The Mesoporous Metal-Organic Framework MIL-101 at High-Pressure

Supplementary Information

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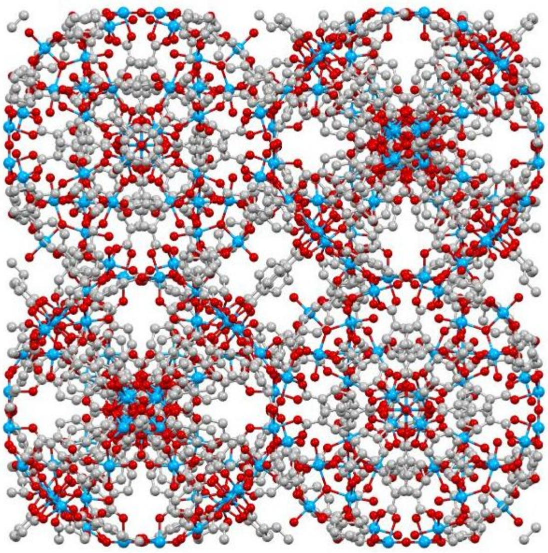


Figure S1. One-fourth of MIL-101 unit cell (space group $Fd\overline{3}m$). Chromium atoms are depicted in light-blue, oxygens in dark-red and carbons in grey. Hydrogens are hidden for sake of clarity.

The synthesis process of MIL-101 can be resumed as follows. The reaction mixture, obtained from terephthalic acid (98 wt.%) and $CrCl_3 \cdot 6H_2O$ (96 wt.%) and water, in ratio 1:1:500, was loaded into a TFE pot which was placed in a stainless-steel autoclave. Then, the autoclave was placed in an electric oven and heated at a temperature of 190°C for 16 hours, with a heating ramp of 6h. After cooling, the resulting solid (green) was separated by filtration and dried at room temperature. For activation the as-synthesized MIL-101 was heated in ethanol under reflux for 72 hours. The activated sample was filtered and dried at 150^{o}C. The textural properties of samples were estimated from nitrogen adsorption/desorption isotherms at 77.3 K using a Sorptomatic 1990 (Thermo Electron Corporation) apparatus. Each sample was degassed at 220°C for 18 hours under dynamic vacuum before measurement. The Brunauer-Emmett-Teller (BET) surface area (SBET) was calculated using the multiple-point method in the relative pressure range p/p_0 of 0.02-0.25. The specific pore volume was determined according to Gurvich's rule at p/p_0 of 0.95. The pore size distribution, shown in Fig. S2, has been calculated from nitrogen adsorption/desorption isotherms data using the software of the AutoSorb IQ instrument from Quantachrome, which is based on the Quenched Solid Density Functional Theory.

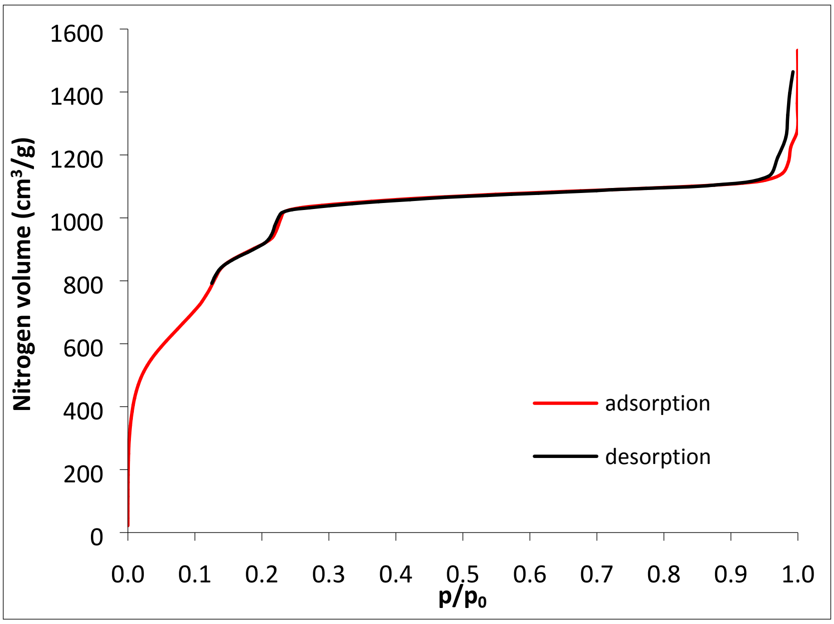


Figure S2. N_2 adsorption and desorption curves of MIL-101.

