Electronic Supporting Information

A lithium organic framework with coordinatively unsaturated metal sites that reversibly binds water by Racha El Osta, Michel Frigoli, Jérôme Marrot, Nathalie Guillou, Hubert Chevreau, Richard I. Walton and Franck Millange*

S1: Experimental Details

A number of X-ray diffraction methods were used to characterize the solid.

A single crystal of MIL-145(Li)[DMF] or $Li_4[C_{12}H_6N_2(CO_2)_4].(C_3H_7N_1O_1)_2$ was carefully selected, mounted onto a cryoloop with the viscous oil-drop method for the structure determination by X-ray diffraction. The X-ray data were recorded at room temperature on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector (monochromated Mo Kα radiation). Slightly more than one hemisphere of data was collected. The frames were recorded with a scan width of 0.3° in ω and an exposure time of 60 s. Data reduction was performed with SAINT software. Data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction based on symmetry equivalent reflections was applied by using SADABS program [1] based on the method of Blessing [2]. The structure was solved by direct methods (SHELXS) in the triclinic space-group P-1 and refined by full-matrix least-squares based on F^2, using the SHELX-TL package [3]. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom). The terminal DMF coordinated molecules were found highly disordered in this structure (large displacement parameters for these atoms) so some constraints have to be applied during the refinement process.

Crystal structure analysis of MIL-145(Li)[DMF]: triclinic, space group *P*-1; dimensions $a = 9.666(4)$ Å, $b = 11.692(5)$ Å, $c = 12.366(5)$ Å, $\alpha = 72.750(9)°$, $\beta = 67.912(8)°$, $\gamma = 76.869(9)°$, $V = 1226.0(8)$ Å^3; $Z = 2$; total reflections collected: 6740; independent reflections: 4296 (3057 $Fo > 4\sigma(Fo)$); a hemisphere of data was collected up to a 2Θmax value of 50° (99.7 % coverage). Number of variables: 384; $R_1 = 0.0724$, $wR_2 = 0.2212$ (all: 0.0977 – 0.2383), S = 1.164; the final difference map displayed no peaks of chemical significance ($\Delta\rho_{max} = 0.79$, $\Delta\rho_{min} = -0.72$ e.Å^{-3}).

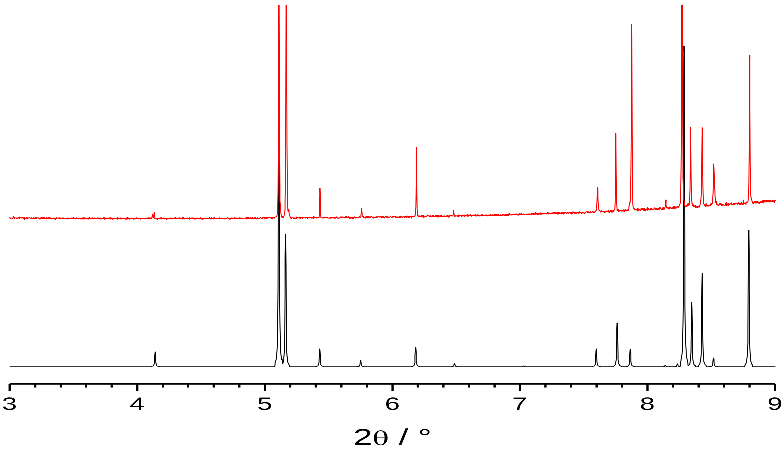

Figure S1: Zoom on the low part angle X-ray diffraction data showing the good agreement between the simulated powder pattern from single crystal data (black) and the experimental powder pattern recorded at ESRF on ID31 (λ ~0.8 Å).

