

Electronic Supplementary Information for  
**Synthesis of amine-tagged metal-organic  
frameworks isostructural to MIL-101(Cr)**

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## S1. Experimental Procedures

**Starting Reagents.** Chromium nitrate nonahydrate (Sigma-Aldrich, 99%), terephthalic acid (Acros Organics, >99%), 2-aminoterephthalic acid (Acros Organics, >99%) and fluorhydric acid (Vetec, 48 wt% P.A. ACS) were used as-received without further purification.

**Synthesis of MIL-101(Cr).** An amount of terephthalic acid (Table S1) and the chromium nitrate,  $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ , (0.7663 g) were dissolved in distilled water (10.0 mL) and stirred. While the reaction was stirring, fluorhydric acid 48 wt% (69  $\mu\text{L}$ ) was added in two portions. The stir bar was then removed from the half full Teflon<sup>®</sup> cup, and the cup was sealed inside a steel autoclave. The system was placed inside a 180 C oven and was heated for 8 h. Afterwards, the autoclave was removed and left to cool to room temperature. Once cooled, the steel autoclave was open and the reaction carefully vented. The resulting solution contained a suspension of green solid and green liquid. The suspension was then filtered through a stainless metal sieve to extract the excess terephthalic acid from the reaction mixture. The newly filtered suspension was left to settle during 6 h. The suspension was then vacuum filtered to yield a green solid. The solid was removed and dried inside a desiccator to prepare for purification.

**Synthesis of amine-tagged MIL-101(Cr).** A similar procedure was employed to the synthesis of amine-tagged MIL-101(Cr). Instead of the amount of terephthalic acid used in the synthesis of MIL-101(Cr), we used a mixture of different amounts of terephthalic acid and 2-aminoterephthalic acid, as indicated in Table S1. The rest of the amounts and the procedure was carried as described before.

Table S1: Molar fraction and mass amounts of organic acids used in the synthesis of the samples, where  $X_{ta}$  and  $X_{nh2}$  represent the molar fraction of terephthalic acid and 2-aminoterephthalic acid, respectively.

Samples	$X_{ta}$	$m_{ta}$ (g)	$X_{nh2}$	$m_{nh2}$ (g)
MIL-101(Cr)	1.0	0.319	0	0
10%NH <sub>2</sub> -MIL-101(Cr)	0.9	0.287	0.1	0.035
20%NH <sub>2</sub> -MIL-101(Cr)	0.8	0.255	0.2	0.070
30%NH <sub>2</sub> -MIL-101(Cr)	0.7	0.223	0.3	0.104

**Purification of the materials.** The materials underwent purification three times with three different solvents. In the first purification, distilled water (20.0 mL) was added to the dry green solid. The reaction was refluxed over an approximate heat of 70 C for 5 h, and then vacuum filtered. The

second purification used ethanol (20.0 mL) as the solvent, and the solution was refluxed over the approximate heat of 60 C for 3 h. The solution was once again vacuum filtered. The final purification used the solvent  $\text{NH}_4\text{F}$  30  $\text{mmol}\cdot\text{L}^{-1}$  (20.0 mL). This solution was refluxed over about 70 C for 10 h. The resulting solution was vacuum filtered to yield a final green solid. The green solid was dried inside the desiccator. After the sample was completely dried, the compound was scraped from the surface of the filter paper and ground into a fine powder using a mortar and pestle. The green powder was transferred to a plastic tube for storage and submitted to vacuum drying.

**Powder X-Ray Diffraction.** Powder X-Ray Diffraction data were collected with a Shimadzu XRD-7000 diffractometer with Bragg-Brentano geometry and graphite monochromator. The  $\text{CuK}\alpha$  (1.5406 Å) X-Ray radiation source was operated at 40 kV and 30 mA. The collected  $2\theta$  range was from 1.4 to 50.0 under  $2\cdot\text{min}^{-1}(2\theta)$ . The apertures of divergence, scattering and receiving slits were at 0.5, 0.5 e 0.3 mm, respectively.