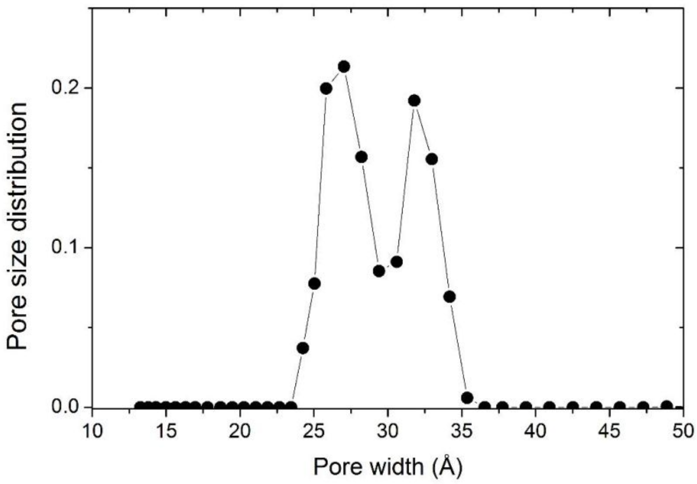


Figure S3. Pose size distribution of MIL-101 calculated from nitrogen adsorption/desorption isotherms data.

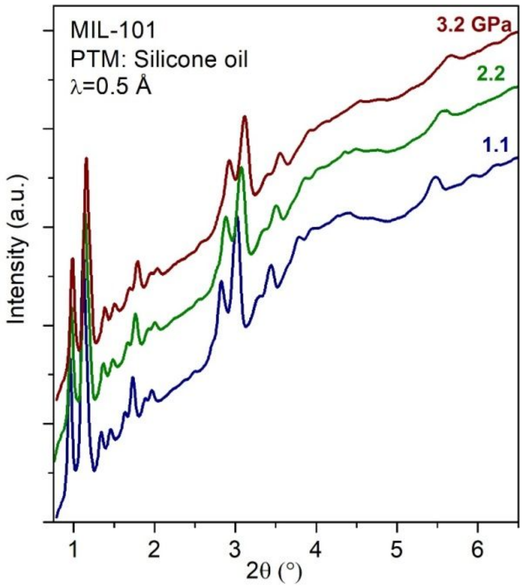


Figure S4. Preliminary X-ray diffraction patterns of MIL-101 under compression with silicone oil as PTM collected at the Xpress beamline in ELETTRA. In this case, sample was exposed to air during loading inside the DAC.

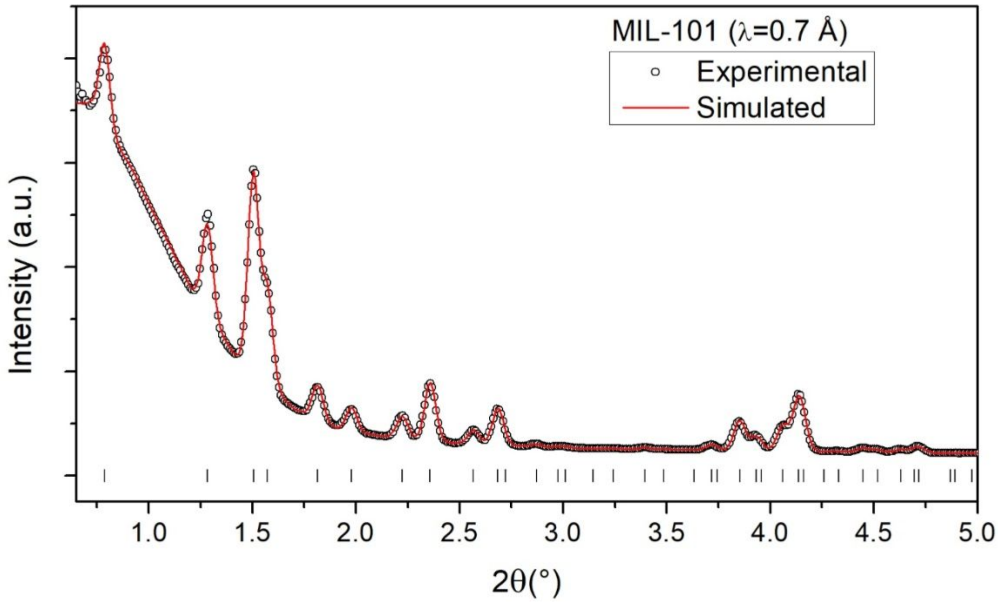


Figure S5. Measured and simulated X-ray diffraction pattern for MIL-101 inside a capillary. The simulated pattern has been obtained through a Le Bail structural refinement.

