Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Single particle Raman spectroscopy analysis of the Metal-Organic Framework DUT-8(Ni) switching transition under hydrostatic pressure

Alexander Krylov,[a]* Irena Senkovska,[b]* Sebastian Ehrling,[b] Mariia Maliuta,[b] Svetlana Krylova,[a]
Evgenia Slyusareva,[c] Alexander Vtyurin[a,c], Stefan Kaskel,[b]

[a]*Kirensky Institute of Physics, Federal Research Center KSC SB RAS, 660036 Krasnoyarsk, Russia*

[b]*Chair of Inorganic Chemistry I, Technische Universität Dresden, Bergstrasse 66, 01069 Dresden, Germany*

[c]*Siberian Federal University, Svobodny Prospect 79, 660041 Krasnoyarsk, Russia*

General Information

Powder X-ray diffraction (PXRD) experiments at room temperature were carried out using STOE STADI P diffractometer with Cu Kα1 radiation (λ = 1.54059 Å) and a 2D detector (Mythen, Dectris) in transmission geometry. Pawley refinements of as made and activated phases were performed using FullProf software.[1, 2]

Sample synthesis and characterisation

The samples were synthesized according to the procedures reported in reference 3. The crystallinity and the phase purity of the synthesized samples were confirmed by powder X-ray diffraction (Fig. S1). To obtain the desolvated DUT-8(Ni)_compound (*cp*), the as-made DUT-8(Ni) was washed with DMF several times, the solvent was exchanged to DCM, and the sample was dried at 120 °C in dynamic vacuum overnight. The porosity and switching ability for desolvated material were confirmed by nitrogen adsorption at 77 K.

High hydrostatic pressure Raman spectroscopy

The spectra in backscattering geometry were recorded on a Horiba Jobin-Yvon T64000 spectrometer equipped with an LN cooled charge-coupled device detection system in subtractive dispersion mode. Ar$^+$ ion laser Spectra-Physics Stabilite 2017 with = 514.5 nm and power of 2 mW on a sample was used as an excitation light source. During experiments, an incident laser beam focused on the sample by a 50x Olympus objective lens with a numerical aperture of 0.35 and a working distance of 18 mm. The scattered light was collected by the same objective lens. The deformation of the low-wavenumber spectral edge by an optical slit, that sometimes smears the true features of low-wavenumber spectra, was carefully eliminated by rigorous optical alignment, which attained a low-wavenumber limit of 10 cm^{-1} in the present setup. The lines of recorded Raman spectra had a very well definite shape, so the standard fitting procedure for accruing quantitative spectral lines parameters was carried out with Lorentz function.

The gas membrane-driven diamond anvil cell (DAC) device Diacell µScope DAC HT(G) type (EasyLab, UK) with IIa diamond Diacell design with 500 µm culets was used for Raman study of processes under high hydrostatic pressure. A stainless-steel gasket with an initial thickness of 0.25 mm is used in this DAC. Holes with a diameter of about 200 – 220 µm were drilled in the gaskets pre-indented to a thickness about 84 µm, for measuring at pressures up to

1 GPa by electro-discharge-machine Boehler µDriller (EasyLab, UK). The pressure was monitored by the shift of the $^5D_0$–$^7F_0$ fluorescence band of Sm^{2+} ion in a small SrB_4O_7:Sm^{2+} crystal placed in the vicinity of the sample. The pressure determination experimental error was about 0.02 GPa. Methanol and silicone oil (CAS: 63148-58-3 AP 100) were used as hydrostatic pressure transmission media. The cell was pressurized to 0.05 GPa (for silicone oil) or 0.1 GPa (for methanol) initially and was allowed to stabilize for 2 hours before data acquisition. During experiments after increasing pressure at least 30 minutes was delayed to stabilize the pressure in the DAC (Figures S2, S3).

We performed multiple scans measurement (124 in total) and integration to estimate the uncertainty of measurement and integration, which amount to ±0.6 %.

To calculate the phase fractions, the integration of the peaks centred around 23 and 59 cm^{-1} (to obtain the peak areas A and B, correspondingly) was performed by PeakFit software[4] after the baseline subtraction. The sums of the integrals were scaled to 100%. The *op* and *cp* phase fractions (ω) were calculated as the contributions of the individual peak areas:

$$\omega(A) = \frac{A}{A+B}100\%; \ \omega(B) = \frac{B}{A+B}100\% \ ;$$

The overall relative uncertainties (ΔY) shown in Fig. 3. were estimated as follows:[5]

$$\Delta Z = \sqrt{(\Delta A)^2 + (\Delta B)^2}$$

$$\Delta Y = Y(\sqrt{(\frac{\Delta B}{B})^2 + (\frac{\Delta Z}{Z})^2})$$

Where ΔA and ΔB are standard errors for peak areas calculation.