**Nitrogen Sorption Measurements.** Nitrogen sorption at 77 K was performed in a volumetric ASAP 2010 (Micrometrics) analyzer or using NOVA 4200 (Quantachrome). Surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. The samples were pre-treated at 150 C during 12 h.

**Fourier Transform Infrared Absorption Spectroscopy.** The samples were prepared as pellets with *ca.* 1 wt% of material using KBr. The infrared spectra were obtained with FT-IR ABB Bomen MB-100E Infrared Spectrometer using resolution of  $4\text{ cm}^{-1}$  and accumulation of 20 scans.

**Elemental Analysis.** The samples were analysed in a Perkin Elmer 2400 II Series CHNS/O Elemental Analyzer.

**$^1\text{H}$  Nuclear Magnetic Resonance.** About 1 mg of the samples were digested using 0.4 mL of  $\text{D}_2\text{O}$  and 0.2 mL of a solution of NaOD *ca.* 1 wt%. The resulting solution was submitted to analysis in Bruker equipments, models 300 and Avance III 400.

**Scanning Electron Microscopy.** Scanning electron microscopy (SEM) images were obtained after dispersing the samples in acetone with an ultrasound bath, drying on a stub and then coating with gold. The images were performed in a Jeol 6360-LV, operating at 20 kV.

## S2. Nitrogen Sorption Measurements

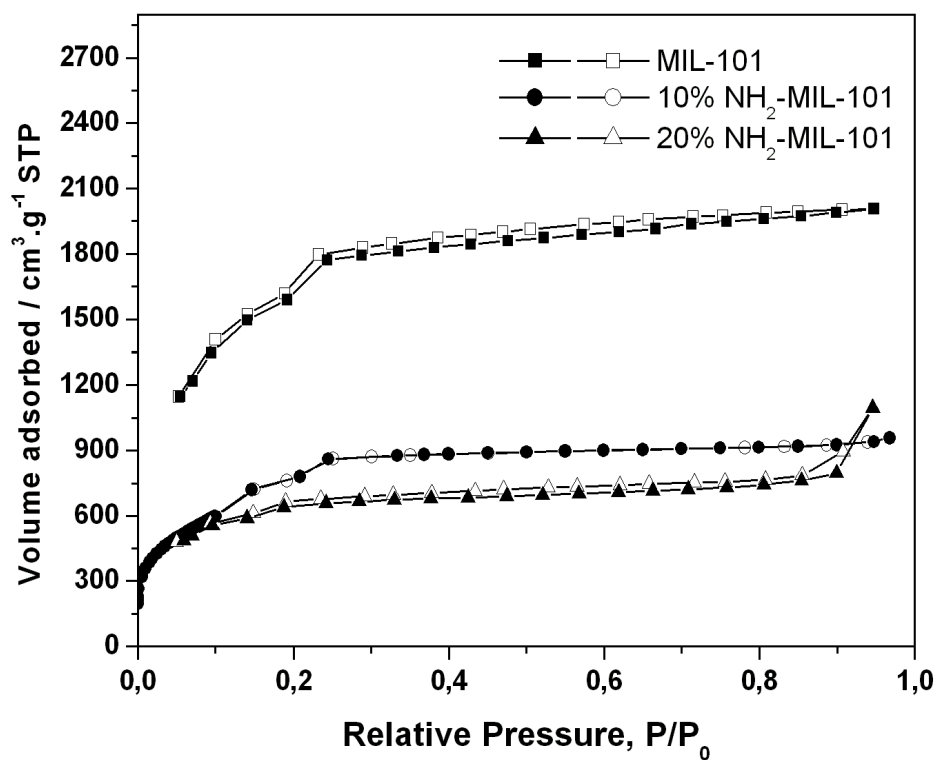


Figure S1: Nitrogen adsorption and desorption isotherms obtained for MIL-101(Cr), 10%NH<sub>2</sub>-MIL-101(Cr) and 20%NH<sub>2</sub>-MIL-101(Cr).

Table S2: Surface area values ( $S_{BET}$ ) obtained from N<sub>2</sub> sorption isotherms using BET model.

