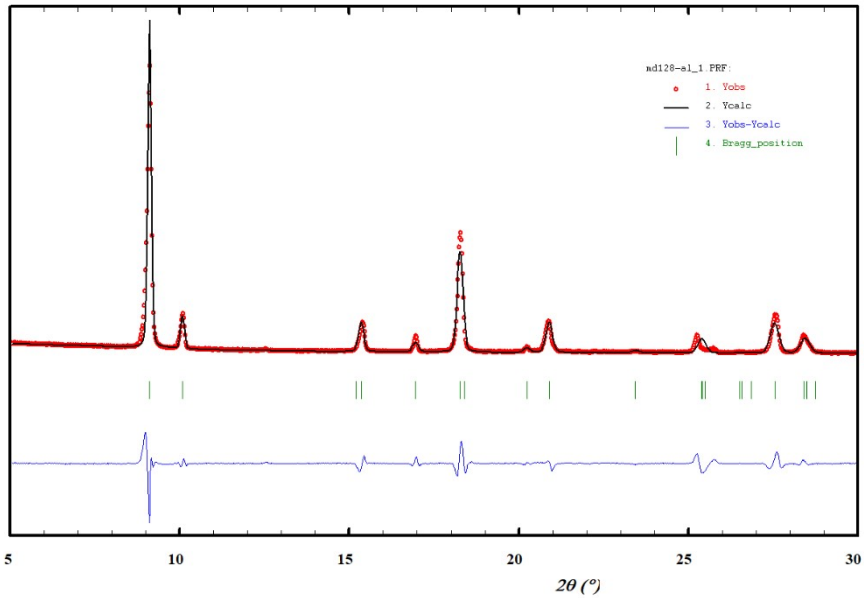


Figure S2. Le Bail fit of MIL-53(Al)-$(OH)_2$ fully hydrated.

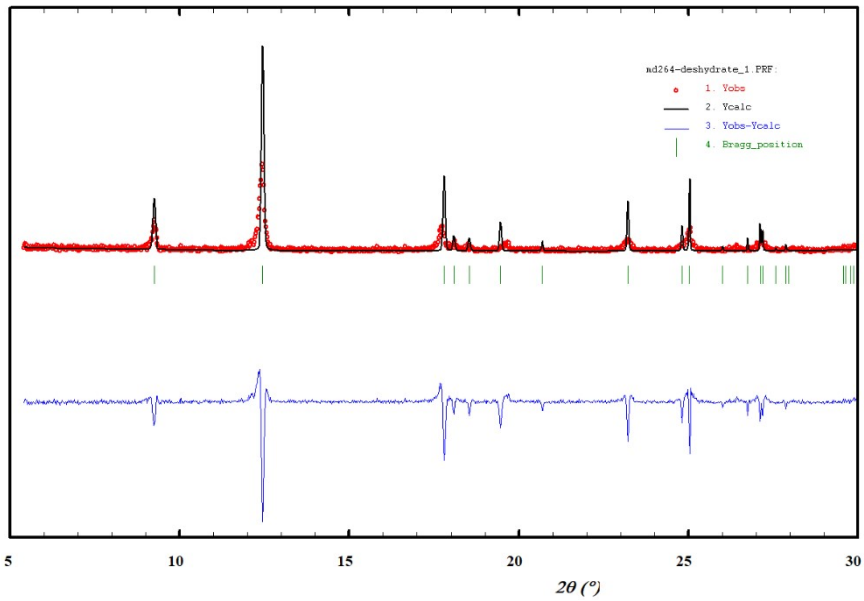


Figure S3. Le Bail fit of MIL-53(Al)-$(OH)_2$ partially hydrated.

