Supporting Information

Indomethacin Embedded into MIL-101 Frameworks: A Solid-state NMR Study

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CHARACTERIZATION OF MATERIALS

1. Nitrogen sorption isotherms

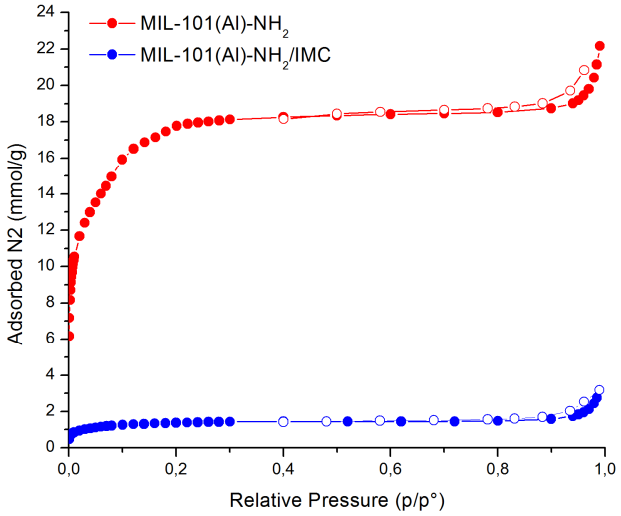

Figure S1. Nitrogen adsorption and desorption isotherms of MIL-101(Al)-NH_2 and MIL-101(Al)-NH_2/IMC. The isotherms were measured on a Micromeritics ASAP 2020 volumetric adsorption analyzer at 77 K. Before the sorption analysis, the samples were thermally treated in dynamic vacuum as follows: MIL-101(Al)-NH_2 at 130 °C for 12 hours and MIL-101(Al)-NH_2/IMC at 40 °C for 3 hours.

2. XRD

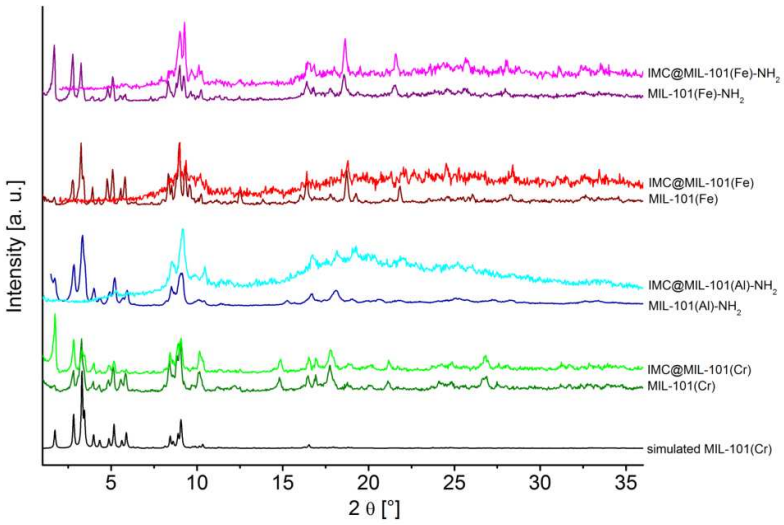

Figure S2. X-ray powder diffraction patterns of MIL-101 matrices before and after loading with IMC. The patterns were recorded on a PANalytical X'Pert PRO high-resolution

diffractometer using $CuK_{\alpha 1}$ radiation (1.5406 Å) in the 2θ range between 1° and 36°, taking 100 s for a step of 0.033°.

3. Elemental analysis

The distribution and quantity of chlorine, aluminum, chromium and iron within the MIL-101 matrices loaded with IMC were observed by energy dispersive X-ray analysis mapping (EDX) with an INCA Energy system (Oxford Instruments) attached to the Zeiss Supra 3VP field-emission microscope. All mapping analyses were performed on the surfaces of the samples with an approximate area of 900 μm^2 and exposure time of 1600 s. For each sample several surfaces were examined. The quantity of chlorine is directly related to the quantity of IMC within the MIL-101 matrix. Figures S3-S6 show even distribution of chlorine throughout the observed agglomerate of MIL-101 matrices, indicating that indomethacine is finely dispersed within the samples. Table 1 shows chlorine/metal atomic ratios obtained by mapping analysis.

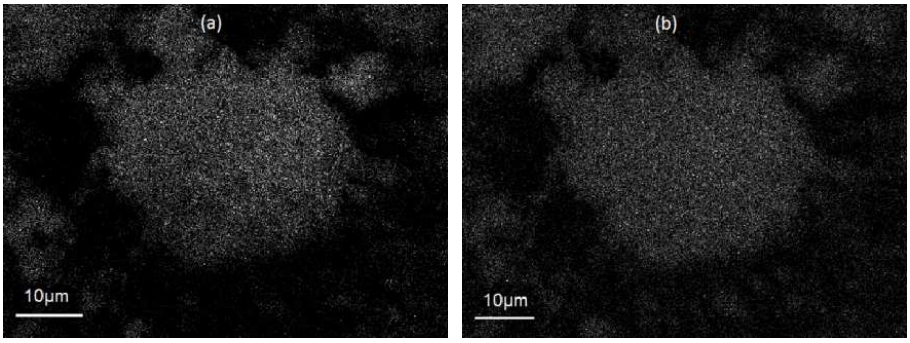

Figure S3. Distribution of Al (a) and Cl (b) atoms in MIL-101(Al)-NH_2/IMC sample.

