# **Supplementary Information**

## Chloromethylation: a Route to Generic Post-Synthetic Functionalisation of Metal-Organic Frameworks

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## Experimental

#### MOF synthesis

All chemicals were obtained from Sigma-Aldrich and used without further purification. Amino MIL-53 (Al) was synthesized mixing 1.97 g of aluminium chloride hexahydrate, 1.50 g of 2-aminoterephthalic acid, and 20.00 g distilled water in a Teflon insert, which is placed in an autoclave. The closed autoclave is heated under autogenous pressure for 8 hours at  $150^{\circ}$ C<sup>1</sup>. The resulting yellow powder is filtered off, then washed in the same autoclave with DMF at  $150^{\circ}$ C overnight.

MIL-101(Cr) was synthesized mixing 1.63g of chromium nitrate hexahydrate, 0.97g of terephthalic acid, 0.20 g hydrofluoric acid (60%) and 12 g water in a Teflon insert, which is placed in a microwave autoclave. The mixture is heated in a microwave to 210 °C within 4 minutes and kept for 45 minutes at that temperature<sup>2</sup>. The resulting green powder is filtered off and washed in DMSO at 80 °C overnight.

#### **Chloromethylation**

Chloromethylation was carried out using selected amounts per gram of MOF shown in the table below:

	Amino MIL-53(Al)	MIL-101(Cr)
Aluminium chloride hexahydrate (g)	1.1	1.9
Methoxyacetyl chloride (g)	0.7	0.4
Nitromethane (g)	80	80
Temperature ( <sup>0</sup> C)/Duration (h)	75/3	100/5

Table 1. Amounts of chemical used and applied conditions in the chloromethylation of MOFs

The reaction is carried out under reflux with continuous stirring. It is vital to use the hexahydrate form of aluminium chloride as it offers protons necessary in the mechanism for the initiation (see: reaction mechanism). The reason MIL-101 (Cr) has to be chloromethylated under harsher conditions lies in the absence of activating amino species in the aromatic ring to be chloromethylated. Any solid product of chloromethylation was washed overnight with boiling, distilled water and followed by boiling THF for 3 hours, before being 'activated' in a furnace at  $100^{\circ}$ C under air.

#### **Diphenylphosphination**

Before the reaction was started, MIL-101 (Cr) was dispersed in THF at  $-78^{\circ}$ C under nitrogen. 2 mol/mol of LiPPh<sub>2</sub> per MOF in THF solution was added dropwise before the reaction was carried out under slow stirring for 12 h. The resulting product was washed in THF at 50 °C before being activated under vacuum.

#### Solid-state NMR

Solid-state <sup>27</sup>Al, <sup>13</sup>C, and <sup>1</sup>H NMR studies were performed on a Bruker AV-750 spectrometer with a 17.6 Tesla magnetic field, in which these nuclei resonate at 195.46, 188.64, and 750.13 MHz, respectively. A H/X/Y 2.5 mm MAS probe-head and a standard ZrO<sub>2</sub> rotor spun at 20 kHz were used. For the acquisition of <sup>27</sup>Al MAS spectra, the RF field frequency, pulse duration, number of scans, and repetition time were 55 kHz, 1.5 µs, 1024 scans and 1 s, respectively. The corresponding parameters were 78.1 kHz, 3.2 µs, 32scans, and 1s for <sup>1</sup>H MAS spectra. For <sup>1</sup>H to <sup>13</sup>C CPMAS with TPPM decoupling, we used 62.5 and 89 kHz RF field frequencies in the <sup>13</sup>C and <sup>1</sup>H channels, respectively. For cross-polarization (CP), the contact time was 3 ms, and the repetition time was 2 s for 1024 scans. Chemical shift references (0 ppm) are Al(NO<sub>3</sub>)<sub>3</sub> in aqueous nitric acid solution for <sup>27</sup>Al, TMS for <sup>1</sup>H, Glycine for <sup>13</sup>C. <sup>27</sup>Al spectra were fitted with the DMFIT software package to obtain approximations for quadrupolar coupling constant  $C_q$  and asymmetry factor  $\eta q$ .<sup>3 31</sup>P MAS NMR studies were performed on a Bruker DMX-400 spectrometer with a 9.6 Tesla magnetic field, in which 31P and 1H resonate at 161.69 and 399.42 MHz, respectively. A triple resonance 4 mm MAS probe with standard ZrO<sub>2</sub> rotor with spinning frequency of 12 kHz was used. A single pulse of 78.12 kHz was applied with a repetition time of 2 s, 5120 scans were collected. The chemical shift reference for <sup>31</sup>P used was 85 % H<sub>3</sub>PO<sub>4</sub>. All the spectra were processed with Bruker Topspin 1.3.