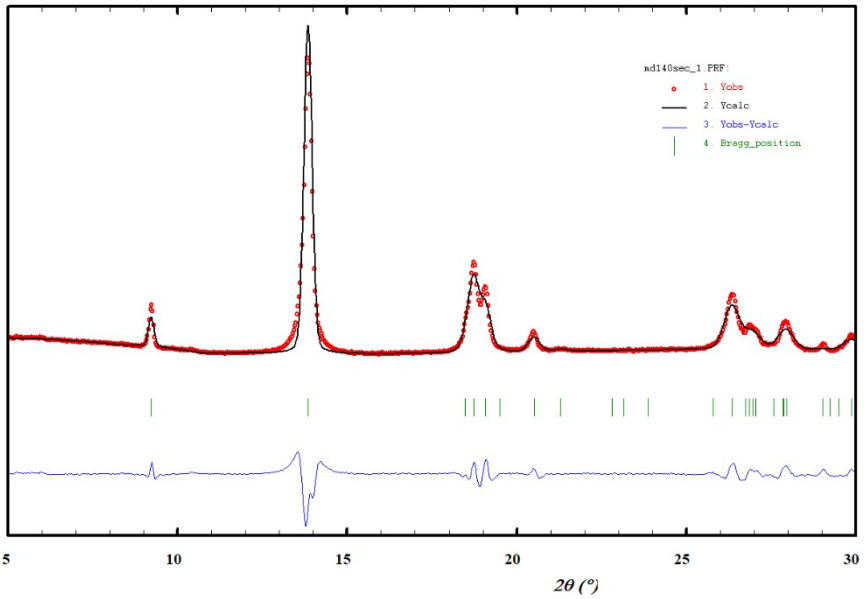


Figure S4. Le Bail fit of MIL-53(Al)-$(OH)_2$ dried.

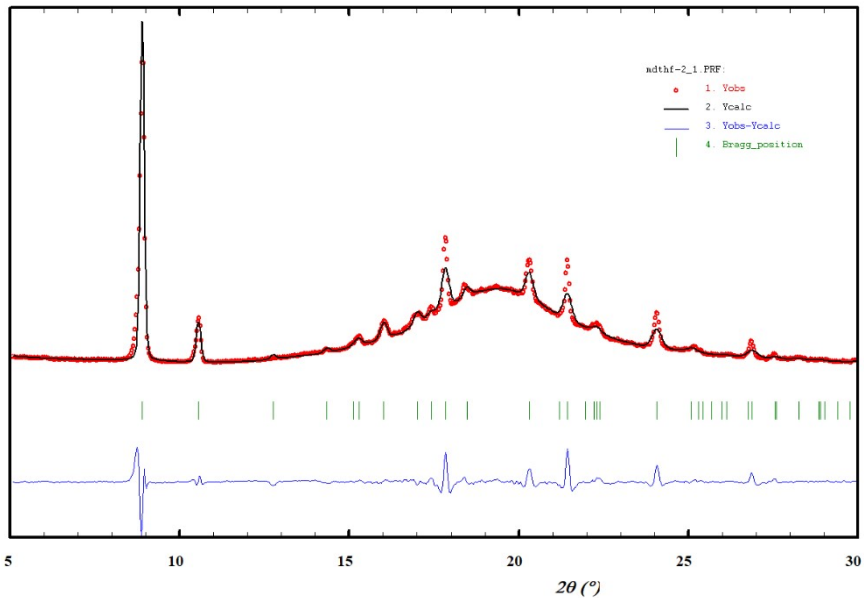


Figure S5. Le Bail fit of MIL-53(Al)-$(OH)_2$ suspended in THF.

Compound	**a (Å)**	**b (Å)**	**c (Å)**	**β (°)**	**V (Å^3)**	**SG**	**form**
as-prepared	17.201(5)	12.251(3)	6.646(2)	-	1400.4(6)	*Imcm*	LP
fully hydrated	17.540(6)	11.650(2)	6.636(2)	-	1355.9(6)	*Imcm*	LP
partially hydrated	19.702(7)	7.656(2)	6.585(2)	103.85(2)	964.4(5)	*C2/c*	NP
dry	19.22(1)	6.761(3)	6.646(4)	93.75(5)	862.0(7)	*A2/m*	CP
in THF	16.759(7)	12.347(5)	6.654(4)	-	1377(1)	*Pnam*	LP

Table S1 Unit-cell parameters of MIL-53(Al)-$(OH)_2$ with various pore fillings determined from PXRD. SG = possible space group; CP = close pore, NP = narrow pore, LP = large pore. λ = 1.5406 Å.