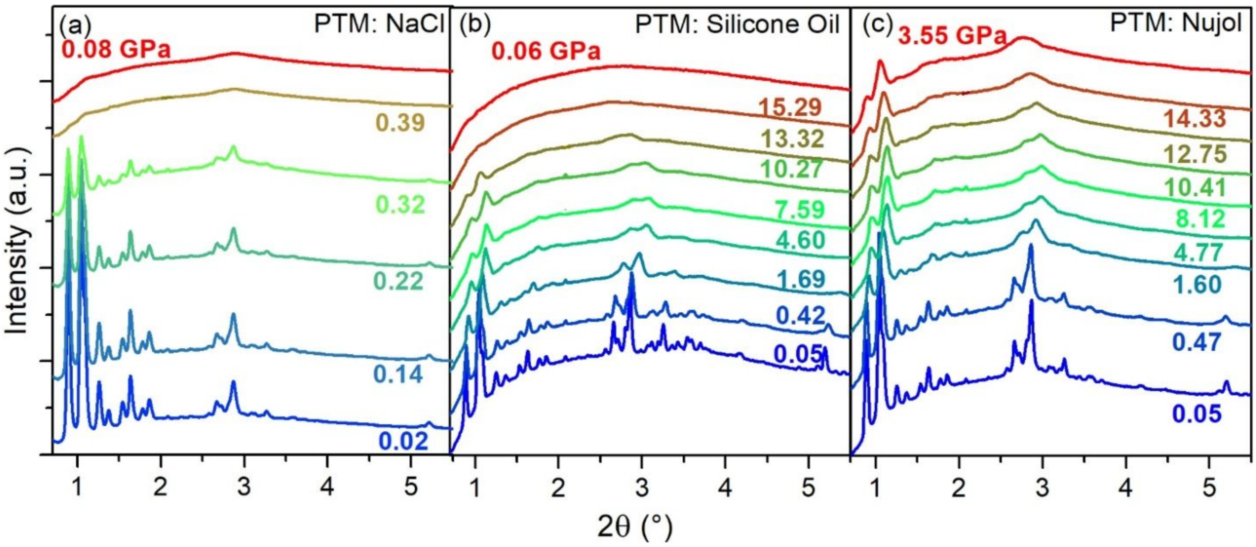


Figure S6. X-ray diffraction patterns *(λ=0.48593 Å)* of MIL-101 under compression with (a) NaCl, (b) Silicone Oil and (c) Nujol as PTM. Patterns collected when the pressure was released are shown in red.

X-ray diffraction patterns of the MIL-101 under pressure without pressure transmitting medium are shown in Fig. S6. The measurements have been performed on the PSICHE beamline at the SOLEIL Synchrotron with a 0.3738 Å X-ray beam and using Au as pressure gauge.

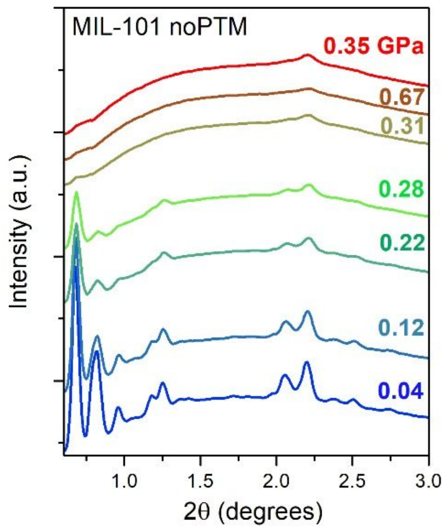


Figure S7. X-ray diffraction patterns (λ=0.3738 Å) of MIL-101 under compression without any pressure transmitting medium. Pattern collected when the pressure was released is shown in red.

