STRUCTURAL CHEMISTRY

Supporting information for article:

NMR crystallography to probe the breathing effect of the MIL-53(Al) metal–organic framework using solid-state NMR measurements of ^{13}C–^{27}Al distances

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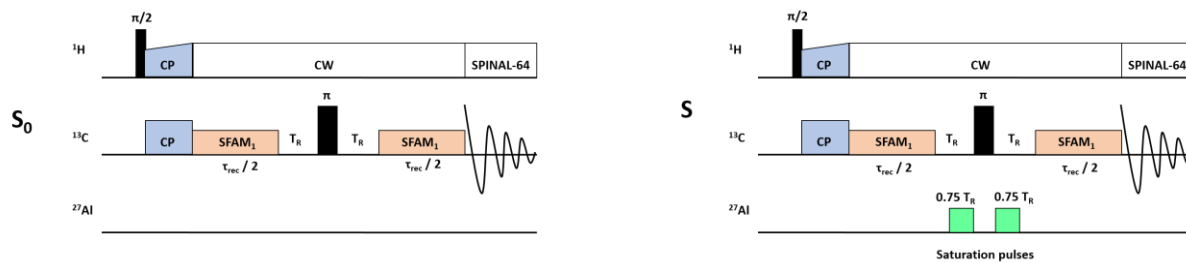**S1.**

S2. Method : SFAM-RESPDOR experiment

Figure S1: Pulse sequences employed for the acquisition of S_0 (left) and S (right) signals of ^{13}C-$\{^{27}Al\}$ SFAM-RESPDOR experiment.

S2. Synthesis

S2.1. MIL-53(Al)-*as*

The MIL-53(Al)-*as* was hydrothermally synthesized under autogenous pressure condition from a mixture of (i) aluminum nitrate nona-hydrate (Al(NO$_3$)$_3$.9H$_2$O, > 98%, Sigma-Aldrich), (ii) 1,4-benzenedicarboxylic acid (C$_6$H$_4$ -1,4-(CO$_2$H)$_2$, 98%, Sigma-Aldrich, noted H$_2$bdc), and (iii) deionized water. These chemical reactants are commercially available and they have been used without any further purification. 40 mmol of Al(NO$_3$)$_3$.9H$_2$O and 45.2 mmol H$_2$BDC were dissolved in 200 mL of H$_2$O and placed in a 500 ml Teflon-liner within a Parr-type autoclave. The mixture was heated for 24h at 200°C. The resulting product was first recovered by filtration, then washed with *N,N*-Dimethylformamide (HCON(CH$_3$)$_2$, 99.8%, Verbièse, denoted DMF hereafter). Finally, the final MIL-53(Al)-*as* was dried at room temperature without any further treatment.

S2.2. MIL-53(Al)-*lp*

The high-temperature form of MIL-53(Al), i.e. the *lp* form, was synthesized first by eliminating the unreacted species inside the pores of the MIL-53(Al)-*as*. About 2 g of the MIL-53(Al)-*as* and 45 ml of DMF were placed in a 120 ml Teflon-liner within a Parr-type autoclave and heated for 12 h at 150°C. The resulting product was first filtered, washed with deionized water and then dried at room temperature. Finally, the sample was heated for 24 h at 200°C in an open vial to evaporate off the DMF.