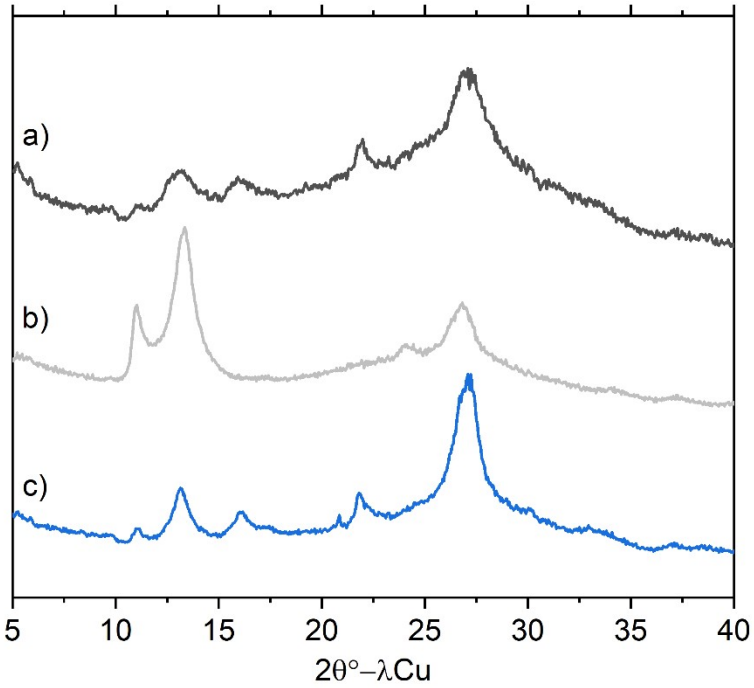


Figure S6. PXRD patterns of the products of the reaction between MIL-53(Al)-$(OH)_2$ and LiOMe in MeOH/THF under various conditions: a) 8 eq., 50°C, 16 hours; b) 3 eq., 15 days, 50°C; c) Li_4(DOBDC) prepared in MeOH/THF.

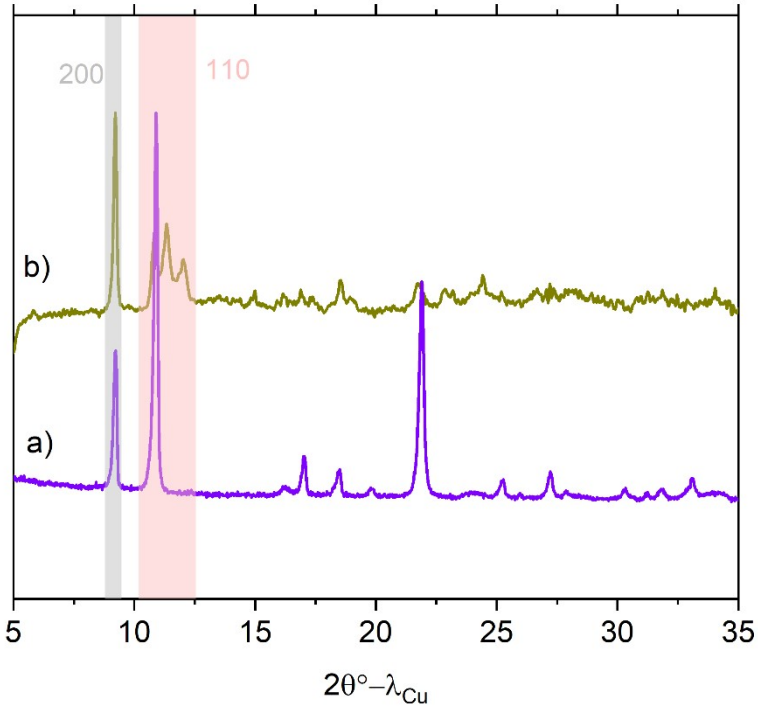


Figure S7. PXRD patterns of MIL-53(Fe)-$(OH)_2$: hydrated (violet) and dried (khaki) at 155°C under vacuum. The positions of the 200 and 110 Bragg peaks are highlighted. The multiplicity observed for the dried solid indicates the presence of a mixture of pore opening (at least NP-H_2O and CP).

2. Optical images

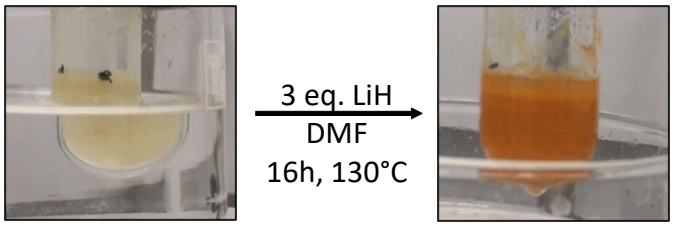


Figure S8. Evolution of the color of the suspension of MIL-53(Al)-$(OH)_2$ in DMF in the presence of 3 eq. of LiH with time.