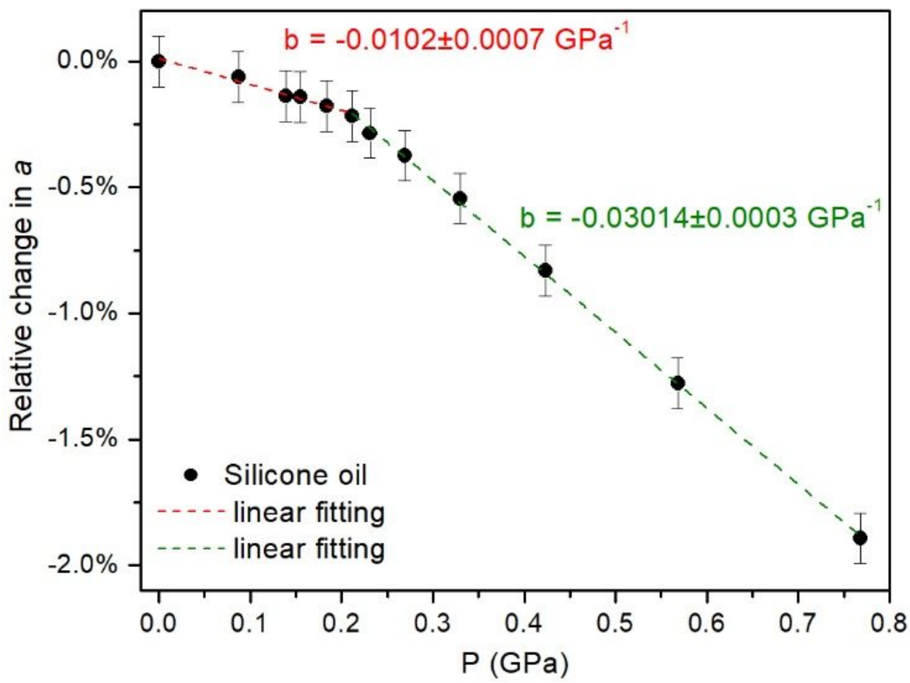


Figure S8. Linear fit of the relative change in the lattice parameter *a* when silicone oil is used as PTM.

Bulk moduli have been calculated for MIL-101 with silicone oil and Nujol using a second-order Birch-Murnaghan equation-of-state. Values obtained are listed in table S1 and the equations-of-state modeled to the data are shown in Fig. S8-S10. However, since we clearly demonstrated the PTM hyperfilling the MIL-101 pores, the obtained bulk moduli reflect the response of a hybrid material (MIL-101 + polymer), thus it is not characteristic of pure MIL-101.

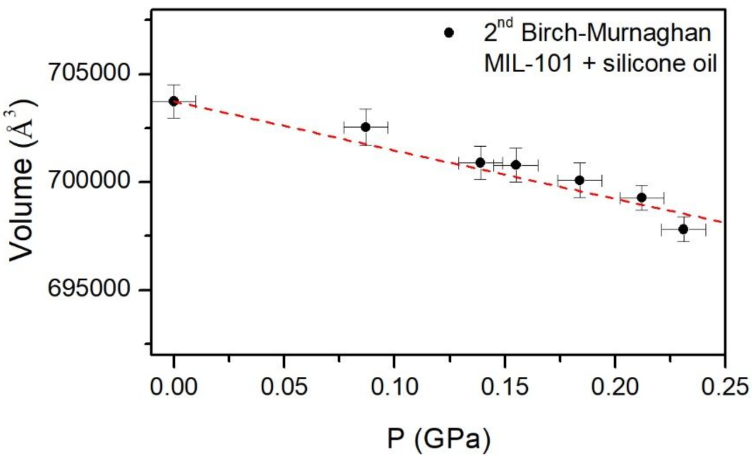


Figure S9. Unit cell volume of MIL-101 in the 0-0.25 GPa pressure range when silicone oil is used as PTM. Dashed line represents the second-order Birch-Murnaghan equation-of-state fit to the experimental points.