S2.3. MIL-53(Al)-*np*

The MIL-53(Al)-*lp* was cooled to room temperature. During this process the sample absorbed one equivalent of water molecule per Al, thus leading to the MIL-53(Al)-*np*.
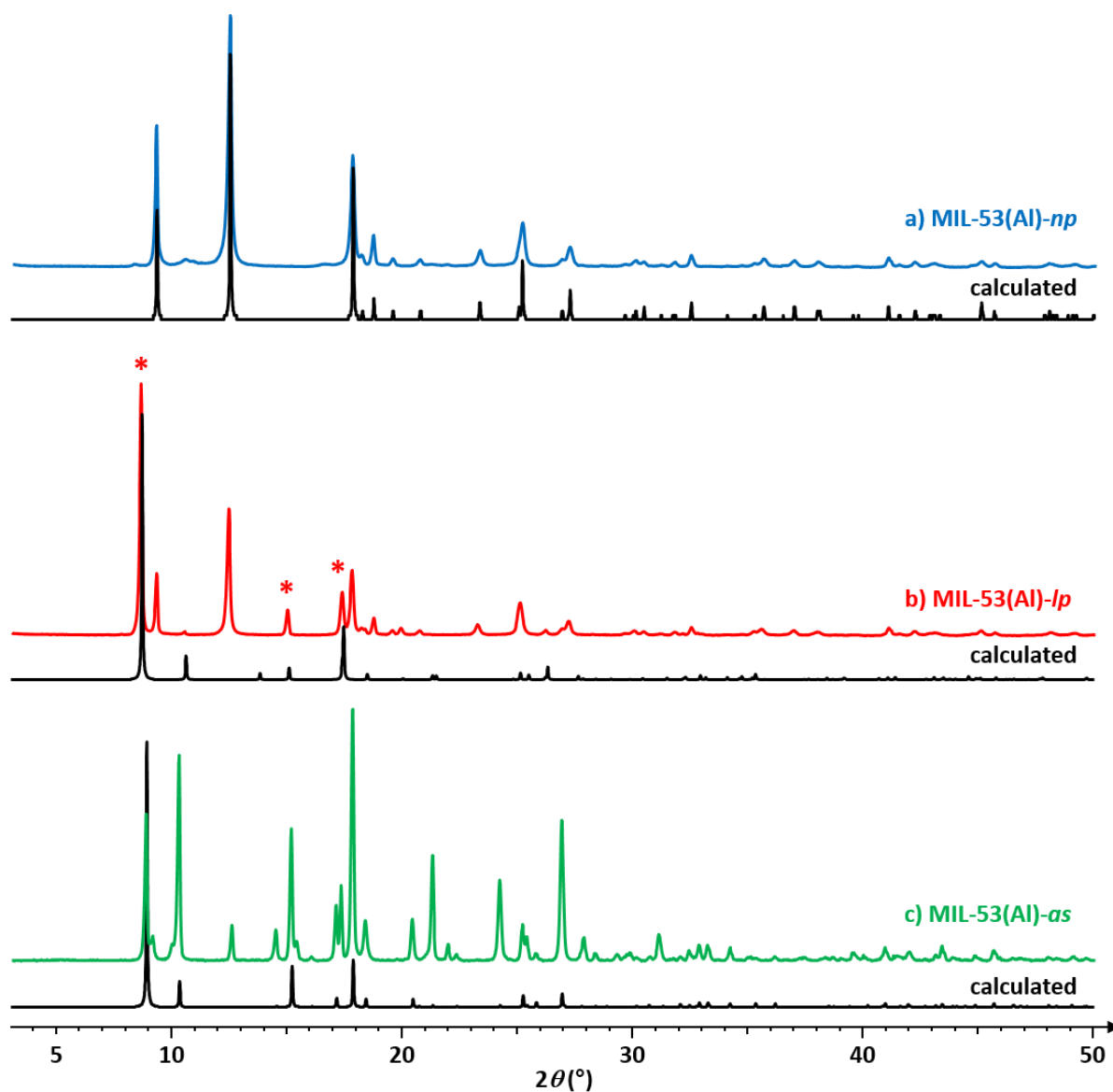
S3. PXRD