#### XRD

XRD was carried out using a Bruker-AXS D5005 with CuKa radiation.

#### Diffuse Reflectance IR Spectroscopy:

DRIFT spectra of the chloromethylated and phosphinated samples were recorded on a Nicolet model 8700 spectrometer, equipped with a high-temperature DRIFT cell, DTGS-TEC detector and a 633 nm laser. The spectra were registered from 4000 to 600 cm<sup>-1</sup> after accumulation of 128 scans and a resolution of 4 cm<sup>-1</sup>. A flow of helium at 20 mL min<sup>-1</sup> was maintained during the measurements. Before collecting the spectra, the different samples were pre-treated in the same helium flow at 393 K for 30 min. KBr was used to perform background experiments.

#### Transmission FTIR

IR analysis on the chloromethylated samples was carried out using a Thermo Nicolet Nexus FTIR spectrometer. The samples (1 mg) were mixed with KBr and pressed into self-supported pellets (50 mg/cm<sup>2</sup>). The spectra were taken in an in-situ cell equipped with CaF<sub>2</sub> windows. Prior to the measurements, the samples were degassed under vacuum ( $10^{-5}$  mbar) at 473 K for 30 min to remove adsorbed molecules.

#### Temperature programmed desorption (TPD)

The thermal decomposition of modified MOF was followed by mass spectrometry. The sample, about 0.05 g, was heated in a quartz reactor at a rate of 5 K min<sup>-1</sup> under a helium flow of 50 cm<sup>3</sup>min<sup>-1</sup>. The released gases were analyzed by a mass spectrometer.

#### CO<sub>2</sub> sorption

High-pressure adsorption isotherms of pure  $CO_2$  (purity of 99.995%), were determined volumetrically using an apparatus from BEL Japan (Belsorp HP). 0.5 gram of adsorbent was placed in the sample container. Before every measurement, the adsorbent was pretreated/regenerated by increasing the temperature to 473 K at a rate of 10 K/min under vacuum and maintaining this temperature for two hours.

#### N<sub>2</sub> adsorption

Nitrogen adsorption at 77 K was measured in a Quantachrome Autosorb-6B unit gas adsorption analyzer. The specific BET surface area was calculated between 0.05-0.15 relative pressures and the pore volume at 0.95 relative pressure.

#### Elemental analysis

Elemental analysis was carried out by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The samples were digested in a mixture of 1% HF and 1.25% H2SO4 and were analyzed with an ICP-OES Perkin Elmer Optima 3000 dv in order to determine the amount of phosphorus present in the structure. The procedure was carried out in duplo with the average taken as result.

## Solid-state NMR

Solid-state NMR is the key technique for the characterization of successful post-synthetic functionalization. It is in many cases the only technique able to show functionalities are attached through covalent bonds, and may also provide information about the solid-state interactions taking place.

Solution-state NMR has not been performed since the only solvents to dissolve these frameworks, HF, and (M)OH (M being a metal), lead to unwanted  $S_n$  reactions with the chloromethyl group, and would therefore change the result of analysis.

## <sup>13</sup>C CPMAS NMR

In extension to information described in the paper, chemical shift values and peak assignments for the <sup>13</sup>C CPMAS experiment are shown below.