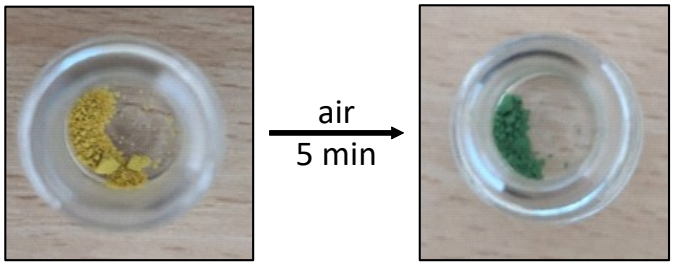


Figure S9. Evolution of the color of the MIL-53(Al)-$(OH)_2$ treated with 3 eq. of LiOMe in MeOH/THF upon exposure to air.

3. Thermogravimetric analysis

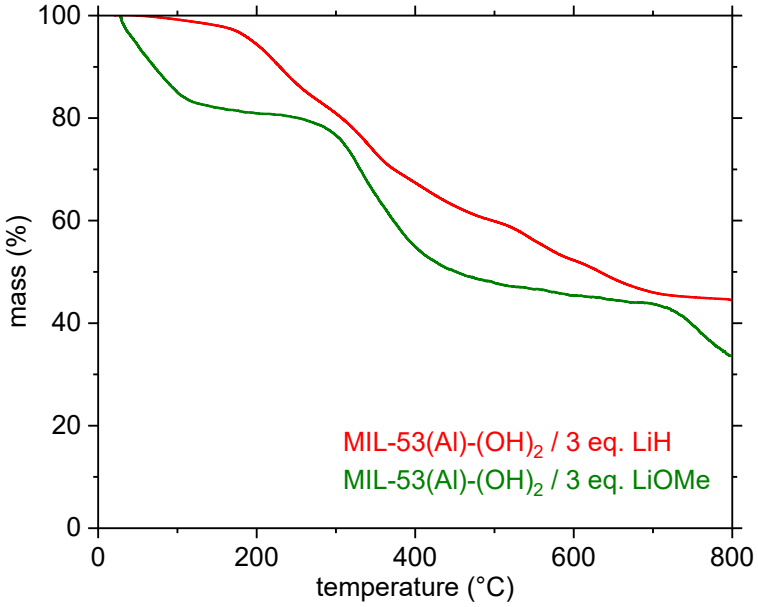


Figure S10. TG curves of the product of the reaction between MIL-53-(Al)$(OH)_2$ and 3 eq. of LiH in DMF (red) and 3 eq. of LiOMe in MeOH/THF (green), measured at a heating rate of 5°C min^{-1} under Ar.

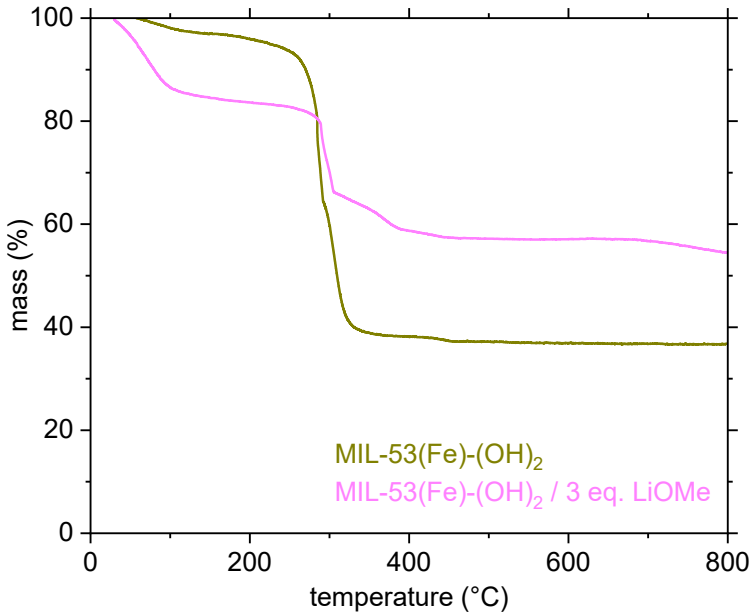


Figure S11. TG curves of MIL-53-(Fe)$(OH)_2$ (khaki) and of the product of the reaction between MIL-53-(Fe)$(OH)_2$ and 3 eq. of LiOMe in MeOH/THF (pink), measured at a heating rate of 5°C min^{-1} under Ar.