Figure S2 X-Ray diffractograms of: a) MIL-53(Al)-*np* (blue), b) MIL-53(Al)-*lp* (red) and c) MIL-53(Al)-*as* (green). It is noted that the MIL-53(Al)-*lp* was partially hydrated into MIL-53(Al)-*np* because the PXRD analysis lasted for 12 min without any precaution. However, the amount of the MIL-53(Al)-*lp* phase was predominant (* peaks) compared to that of the MIL-53(Al)-*np* phase. For each phase, the calculated diffractogram is represented in black.
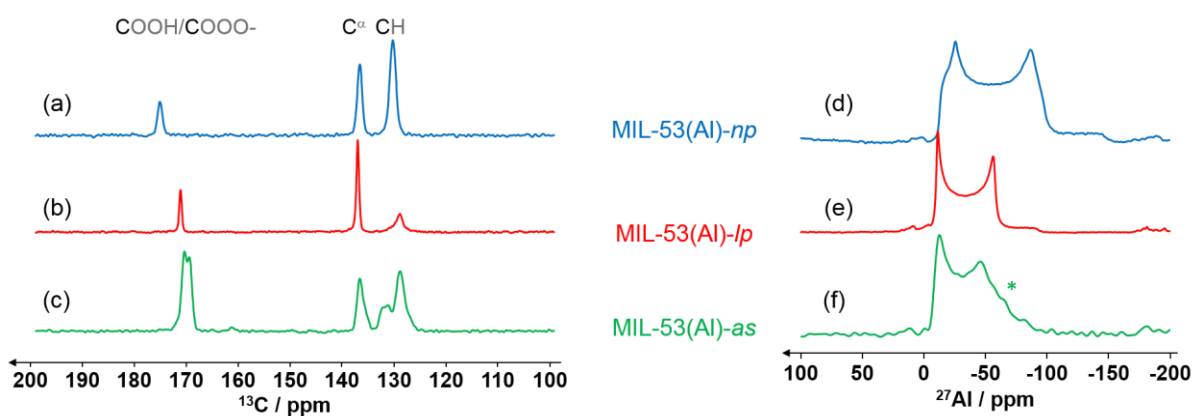
S4. SS-NMR

S.4.1. 1D SS-NMR spectra

Figure S3. a-c) $^1H \rightarrow ^{13}C$ CP-MAS and d-f) ^{27}Al DE-MAS 1D spectra, of MIL-53(Al)-*np* (blue), MIL-53(Al)-*lp* (red) and MIL-53(Al)-*as* (green) recorded at 9.4 T and ν_R = 20 kHz. The asterisk on the spectrum (f) corresponds to remaining $Al(OH)_3$ (see main text for details).
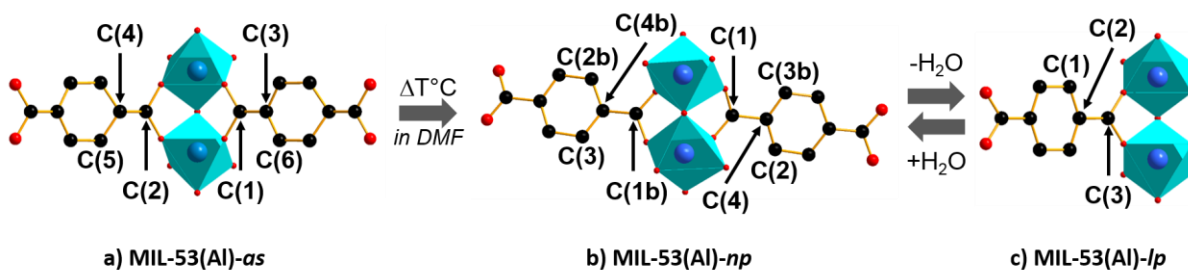
S.4.2. Analysis of ^{13}C-{^{27}Al} SFAM-RESPDOR data

Figure S4 Local structures of a) MIL-53(Al)-*as*, b) -*np*, c) -*lp* determined by PXRD showing the labels of carbon and aluminum atoms.

Table S1 Geometric parameters (C-Al distances and $\widehat{AlCiAl}$ angle) of all ^{13}C-$^{27}Al_2$ spin systems used to simulate the ^{13}C-$\{^{27}Al\}$ SFAM-RESPDOR signal fractions of the *np* form (see Fig. 3). These parameters were determined from the PXRD structure of *np* form. (Loiseau *et al.*, 2004)

Crystallographic sites	Site (δ_{iso} / ppm)	$d_1(Ci\text{-}Al)^a$ /Å	$d_2(Ci\text{-}Al)^b$ /Å	$\widehat{AlCiAl}$ /°
C(1)	COOH (172.9)	2.9064 (325)	2.9972 (295)	67.670 (607)
C(1b)	COOH (172.9)	2.8779 (308)	2.9316 (279)	68.932 (537)
C(2)	CH (128)	4.3552 (234)	5.3892 (220)	37.583 (301)
C(2b)	CH (128)	4.2500 (244)	5.2975 (221)	38.346 (313)
C(3)	CH (128)	4.5733 (223)	5.1672 (243)	38.856 (282)
C(3b)	CH (128)	4.6094 (252)	5.1659 (282)	38.786 (304)
C(4)	C^{α} (134.4)	4.0592 (267)	4.2640 (243)	46.456 (380)
C(4b)	C^{α} (134.4)	4.0636 (255)	4.2140 (233)	46.764 (348)