Carbon no. / <sup>13</sup> C chemical shift (range) (ppm)	Structural representation
1a / 58.5	
1b / 72.5	
2 / [112 - 152]	
3a / 165.5	
3b / 172.5	

Table I: Chemical shift values for the <sup>13</sup>C CPMAS experiment on CMNH2-MIL-53(Al)

## <sup>1</sup>H MAS NMR

For chloromethylene protons, there is no visible difference in peaks for *ortho* and *parasubstituted* CM groups; the result is a broad peak centered at approximately 3.5 ppm, typical for chloromethylene protons, overlapping the aluminium hydroxide proton signal as well (figure I). The experiment is useful and confirmative in combination with the HETCOR experiment given in the paper.



Figure I. <sup>1</sup>H MAS NMR spectrum of NH2-MIL-53(Al) {grey} and CMNH2-MIL-53(Al) {black}.

## <sup>27</sup>AIMAS NMR

The aluminium nucleus possesses a spin of 5/2, every nucleus with spin > 1/2 is quadrupolar of nature. Quadrupolar nuclei have a non-spherically symmetrical distribution of nuclear charge and possess, in addition to their magnetic moment  $\mu$ , also an electric quadrupole moment eQ. This quadrupolar moment interacts strongly with any electric field gradient (EFG) at the position of the nucleus, and is therefore strongly dependent on the shape of the electron cloud within the crystal. In Cartesian form the quadrupolar Hamiltonian is given by:

$$\widehat{H}^{\mathcal{Q}} = \frac{eQ}{2I(2I-1)}\widehat{I} \cdot \overrightarrow{V} \cdot I$$

where V represents the EFG in tensor notation. From this Hamiltonian two important crystallographic parameters can be defined, the quadrupolar coupling constant  $C_Q$  (MHz) and the asymmetry factor  $\eta_Q$  (dimensionless):

$$C_Q = e^2 q Q / \hbar$$
$$\eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

Here, *Q* represents the quadrupole moment and  $\hbar = h/2\pi$ .

Recently, Lieder et al. (2010) showed the effect of adsorbates on the quadrupolar coupling constant and asymmetry factor for MIL-53(Al).<sup>4</sup> It seems this NMR based approach can be very useful to determine characteristics of porous coordination polymer materials. In this case, the use was limited to the effect of the opening of the structure on these parameters.

As shown recently by Stavitski et al. (2011), in the case of NH<sub>2</sub>-MIL-53(Al) the interaction between the amine group and  $\mu_2$ -aluminium-bridging hydroxyl groups of the MIL-53 structure results in the stabilization of the narrow pore structure after solvent removal. As a result, the EFG in NH<sub>2</sub>-MIL-53(Al) is much larger, considering the increased proximity of electron clouds in the narrow pore form. The asymmetric nature of the electric field experienced by the aluminium node increases too as any amine group interacts with only one side of the most-nearby aluminium atom from x-axis perspective.



**Figure II.** DFT optimization of NH<sub>2</sub>-MIL-53 in the narrow pore form (np) showing the interaction between the Alcuster and the amine group, adapted from Stavitski et al. (2011)<sup>5</sup>

CM opens the MIL-53 structure, and therefore decreases the EFG, but also increases the distance between the amine group (see: Transmission FTIR) and the  $\mu_2$ -aluminium-bridging hydroxyl groups, with a decrease of the asymmetry factor as result (figure III).

Finally, and even more observable, there is a large change in chemical shift. A similar effect has been reported before by Loiseau et al.  $(2004)^6$  in the case of MIL-53 and matters the increased electron density in the closed form of MIL-53, which presents a shielding effect, which causes the aluminium signal to move upfield in the case of the closed (unfunctionalized) form.



Figure III. <sup>27</sup>Al MAS NMR spectrum of NH<sub>2</sub>-MIL-53(Al) {grey} and CM NH<sub>2</sub>-MIL-53(Al) {black}.

## <sup>31</sup>P MAS NMR

<sup>31</sup>P MAS NMR was used to prove successful diphenylphosphination of MIL-101(Cr) after chloromethylation. It might arise as a surprise that MIL-101(Cr) was successfully tested as it is a structure for which NMR is normally a problem due to paramagnetism of the Cr nodes: paramagnetic electrons are able to enter the aromatic ring and act like delocalized aromatic electrons, Relaxation of the excited nuclei in the ring is then so fast that it's a large challenge or even nearly impossible to obtain a proper FID (Free Induction Decay). Refocusing of the signal can be done by solid-echo based sequences but implementation of this is usually time-consuming.