4. Infrared spectroscopy

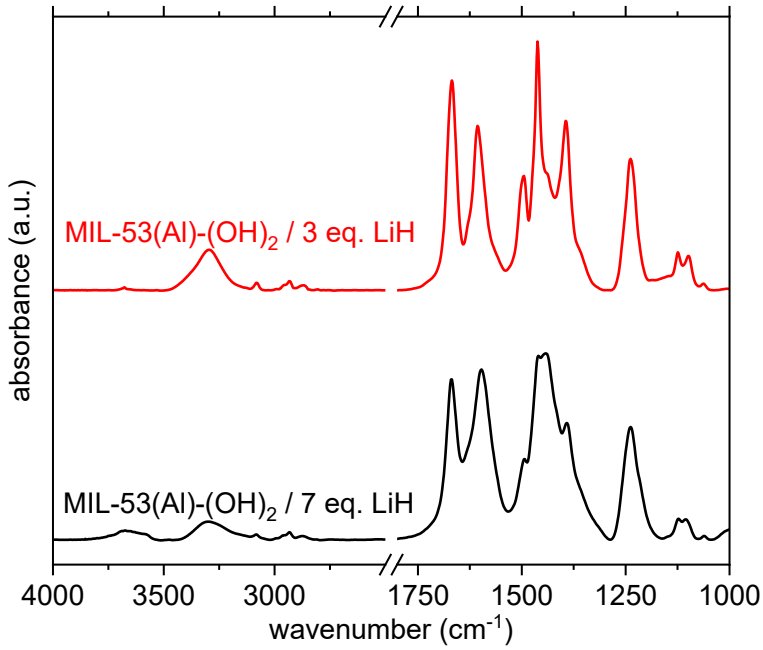


Figure S12. IR spectra of the of the products of the reaction between MIL-53-(Al)$(OH)_2$ and 3 eq. of LiH in DMF (red) and 7 eq. of LiH in DMF (pink). Even with excess of hydride, OH vibration bands remain visible, as well as bands characteristics of DMF (e.g. C=O vibration band at ~1660 cm^{-1}).

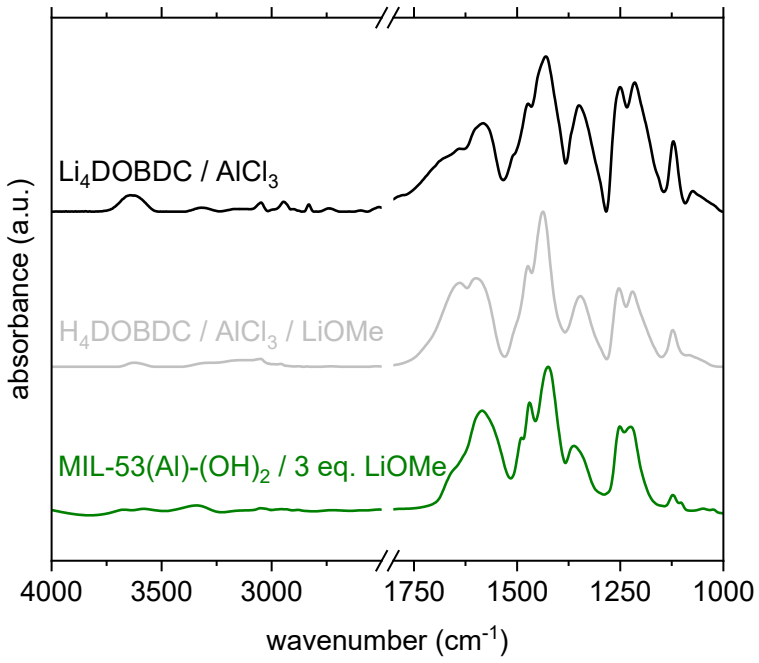


Figure S13. IR spectra of the of the products of the direct reaction between H_4DOBDC, $AlCl_3$ and LiOMe (grey), and Li_4(DOBDC) and $AlCl_3$, both in MeOH/THF, compared to the one of MIL-53(Al)-$(OH)_2$ treated with 3 eq. of MeOH/THF (green). The shoulder at ~ 1650 cm^{-1} indicates the presence of free carboxylic groups for direct syntheses.