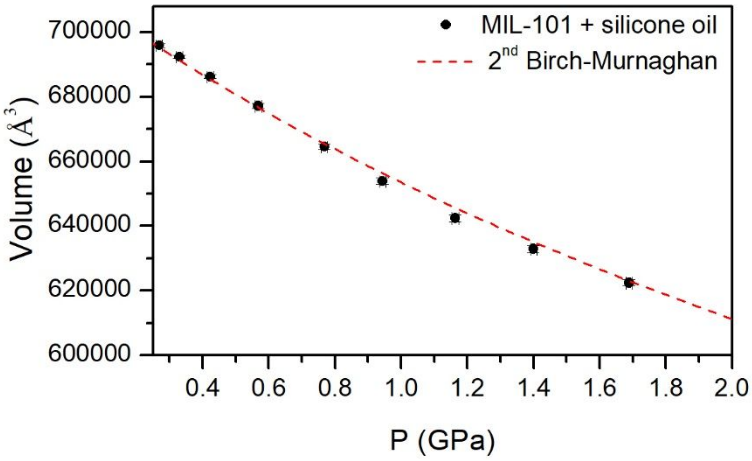


Figure S10. Unit cell volume of MIL-101 in the 0.25-2.0 GPa pressure range when silicone oil is used as PTM. Dashed line represents the second-order Birch-Murnaghan equation-of-state fit to the experimental points.

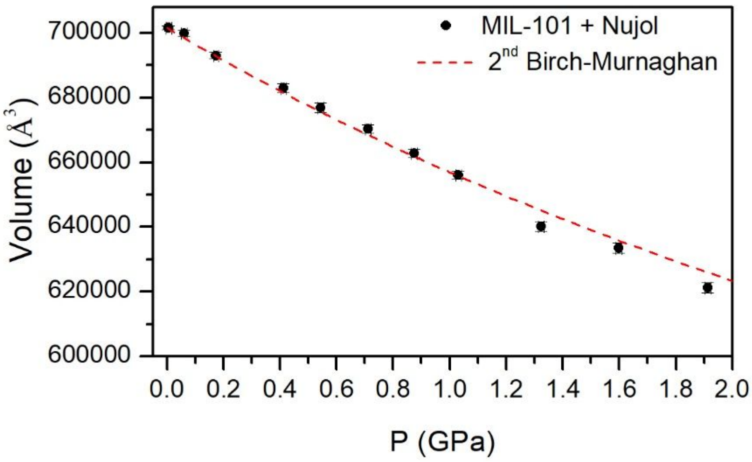


Figure S11. Unit cell volume of MIL-101 in the 0-2.0 GPa pressure range when Nujol is used as PTM. Dashed line represents the second-order Birch-Murnaghan equation-of-state fits to the experimental points.

Table S1. Summary of the values of the bulk moduli for different PTM as obtained by a second order Birch-Murnaghan equation-of-state.

PTM	Pressure range (GPa)	Bulk modulus (GPa)
Silicone oil	0 0.25	31±2
Silicone oil	0.25 2.0	9.4±0.4
Nujol	0 2.0	13.4±0.2