Additionally, for the newly activated anhydrous form of MIL-146(Li) or $Li_4[C_{12}H_6N_2(CO_2)_4]$ and activated rehydrated form of MIL-146(Li)[H_2O] or $Li_4[C_{12}H_6N_2(CO_2)_4].(H_2O)_2$, high-resolution powder X-ray diffraction data were collected on the station ID31 at the ESRF from polycrystalline samples contained in 1 mm diameter quartz capillaries. The beam line receives X-rays from the synchrotron source (which operates with an average energy of about 6 GeV and a current beam of typically 100 mA) from an undulator device. The incident X-ray wavelength was 0.79989 Å using an incident beam size of 2.0 mm (horizontal) × 1.0 mm (vertical). The sample was rapidly spun during data collection in order to minimize preferred orientation effects. However, it was not enough since the sample was ground too gently in order to avoid crystallinity damages. Therefore, spherical harmonics were applied for performing preferred orientation correction. For MIL-146(Li), a primitive triclinic cell (a = 5.1830(2) Å, b = 9.3317(4) Å, c = 9.3808(2) Å, α = 104.6941(8)°, β = 95.342(2)°, γ =105.979(8)°, V = 415.39(3) Å^3) was found with very good figure of merit of M_{20} = 201. A similar result was also found for MIL-146(Li)[H_2O] (a = 5.04833(7) Å, b = 9.4401(2) Å, c = 9.3335(2) Å, α = 102.271(1)°, β = 94.1868(9)°, γ = 104.625(1)°, V = 416.77(1) Å^3 and M_{20} = 86.

Extractions of the peak positions, pattern indexing, structural determinations and Rietveld refinements were carried out with the TOPAS program [4]. In both cases, the tetracarboxylate ion was treated as rigid body and its position was determined by simulated annealing. The structural models were completed by difference Fourier calculations.

The final Rietveld plots correspond to satisfactory crystal structure model indicator (R_B = 0.034, 0.033) and profile factors (R_P = 0.066, 0.093 and R_{WP} = 0.054, 0.073) for MIL-146(Li) and MIL-146(Li) [H_2O] respectively.