However, delocalized electrons are unable to move through the methylene group and therefore the <sup>31</sup>P nucleus is "protected" from the paramagnetic effect. Excitation and recording of the FID didn't turn out to provide any problem. The spectrum is shown in figure IV and no organolithium phosphorus signal is seen, which points at removal of the reactant. The signal observed is in the typical chemical shift range for benzyl diphenylphosphines.

However, as expected for uncoordinated trivalent phosphorus moieties, the trivalent phosphorus compound oxidizes readily in air, and this was *in-situ* visible in the solid-state NMR experiment by an increasing chemical shift signal at 48 ppm.



Figure IV. <sup>31</sup>P MAS NMR spectrum of PhP MIL-101(Cr).

#### **Proposed reaction mechanism**

Considering the harsh conditions and hazardous character of chloromethylation under traditional conditions, it was our aim to find a milder and safer replacement. As with the sulfation, presented earlier for MOFs<sup>7</sup>, the choice fell on a very reactive, but non-destructive agent, in this case methoxyacetyl chloride (MeOAcCl). The reagent is activated by aluminium chloride hexahydrate in nitromethane and decomposes into CO and the reactive electrophile  $CH_3OC^+H_2$  which reacts further in a couple of steps towards complete chloromethylation. The presence of amine groups activates the ortho- and para-positions of the ring, since nitrogen's lone pair electrons stabilize these sites in a positively charged aromatic intermediate. Substitution therefore occurs at ortho and para positions with respect to nitrogen. The other reaction products formed are CO, MeOH and HCl and they are all detected. It is important to use a large quantity of nitromethane in order to diminish acidity by the HCl formation, which might be detrimental for some frameworks. Important to note is that we observed that aluminium chloride hexahydrate is essential for the successful completion of the reaction, rather than anhydrous aluminium chloride. Our explanation is that the final two steps only proceed in acidic medium. At the start of the reaction, therefore, traces of water need to be present after which the reaction is autocatalyzed because of the formation of HCl.



Figure V. Proposed reaction mechanism for the mild chloromethylation with methoxyacetyl chloride and aluminium chloride

## CO<sub>2</sub> sorption



Figure VI. High-pressure CO<sub>2</sub> isotherm recorded at 0°C of CM-NH<sub>2</sub>-MIL-53(Al) {green} and NH<sub>2</sub>-MIL-53(Al) {grey}.

One of the most apparent results is obtained by comparing an isotherm of CM NH<sub>2</sub>-MIL-53(Al) with an isotherm of NH<sub>2</sub>-MIL-53(Al). Chloromethylation results in a vnp  $\rightarrow$  lp phase transition, as demonstrated by XRD. In addition, no breathing, as described for NH<sub>2</sub>-MIL-53(Al) is observed. CMNH2-MIL-53(Al) is clearly open from the beginning. As described in the main text, we suggest the reason lies in chloromethylene exerting steric influence on this interaction as they interact with amino groups and reduce their interaction with OH groups, resulting in the opening of the framework.



**Figure VII.** XRD patterns of  $NH_2$ -MIL-53(Al) <sup>8</sup> and CM  $NH_2$ -MIL-53(Al) together with the simulated XRD patterns for NH2-MIL-53(Al) in the vnp and lp configurations.

Shown in figure VII are the XRD patterns of  $NH_2$ -MIL-53(Al) before and after chloromethylation. As it can be observed, a transition between the initial vnp configuration and a lp form of the  $NH_2$ -MIL-53(Al) structure occurs upon chloromethylation.

### **IR** - extension



Figure VIII. Left: IR spectra of NH2-MIL-53(Al)  $^{8}$  and CMNH2-MIL-53(Al) {black}. Right: zoomed in on the amine region for CMNH2-MIL-53(Al).