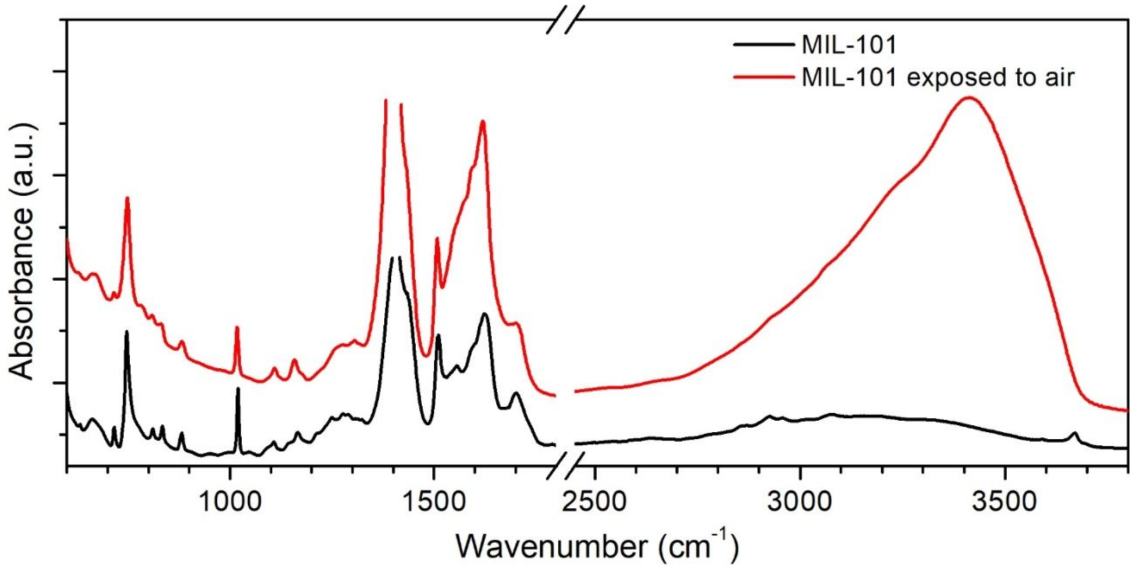


Figure S12. Infrared spectra of MIL-101 in controlled atmosphere (black) and after about 5 minutes of air exposure (red).

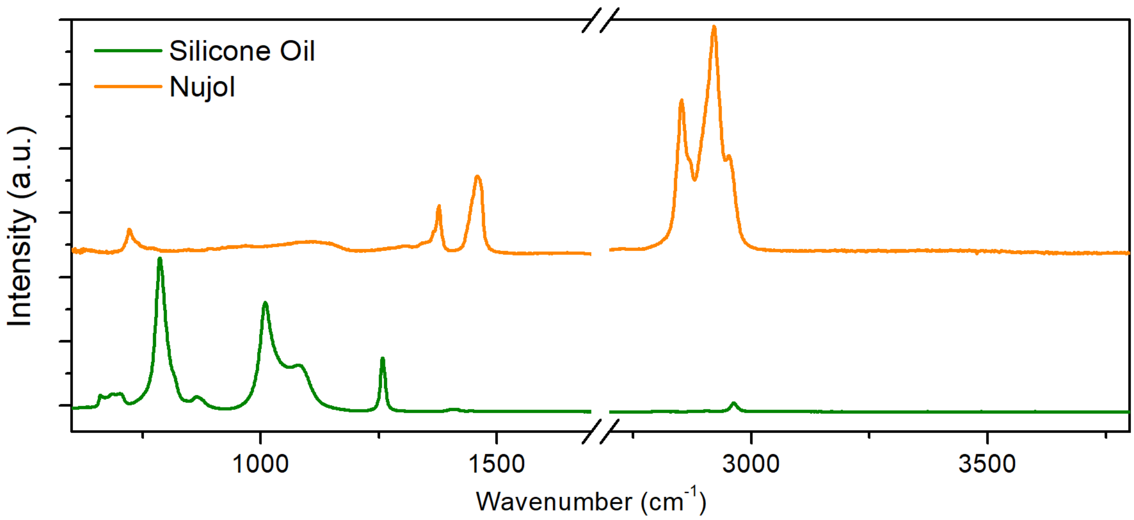
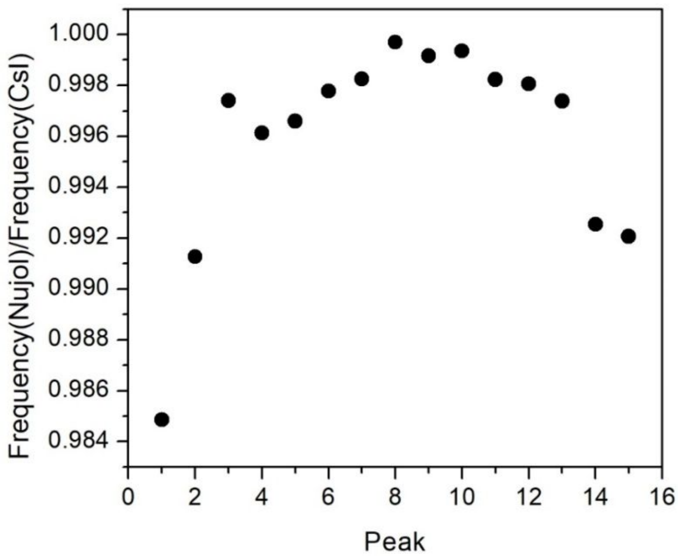


Figure S13. Infrared spectra of silicone oil (green) and Nujol (orange).