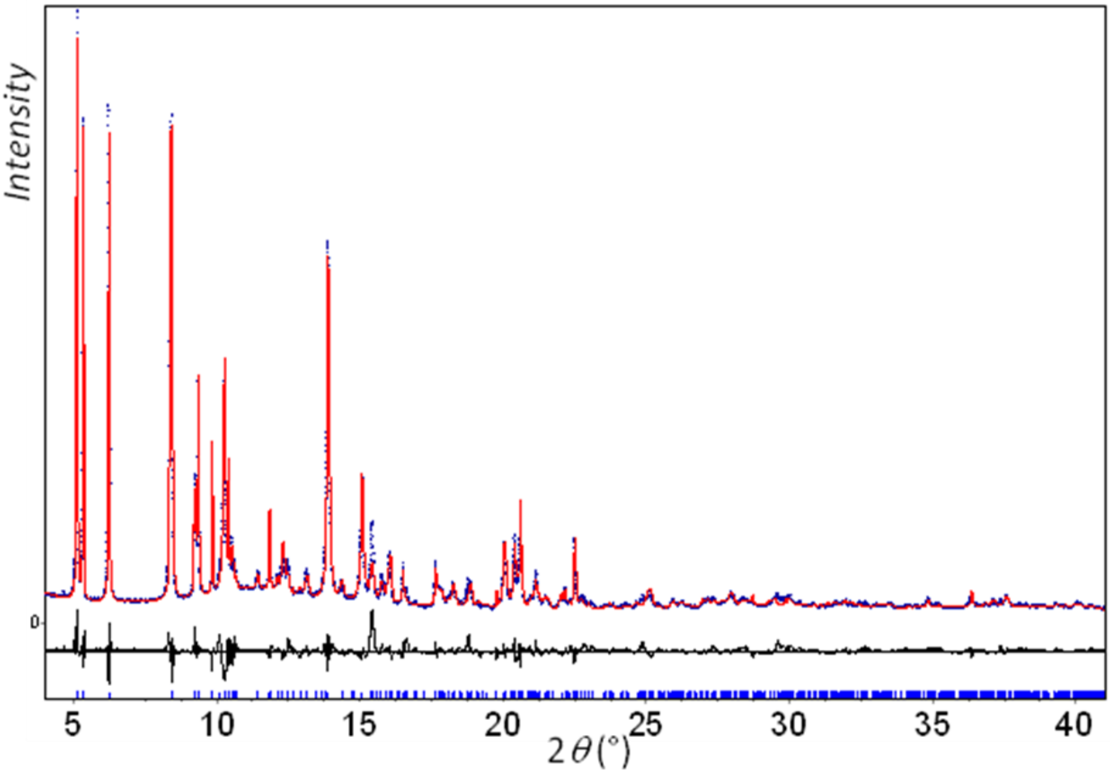

Figure S2: Final Rietveld plot of MIL-146(Li).

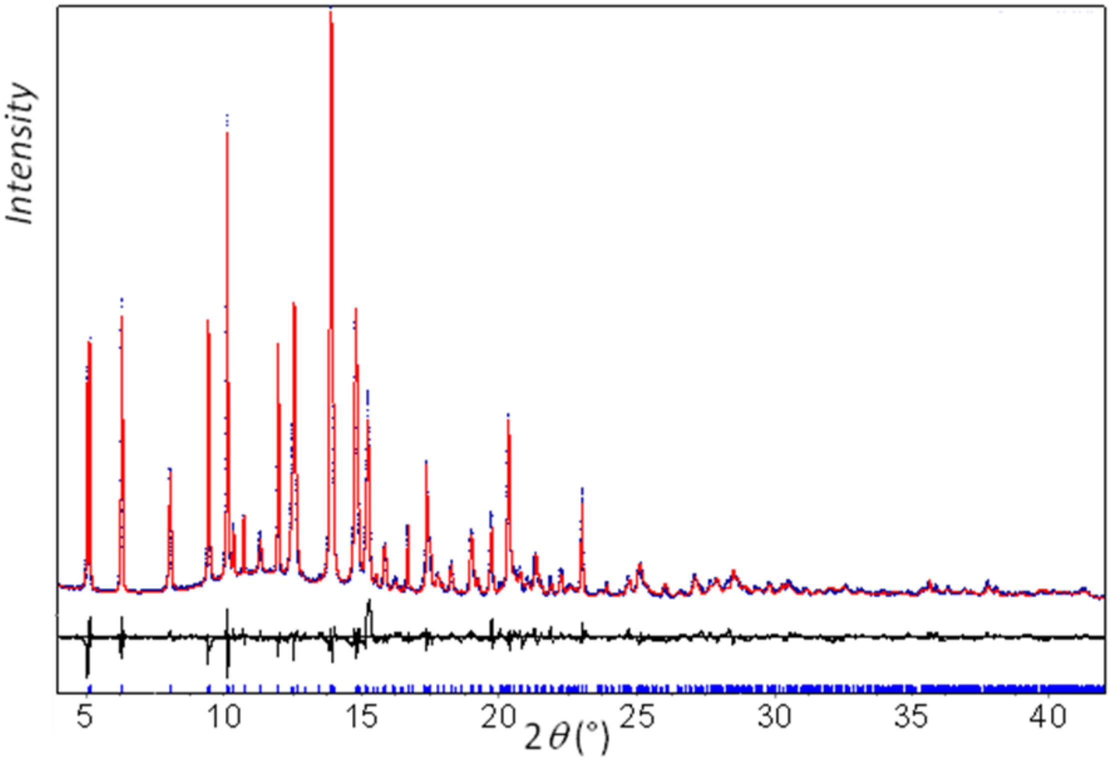

Figure S3: Final Rietveld plot of MIL-146(Li)[H_2O].

Temperature-dependent X-ray powder diffraction measurements were performed using a Siemens D5000 diffractometer (θ-θ mode, Co K_α radiation and a PSD) equipped with an Anton Paar HTK1200 high-temperature device under a N_2 atmosphere.