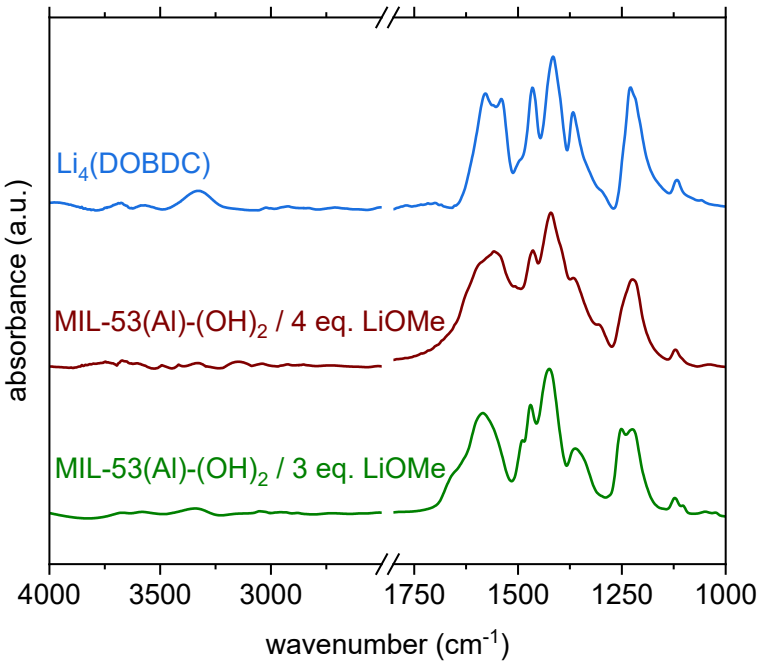
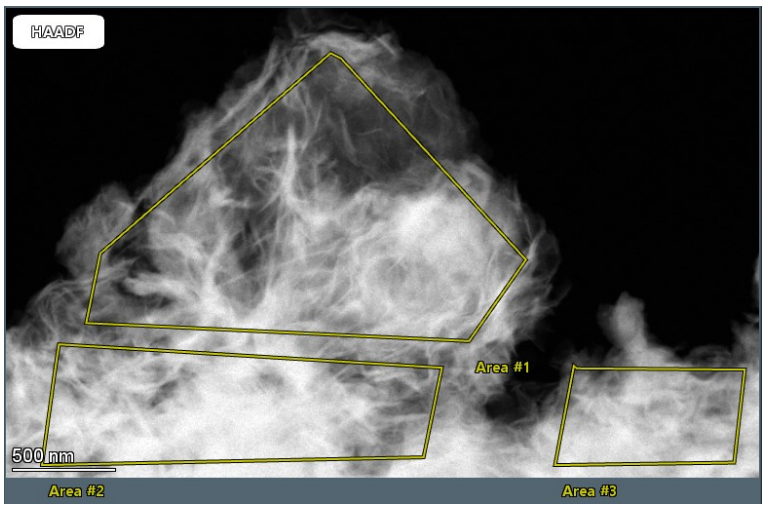


Figure S14. IR spectra of the products recovered after reaction of MIL-53-(Al)$(OH)_2$ with 3 and 4 eq. of LiOMe in MeOH/THF (green and brown, respectively), compared to the one of Li_4(DOBDC) (blue).