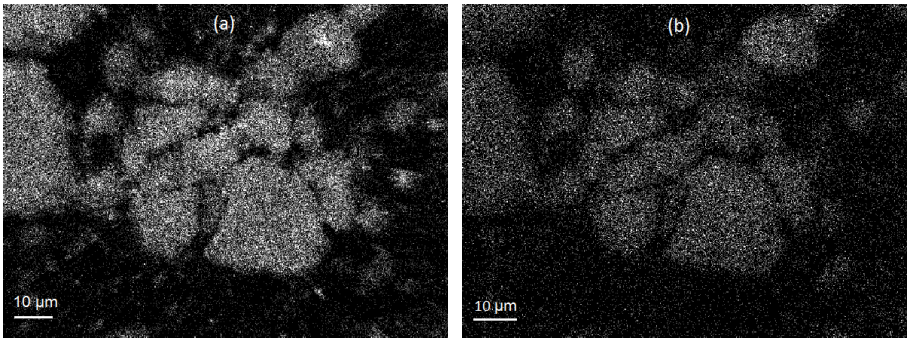

Figure S4. Distribution of Cr (a) and Cl (b) atoms in MIL-101(Cr)/IMC sample.

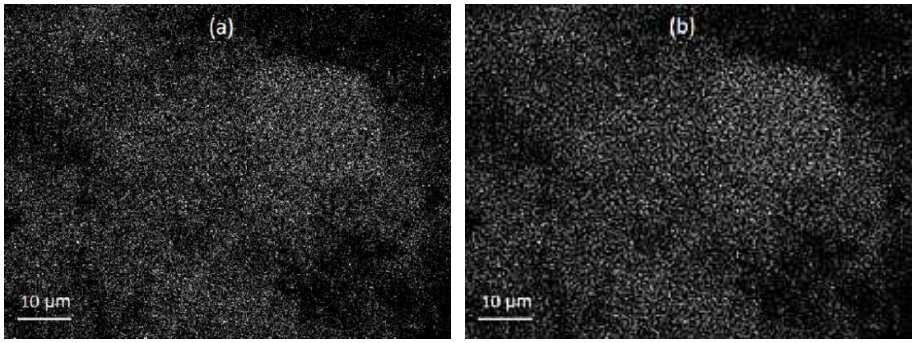

Figure S5. Distribution of Fe (a) and Cl (b) atoms in MIL-101(Fe)/IMC sample.

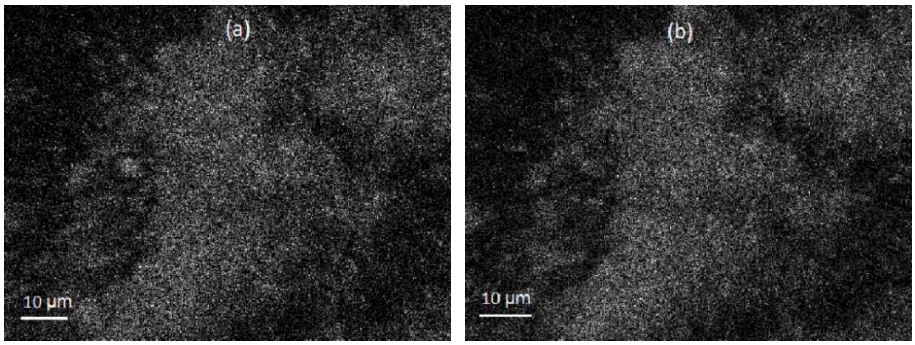

Figure S6. Distribution of Fe (a) and Cl (b) atoms in MIL-101(Fe)-NH_2/IMC sample.

Table 1: Chlorine/metal atomic ratios and the corresponding number of indomethacine molecules per MIL-101 building unit (BU) for all impregnated samples.

sample	**chlorine/metal atomic ratio**	**IMC/BU**
NH_2-MIL-101(Al)/IMC	0.61±0.09	1.8±0.3
MIL-101(Cr)/IMC	0.65±0.09	2.0±0.3
MIL-101(Fe)/IMC	0.54±0.09	1.6±0.3
NH_2-MIL-101(Fe)/IMC	0.74±0.09	2.2±0.3