S2: Analysis of MIL-145(Li)[DMF]

Thermogravimetric analysis of MIL-145(Li)[DMF] shows two weight losses of 26.58 % (cal: 27.68%) below 443 K and 44.72 % (cal: 44.34%) above 723 K corresponding to the departure of the coordinated DMF molecules and the bound tetracarboxylic acid, respectively, ultimately leading to decomposition of the phase.

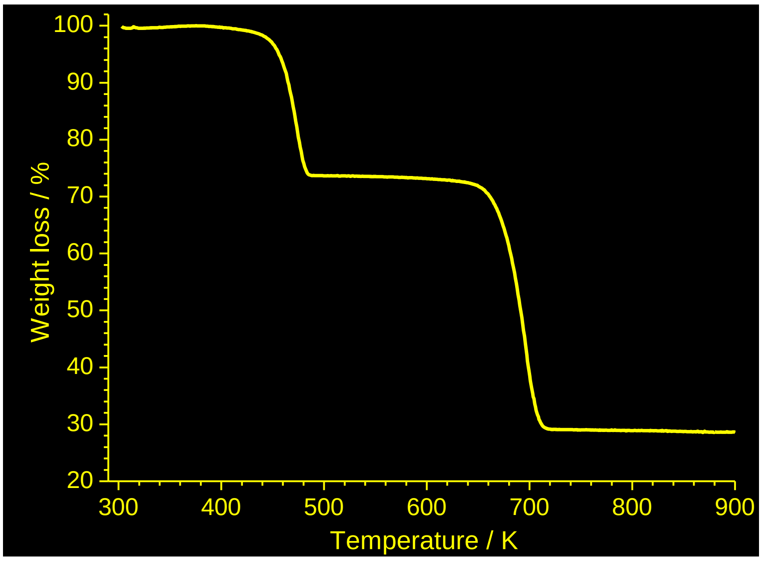

Figure S4: TGA trace of MIL-145(Li)[DMF].

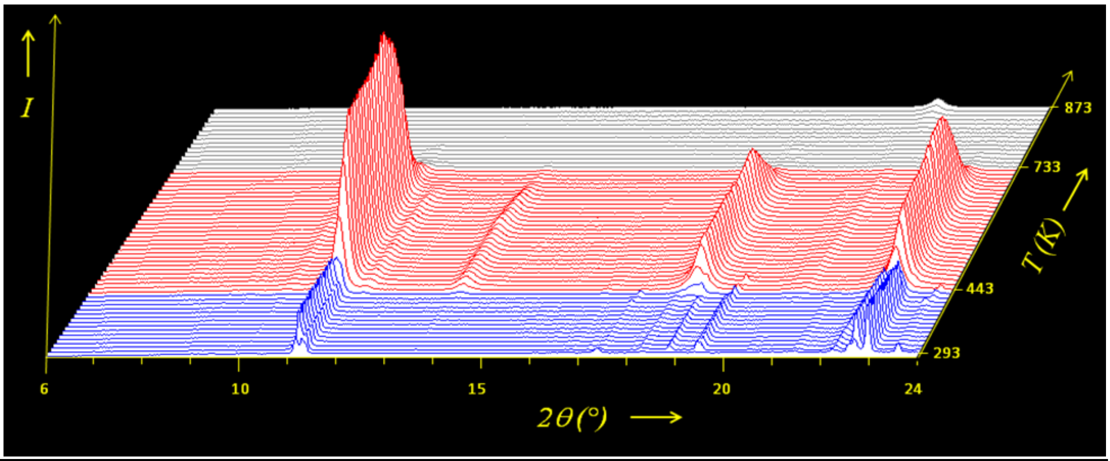

Figure S5: Thermodiffraction (bottom) recorded during the heating of MIL-145(Li)[DMF] showing the departure of the coordinated DMF molecules at 443 K (blue lines) leading to an irreversible phase transition and giving rise to the anhydrous phase MIL-146(Li) (red lines) followed by the destruction of the framework at ~723 K (grey lines).