5. Transmission electron microscopy

a)

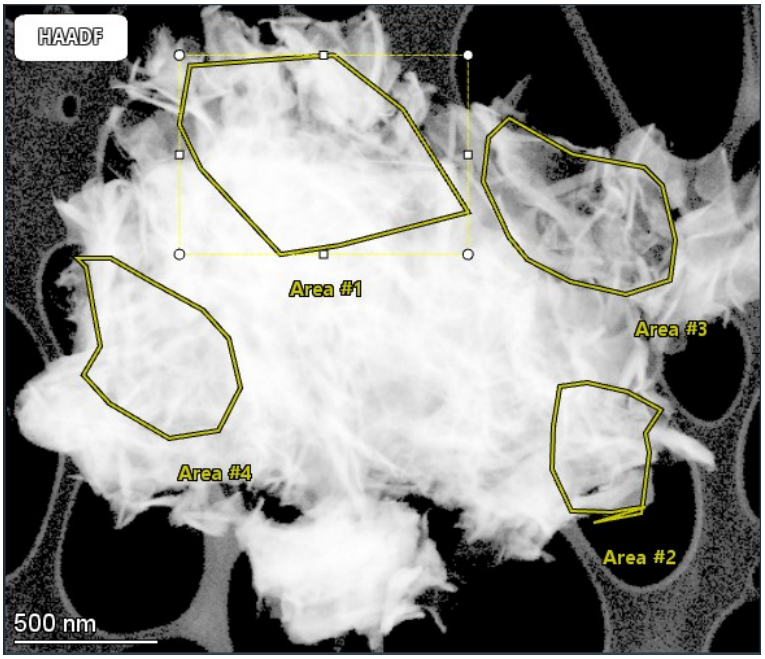


b)

	Area #1	Area #2	Area #3	average	Li_4(DOBDC)
Al/C	0.006	0.005	0.007	0.006	0
O/C	0.75	0.71	0.79	0.75	0.75

Figure S15. STEM-EDX analysis of the reaction product between MIL-53(Al)-$(OH)_2$ and 8 eq. of LiOMe in MeOH/THF at 50°C for 16 hr. a) STEM pictures; b) atomic ratios deduced from the EDX analysis, showing the almost complete departure of Al^{3+}.

a)



b)

	Area #1	Area #2	Area #3	Area #4	average	$Li_7Al(DOBDC)_{5/2}$
C/Al	21	15	25	20	20	20
C/O	1.4	1.3	1.7	1.4	1.4	1.3
O/Al	15	12	15	14	14	15

Figure S16. STEM-EDX analysis of the reaction product between MIL-53(Al)-$(OH)_2$ and 4 eq. of LiOMe in MeOH/THF at 50°C for 16 hr. a) STEM pictures; b) atomic ratios deduced from the EDX analysis, showing that the composition is close to $Li_7Al(DOBDC)_{5/2}$.