Samples	$S_{BET}$ ( $10^3 \text{ m}^2 \cdot \text{g}^{-1}$ )
MIL-101(Cr)	$6.11 \pm 0.09$
10%NH <sub>2</sub> -MIL-101(Cr)	$2.68 \pm 0.02$
20%NH <sub>2</sub> -MIL-101(Cr)	$2.38 \pm 0.03$

### S3. Elemental Analysis

Table S3: Mass percentages of carbon (%C) and nitrogen (%N) obtained from elemental analysis and calculated experimental molar proportion of the functionalized linker (% $_{func}$ ).

Samples	%C (%)	%N (%)	% $_{func}$ (%)
MIL-101(Cr)	39.2	0.28	- %
10%NH <sub>2</sub> -MIL-101(Cr)	35.4	0.65	12.5
20%NH <sub>2</sub> -MIL-101(Cr)	33.5	1.07	21.9

The experimental molar proportion of the functionalized linker (% $_{func}$ ) was obtained using the ratio of mass percentages of carbon (%C) and nitrogen (%N) in the obtained samples. From this ratio and considering the molar mass of each element, we could obtain the molar ratio between nitrogen and carbon (N/C) in the sample. For a hypothetical material that contains 100% of functionalization of benzene rings with NH<sub>2</sub>, we would find a N/C ratio equals to 1/8. Therefore, using the N/C ratios of the samples, and by the division of them by 1/8 we can obtain % $_{func}$  after multiplication by 100. The equations (1) and (2) represent the calculation performed.

$$\frac{N}{C} = \frac{\%N}{M_N} \cdot \frac{M_C}{\%C} \quad (1)$$

$$\%_{func} = \frac{N}{C} \cdot \frac{8}{1} \cdot 100 \quad (2)$$

where  $M_N$  and  $M_C$  stand for the molar mass of nitrogen and carbon respectively.

#### S4. $^1\text{H}$ Nuclear Magnetic Resonance

**MIL-101:**  $\delta$  7.759 (s, 4H)

**10%NH<sub>2</sub>-MIL-101:** signal assigned to terephthalic acid -  $\delta$  7.671 (s, 4H); signals assigned to 2-aminoterephthalic acid:  $\delta$  7.341 (d,  $J = 8.0$  Hz, 1H), 7.968 (dd,  $J = 8.0, 1.2$  Hz, 1H), 8.166 (d,  $J = 1.2$  Hz).

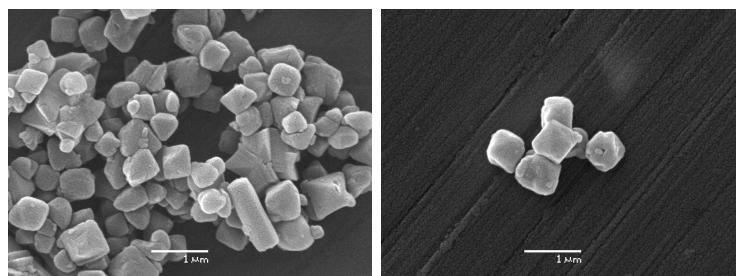
**20%NH<sub>2</sub>-MIL-101:** signal assigned to terephthalic acid -  $\delta$  7.754 (s, 4H); signals assigned to 2-aminoterephthalic acid:  $\delta$  7.424 (d,  $J = 8.0$  Hz, 1H), 8.051 (dd,  $J = 8.0, 1.6$  Hz, 1H), 8.384 (d,  $J = 1.6$  Hz, 1H).

The experimental molar proportion of the functionalized linker ( $\%_{func}$ ) was estimated considering that the relative integration of the signal at 8.0 ppm is related to 4 chemically equivalent hydrogens of terephthalic acid while the relative integration of the signal at 7.7 ppm is referent to 1 hydrogen of 2-aminoterephthalic acid. For this reason, the relative integration of the signal at 8.0 ppm was divided by the sum of this integration and the quarter of the relative integration of the signal at 7.7 ppm. After multiplication by a factor of 100, the value of  $\%_{func}$  was obtained.