The infrared spectrum of MIL-145(Li)[DMF] clearly shows the presence of the vibrational bands characteristic of the –(O–C–O)– groups confirming the presence of the carboxylate within the solids. The absence of OH and/or H_2O groups in MIL-145(Li)[DMF] has been also confirmed (no bands around 3500 cm^{-1}). Other characteristic bands of the C-C, C–H and C-N vibrations have also been observed.

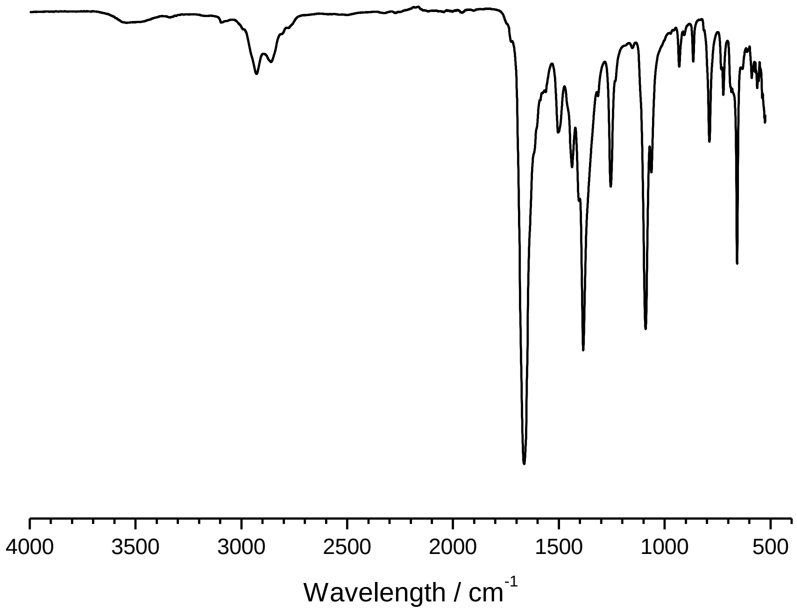

Figure S6: IR spectrum of MIL-145(Li)[DMF].

S3: Analysis of MIL-146(Li) and MIL-146(Li)[H_2O]

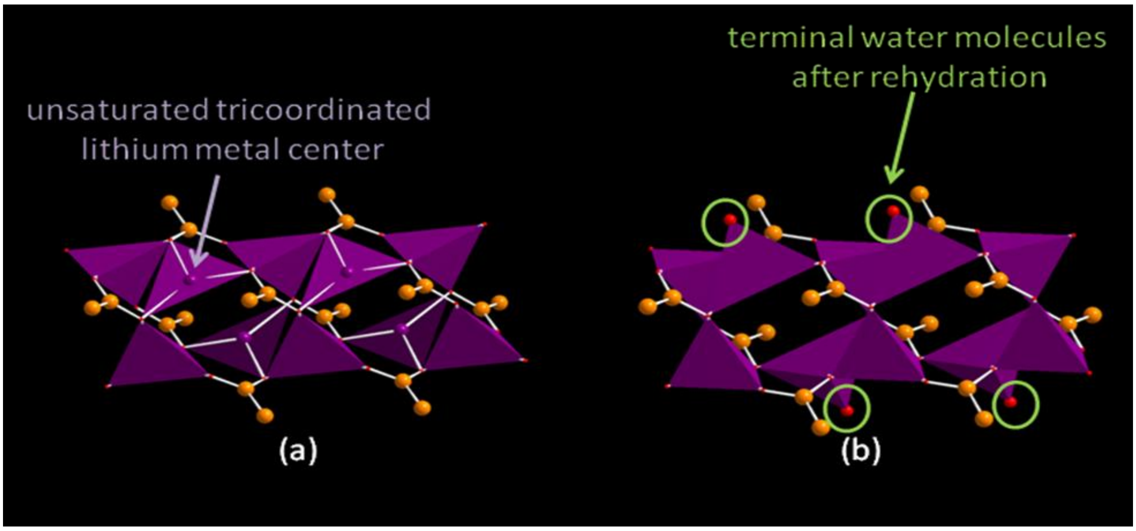

Figure S7: Connectivity seen in the lithium-organic frameworks MIL-146(Li) (left) showing the unsaturated tricoordinated lithium metal center and the terminal water molecules after rehydration in MIL-146(Li)[H_2O] (right).