Table S2   Geometric parameters (C-Al distances and $\widehat{AlC_iAl}$ angle) of all ^{13}C-$^{27}Al_2$ spin systems used to simulate the ^{13}C-$\{^{27}Al\}$ SFAM-RESPDOR signal fractions of the *lp* form (see Fig. 3). These parameters were determined from the PXRD structure of *lp* form. (Loiseau *et al.*, 2004)

Crystallographic sites	Site (δ_{iso} / ppm)	$d_1(Ci\text{-}Al)^a$ /Å	$d_2(Ci\text{-}Al)^b$ /Å	$\widehat{AlC_iAl}$ /°
C(1)	CH (126.7)	4.5929 (121)	5.4295 (108)	37.333 (66)
C(2)	C$^\alpha$ (134.8)	4.4499 (194)	4.4499 (194)	43.588 (1)
C(3)	COOH (168.9)	3.1131 (120)	3.1131 (120)	64.107 (2)

Table S3   Geometric parameters (C-Al distances and $\widehat{AlC_iAl}$ angle) of all ^{13}C-$^{27}Al_2$ spin systems used to simulate the ^{13}C-$\{^{27}Al\}$ SFAM-RESPDOR signal fractions of the *as* form (see Fig. 3). These parameters were determined from the PXRD structure of *as* form. (Loiseau *et al.*, 2004)

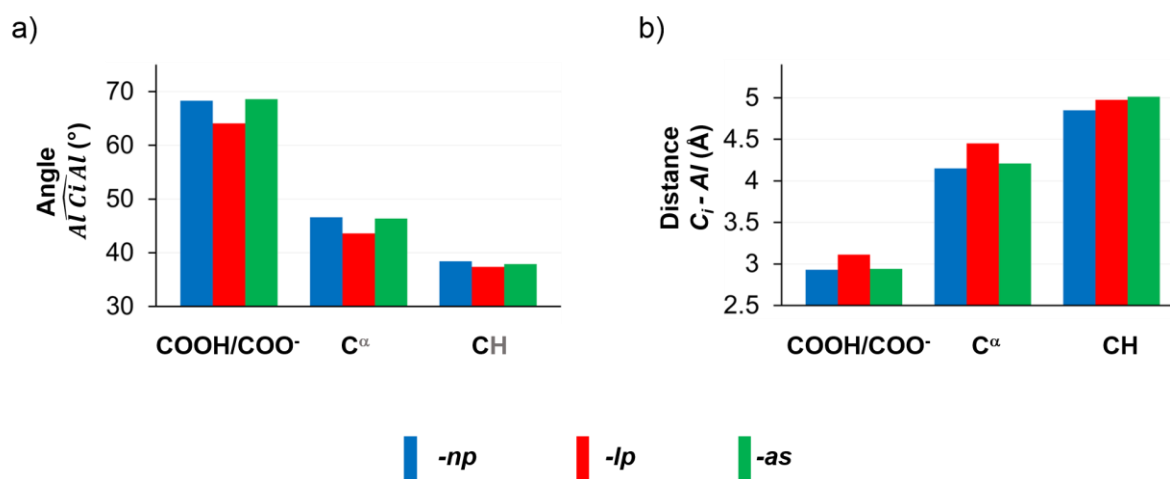| Crystallographic sites	Site (δ_{iso} / ppm)	$d_1(Ci\text{-}Al)^a$ /Å	$d_2(Ci\text{-}Al)^b$ /Å	$\widehat{AlC_iAl}$ /°
C(1)	COOH (170.3)	2.8821 (289)	2.8821 (289)	70.195 (1)
C(2)	COOH (170.3)	3.0022 (291)	3.0022 (291)	67.003 (1)
C(3)	C$^\alpha$ (137.5)	4.1343 (323)	4.1343 (323)	47.259 (1)
C(4)	C$^\alpha$ (137.5)	4.2863 (185)	4.2863 (185)	45.486 (1)
C(5)	CH (129.8)	4.6614 (182)	5.4359 (171)	37.336 (113)
C(6)	CH (129.8)	4.5075 (205)	5.2963 (188)	38.466 (126)