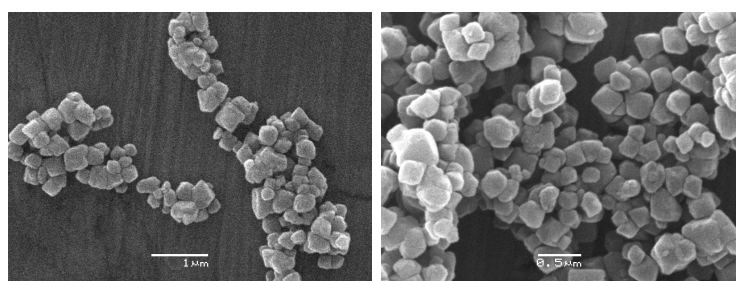
Table S4: Relative integration of signals assigned to both linkers and calculated experimental molar proportion of the functionalized linker ( $\%_{func}$ ).

Samples	Signal at 7.7 ppm	Signal at 8.0 ppm	$\%_{func}$ (%)
MIL-101(Cr)	1.00	0	0
10%NH <sub>2</sub> -MIL-101(Cr)	33.2	1.05	11.2
20%NH <sub>2</sub> -MIL-101(Cr)	16.5	1.06	20.4

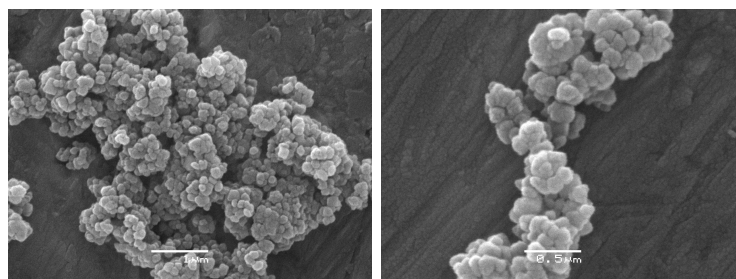
## S5. Scanning Electron Microscopy



(a)



(b)



(c)

Figure S2: SEM images of the samples (a) MIL-101(Cr), (b) 10%NH<sub>2</sub>-MIL-101(Cr), and (c) 20%NH<sub>2</sub>-MIL-101(Cr).

## S6. Molecular Modeling

Molecular modeling was performed using a modified MM+ molecular mechanics force field implemented in HyperChem Professional 8.0<sup>1</sup>, and the structures were optimized with a conjugate gradient using a  $10^{-2}$  kcal mol<sup>-1</sup> Å<sup>-1</sup> criterium for convergence. The inclusion of parameters was necessary to reproduce the geometry of the  $[\text{Cr}_3\text{O}(\text{RCO}_2)_6(\text{H}_2\text{O})_x]$  units, specially the characteristic triangular geometry of the  $\mu_3$ -oxo bridge.

We have constructed the geometries of two different pores found in the unit cell of MIL-101(Cr) as reported by Férey *et al*<sup>2</sup> with a general composition equal to  $[\text{Cr}_3\text{O}(\text{RCO}_2)_6(\text{H}_2\text{O})_3]_x$  in which  $\text{RCO}_2 = \text{terephthalate}$ . The use of three water molecules in place of two water and one fluoride as terminal ligands was used to decrease the number of parameters to be included in the force field. The larger pore modeled reproduces the structure with hexagonal windows (Figure S3) and the other one reproduces the pore with pentagonal windows (Figure S4). The modeled structures are composed of 42 and 30  $\text{Cr}_3\text{O}$  units, respectively.

Inclusion of  $-\text{NH}_2$  groups was made in opposing terephthalate bridges and the structures were reoptimized. For all structures, pore sizes were calculated from the distances of opposing groups, i.e. in MIL-101(Cr) the distances from the *ortho* hydrogens of symmetrically opposing terephthalate groups was used, and for the amine tagged pores, the distance from the  $-\text{NH}_2$  hydrogens pointing inside the pore.