Amine N-H stretching vibrations can be recognized by a doublet of absorbances with a frequency ratio of 0.97 between symmetric and asymmetric stretchings (3390 and 3525 cm<sup>-1</sup>, respectively). Figure VIII displays spectra for unfunctionalized and functionalized MIL-53(Al). A new asymmetric (*left*) –symmetric (*right*) twin of amine absorbances is magnified in the graph on the right. The symmetric stretching absorbance is enhanced after chloromethylation, which infers a decrease in asymmetry for the chemical environment around the amine group, as earlier concluded from the  ${}^{27}$ Al NMR spectrum.

Also, a large difference in the OH stretching region is visible. The unmodified sample presents two clear peaks of which one is centered at 3709 cm<sup>-1</sup> and a second one centered at 3682 cm<sup>-1</sup>. These vibrations are assigned to the free (non-interacting) bridging hydroxyl groups (3709 cm<sup>-1</sup>) and the bridging hydroxyl groups interacting with the amino groups (3682 cm<sup>-1</sup>)<sup>5,9</sup>. As the chloromethylene groups – as shown before – decrease or even nullify the OH-NH<sub>2</sub> interaction, this specific stretching significantly decreases in intensity. This is yet another evidence of strong intra-framework interaction between the different functional groups.



**Figure IX.** *Left:* The characteristic region of the IR spectrum for chloromethylated and diphenylphosphinated MIL-101(Cr). *Right:* IR spectrum of condensed phase of triphenylphosphine showing the characteristic stretchings at 2850-3025 cm<sup>-1</sup>.

Figure IX displays the characteristic region in the IR spectrum of functionalized MIL-101(Cr). After chloromethylation a peak at 2980 cm<sup>-1</sup> appeared which Ma et al. showed to be a characteristic  $-CH_2Cl$  stretching<sup>10</sup>. After further functionalization, the typical aryl phosphine stretchings at 2800-3100 cm<sup>-1</sup> can be observed. As reference an IR of condensed PPh<sub>3</sub> is attached.<sup>11</sup>



## **Temperature Programmed Decomposition – Mass Spectrometry, TPD/MS**



The TPD shows that a part of the chloromethylene groups are released at temperatures above  $210^{\circ}$ C, but most are stable up until the complete collapse of the framework, which occurs at 350 - 450 °C.

## N<sub>2</sub> adsorption @ 77 K



Figure XI. N<sub>2</sub> adsorption isotherm at 77 K of MIL-101(Cr) and PPh<sub>2</sub> MIL-101(Cr).

As visible in Figure XI, diphenylphosphination gives rise to an anticipated decrease in porosity for MIL-101(Cr), but the structure remains very accessible, making the framework an excellent candidate for catalysis. The two characteristic steps in the MIL-101 isotherms are related with the filling of the mesoporous cavities. At very low relative pressures ( $P/P_0 < 0.05$ ) only the supertetrahedra are filled. As pressure increases, the medium ( $P/P_0 = 0.15$ ) and later the large cavities ( $P/P_0 = 0.20$ ) are filled. After diphenylphosphination, it is visible that these steps become less pronounced, and occur at lower relative pressures, suggesting a predictable decrease in pore volume after introduction of the PPh<sub>2</sub> moieties. The BET surface area decreases from 2800 m<sup>2</sup>/g to 1800 m<sup>2</sup>/g. Nitrogen sorption was not performed onNH2-MIL-53(Al) since diffusion limitations for N<sub>2</sub> at 77K in the narrow

Nitrogen sorption was not performed onNH2-MIL-53(Al) since diffusion limitations for  $N_2$  at 77K in the narrow pore form don't make this material suitable for this type of analysis.

## GAUSSIAN® energy/geometry optimization



**Figure XII:** Impressions of an energy/geometry optimized MIL-101(Cr) window functionalized with two -PPh<sub>2</sub> groups. The images are representations at intervals of 20° rotation around a vertical axis.

The images above in figure XII are the result of a GAUSSIAN<sup>12</sup> energy/geometry optimization of the window of MIL-101(Cr) only. Interestingly, these optimizations suggest a close vicinity of phosphorus to the Cr cluster, at a distance of approximately 4 Å.

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