Figure S5. (a) Average $\widehat{AlC_iAl}$ angle and (b) average distance between Ci atom and its two nearest Al neighbors for *np*, *lp* and *as* forms of MIL-53(Al). These distances and angles were determined from the PXRD data (see Tables S1 to 3) and are averaged on all crystallographically inequivalent Ci sites in the unit cell.
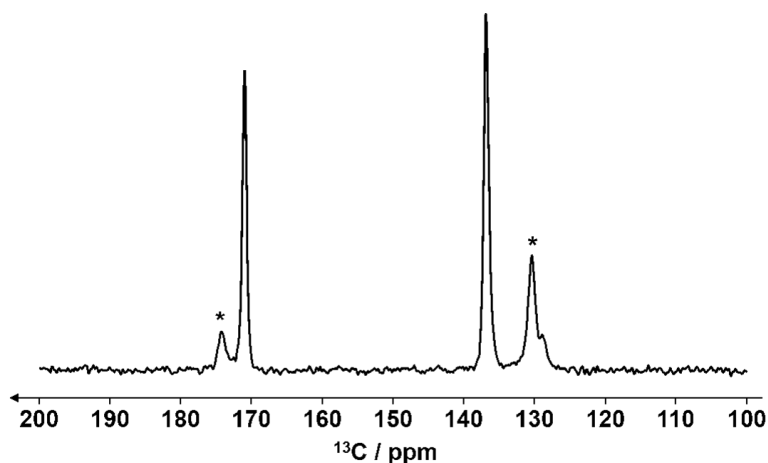
Figure S6. ^{13}C-$\{^{27}$Al$\}$ SFAM-RESPDOR S_0 spectrum with $\tau_{rec} = 3$ ms of MIL-53(Al)-*lp*. The asterisks label the peaks of the hydrated form of the MIL-53(Al).
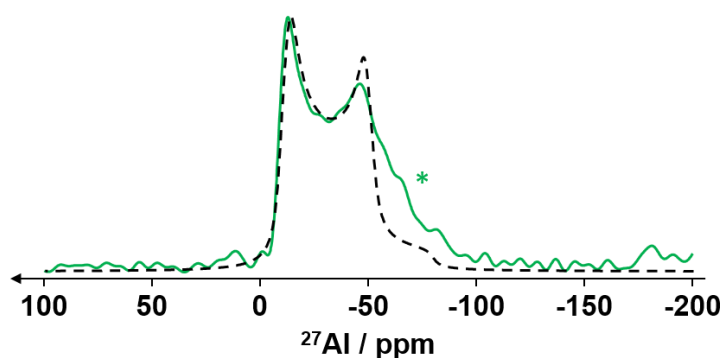

Figure S7. Comparison of ^{27}Al DE-MAS experimental spectrum of MIL-53(Al)-*as* (green spectrum) and the simulated ^{27}Al signal of the MIL-53(Al)-*as* Al site using DMfit software(Massiot *et al.*, 2002) (black dashed lines). The NMR parameters for the simulated signal are δ_{iso} (^{27}Al) = 0.12 ppm, $C_Q = 7.6$ MHz and $\eta_Q = 0.1$. The difference between the experimental spectrum and the simulated one corresponds to the ^{27}Al signal of amorphous Al(OH)$_3$. The asterisk corresponds to remaining Al(OH)$_3$.

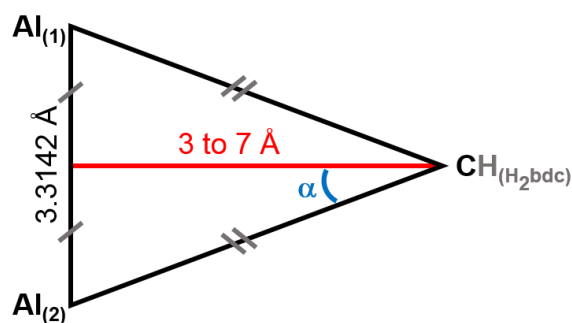**Figure S8.** Illustration of the ^{13}C-^{27}Al$_2$ spin system in which the distance in between the two ^{27}Al is constant and equal to 3.3142 Å. This model is used for the determination of the distance between the CH group of the free ligand and the framework ^{27}Al nuclei in the MIL-53(Al)-*as* form.