Thermogravimetric analysis of MIL-146(Li)[H_2O] shows two weight losses of 7.72 % (cal: 8.62%) below 363 K and 56.64 % (cal: 56.03%) above 723 K corresponding to the departure of the water molecules and the bound tetracarboxylic acid, respectively, ultimately leading to decomposition of the phase.

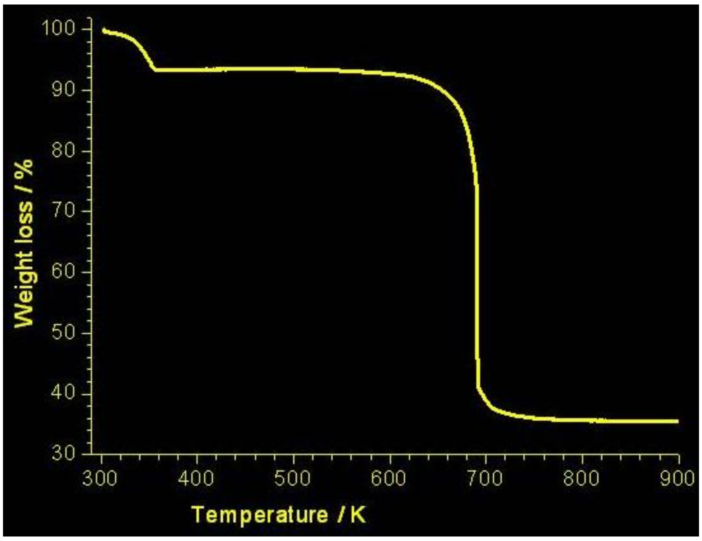

Figure S8: TGA trace of MIL-146(Li)[H_2O].

S4: Low temperature CO_2 Sorption of MIL-146(Li)

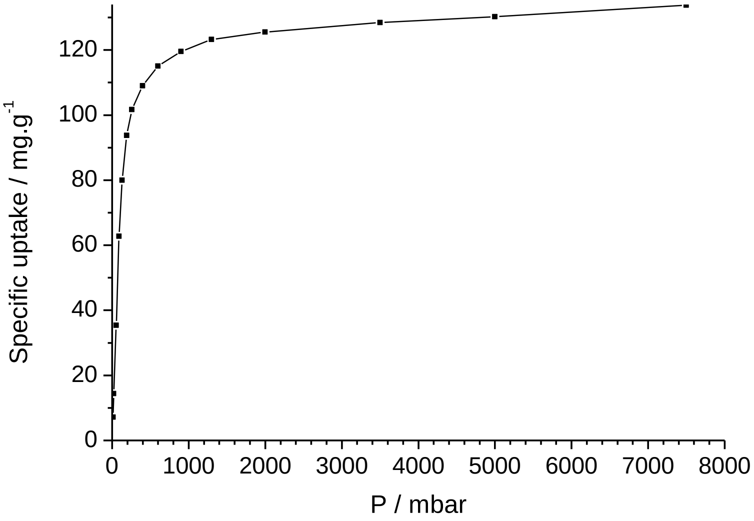

Figure S9: High pressure gravimetric excess of CO_2 isotherm of the MIL-146(Li) material at 233 K.

[1] G.M. Sheldrick, SADABS, a program for the Siemens area detector absorption correction, University of Göttingen, Göttingen, 1994.

[2] R. Blessing, Acta Crystallogr. A 51 (1995) 33.

[3] G.M. Sheldrick, SHELXTL Version 5.03, software package for the crystal structure determination, Siemens analytical X-ray instruments inc., Madison, WI, 1994.

[4] *TOPAS V4.2: General Profile and Structure Analysis Software for Powder Diffraction Data*; Bruker AXS Ltd: Madison, WI, 2004.