4. NMR spectroscopy

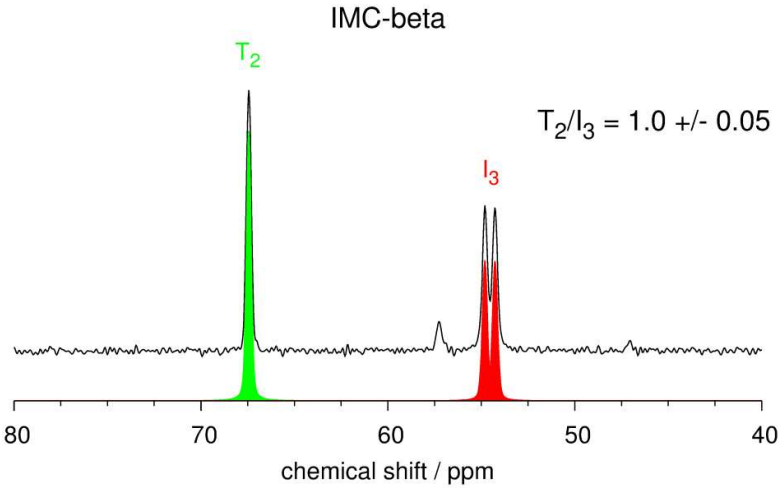

Figure S7. Analysis of the **^{13}C MAS NMR** spectrum of IMC-beta enables quantitative determination of the number of THF molecules and IMC molecules in the crystallographic asymmetric unit of the solvate. THF molecule contains two equivalent T2 carbon atoms and IMC molecule contains only one I3 carbon atom. Two peaks assigned to I3 nuclei belong to two inequivalent IMC molecules within the asymmetric unit of IMC-beta. The ratio of areas under the T2 and I3 peaks provides the number of THF molecules per two molecules of IMC. The spectrum was measured on the Varian 600 MHz spectrometer equipped with a 3.2 mm T3 HX probe. Sample rotation frequency was 20 kHz. Carbon nuclei were excited by a 2 μs 90-degree pulse, repetition delay was 60 s, and number of scans was 2700.

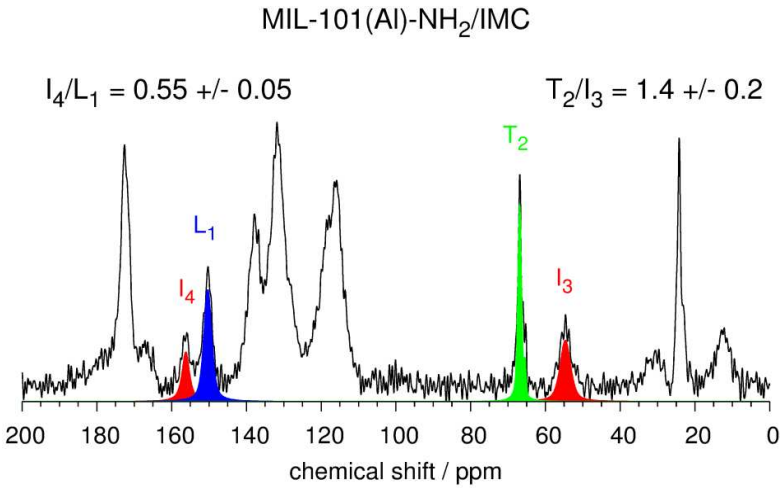

Figure S8. **^{13}C MAS NMR** spectrum of MIL-101(Al)-NH_2/IMC. The ratio of areas under the I4 and L1 peaks provides the number of IMC molecules per one molecule of BDC. The ratio of areas under the T2 and I3 peaks provides the number of THF molecules per two molecules of IMC. The spectrum was measured on the Varian 600 MHz spectrometer equipped with a 3.2 mm T3 HX probe. Sample rotation frequency was 20 kHz. Carbon nuclei were excited by a 2 μs 90-degree pulse, repetition delay was 60 s, and number of scans was equal to 10000.

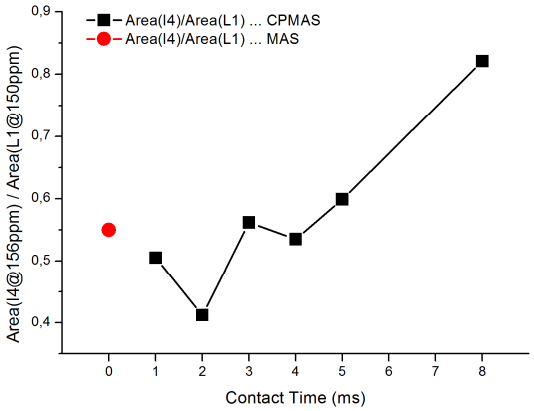

Figure S9. Variation of the ratio of I4 (156 ppm) and L1 (151 ppm) peak intensities with the duration of the cross-polarization block (CP contact time) in the **^{1}H-^{13}C CPMAS NMR** spectrum of MIL-101(Al)-NH_2/IMC. The ratios obtained from the CPMAS spectra are compared to the ratio obtained by the direct-excitation **^{13}C MAS NMR** spectrum of MIL-101(Al)-NH_2/IMC. The latter ratio provides proper loading efficiency that agrees with the one determined by the elemental analysis.