6. Inductively coupled plasma-atomic emission spectroscopy

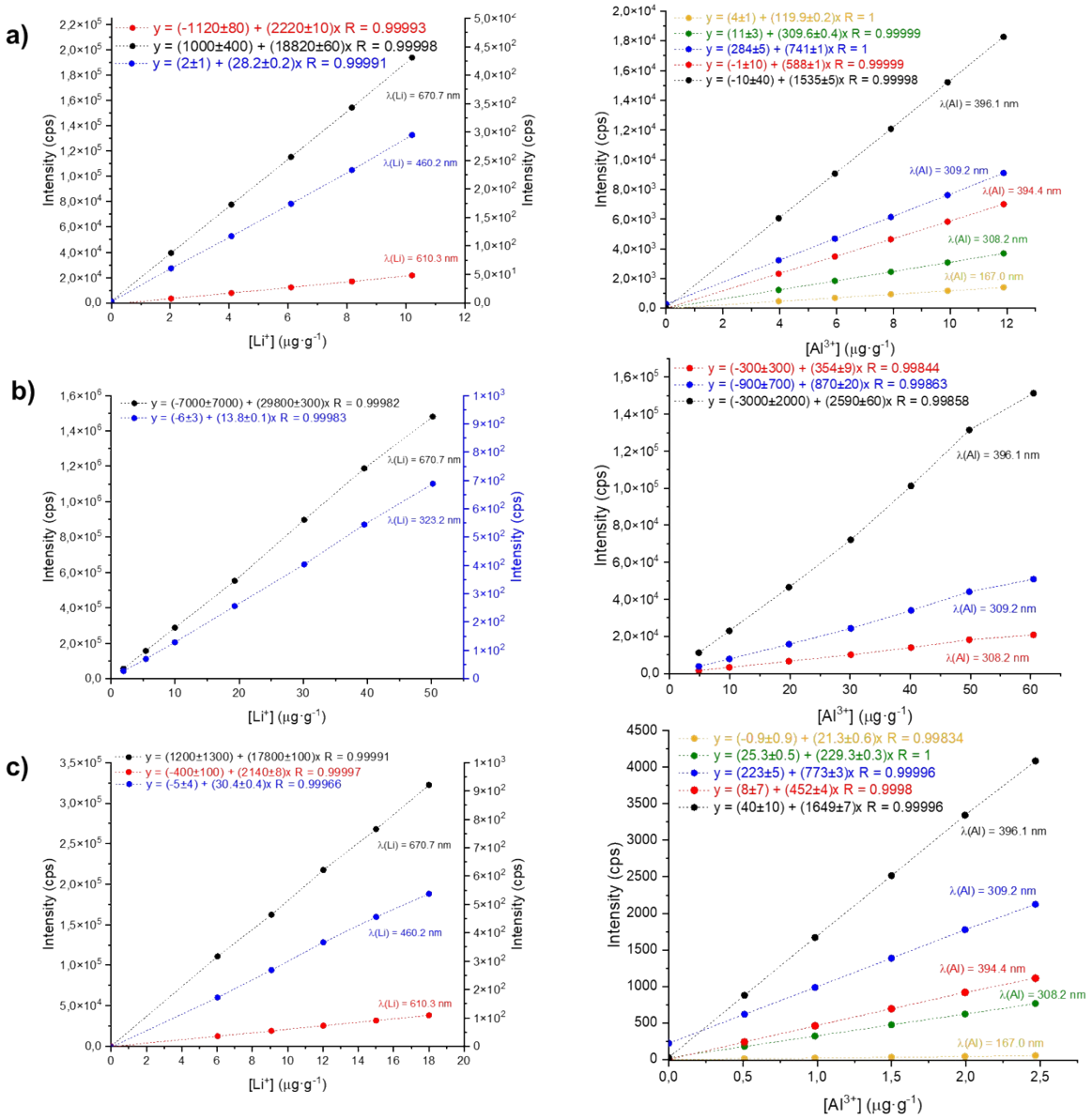


Figure S17. Calibration curves of the ICP-AES used to quantify the elemental composition for the MIL-53(Al)-$(OH)_2$ lithiated with 3 eq. (a), 4 eq. (b) and 8 eq. (c) of LiOMe in MeOH/THF. The composition was quantified by averaging the results obtained with the different curves.

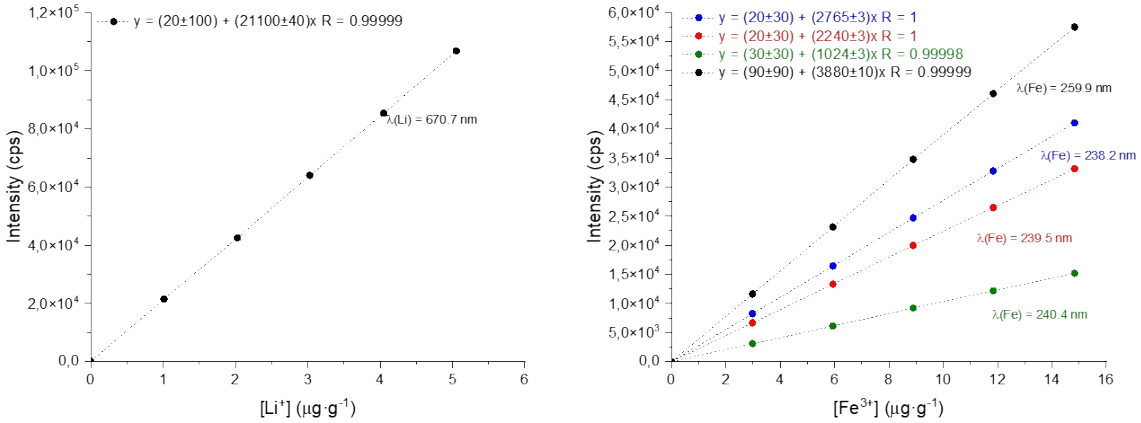


Figure S18. Calibration curves of the ICP-AES used to quantify the elemental composition for the MIL-53(Fe)-$(OH)_2$ lithiated with 3 eq. of LiOMe in MeOH/THF. The composition was quantified by averaging the results obtained with the different curves.