PTM: CsI

Peak frequency (cm^{-1})

1	388.12192
2	588.81222
3	715.84479
4	746.9465
5	811.07498
6	834.29333
7	881.9739
8	1019.9677
9	1108.054
10	1166.5831
11	1510.6654
12	1555.4172
13	1595.9505
14	3590.51
15	3669.543

Figure S14. Frequency shift of the main IR peak of MIL-101 with Nujol relative to the MIL-101 with CsI. Peak frequencies measured when CsI is used as PTM are listed in the table.

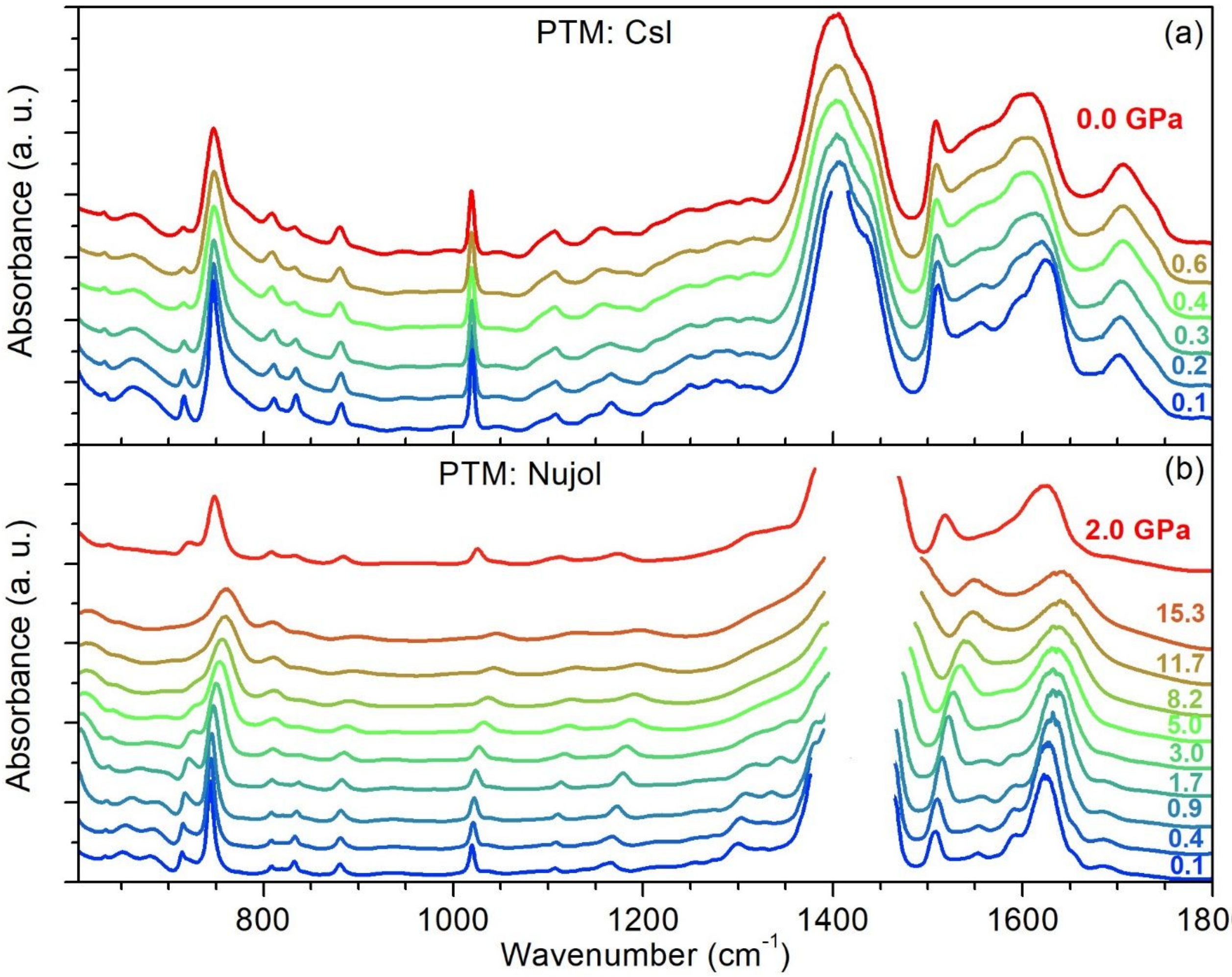


Figure S15. MIR spectra of MIL-101 increasing the pressure with (a) CsI and (b) Nujol used as PTM. Spectra collected when the pressure was released are shown in red.