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<sup>1</sup>Hypercube, Inc. 1115 NW 4th 2006, 56, 167. St. Gainesville, FL 32601, USA.

<sup>2</sup>G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, 309, 2040–2042.



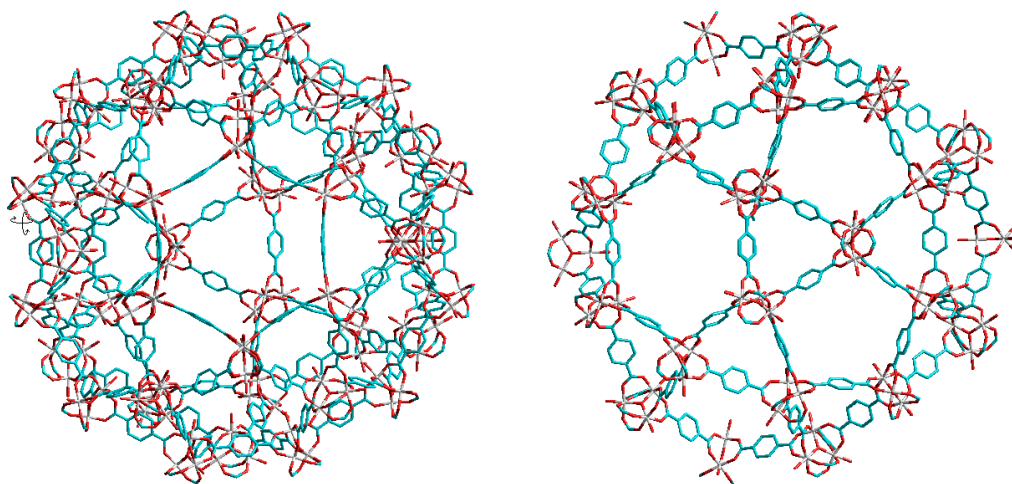


Figure S3: Two views of the structure obtained for the larger pore of MIL-101 with hexagonal windows through two different  $C_3$  axes. The structure is composed of 42  $Cr_3O$  units and hydrogens and terminal therephthalates were omitted for clarity.

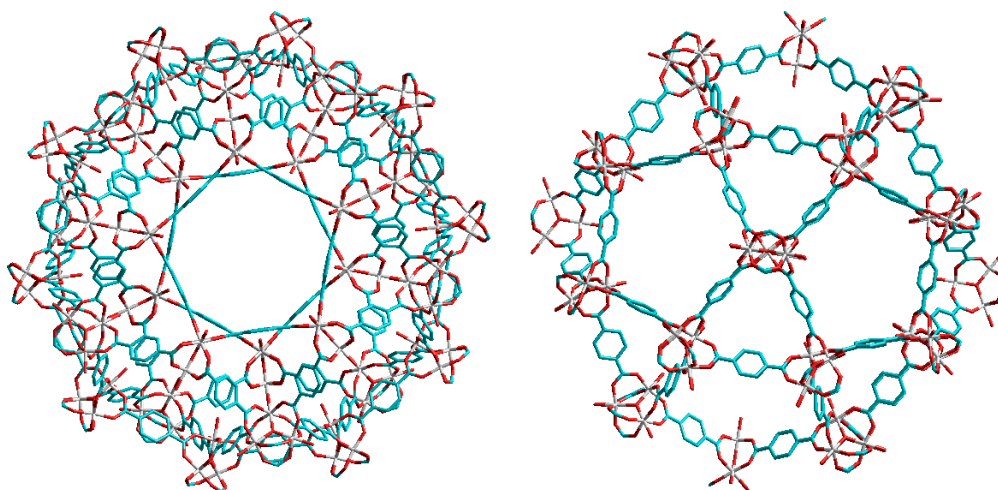


Figure S4: Two views of the structure obtained for the pore of MIL-101 with pentagonal windows. Through one of the  $C_5$  axes (left) and through one of the  $C_2$  axes (right). The structure is composed of 30  $Cr_3O$  units and hydrogens and terminal therephthalates were omitted for clarity.