a)

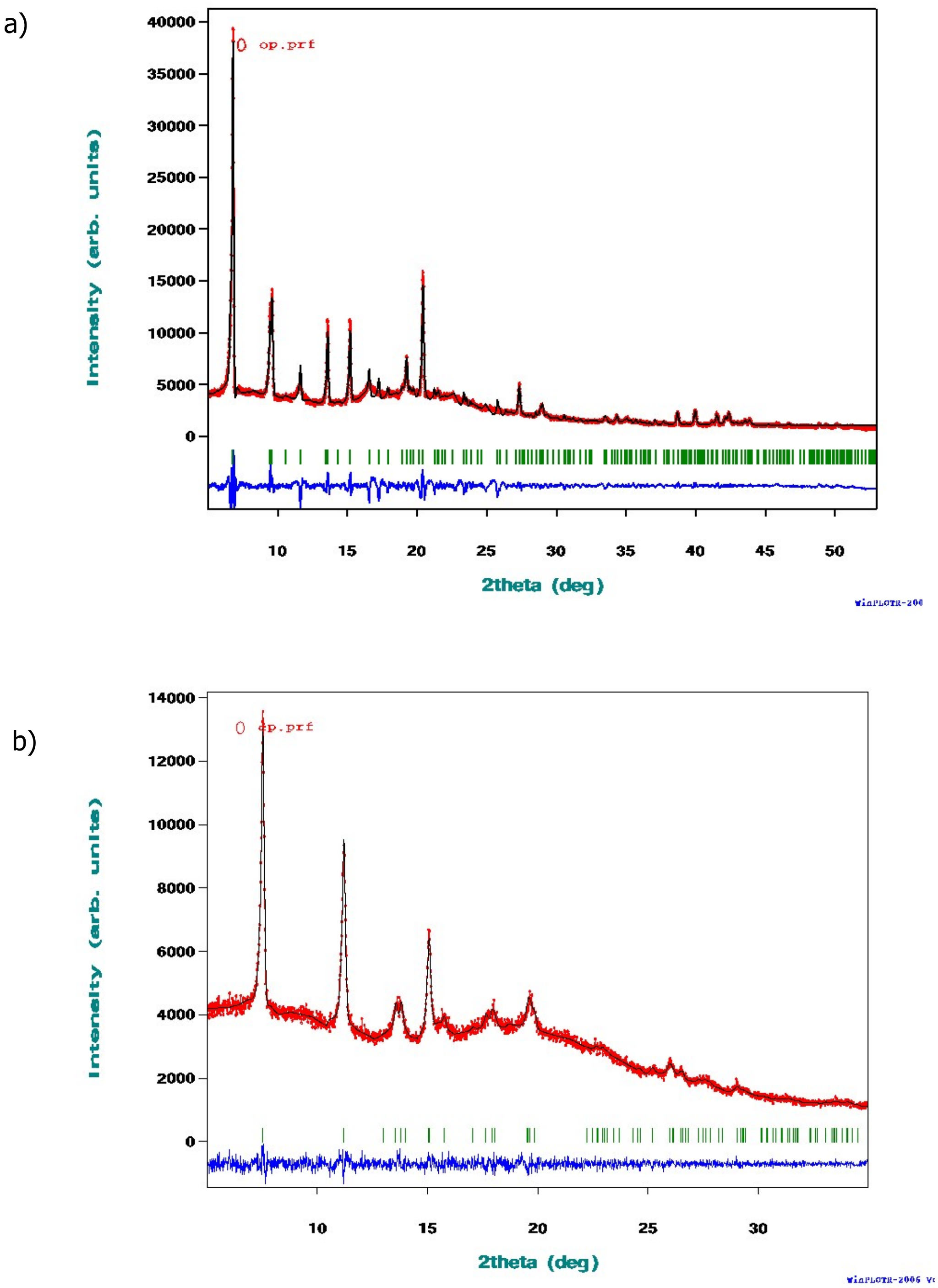

Figure S1. a) Pawley refinement plot for DUT-8(Ni)_*op sample*; b) Pawley refinement plot for DUT-8(Ni)_*cp* sample.

Table S1: Pawley refinement data.

	DUT-8(Ni)_*op*	DUT-8(Ni)_*cp*
Temperature / K	298 K	298 K
Wavelength / Å	1.5406	1.5406
Measurement system	STADI P (Stoe)	STADI P (Stoe)
Geometry	Debye-Scherrer	Debye-Scherrer
Crystal system	tetragonal	Triclinic
Space group	*P*4/*n*	*P*1
Unit cell dimensions / Å	*a* = 18.43812(48)	*a* = 6.96941(88)
	c = 9.37530(38)	*b* = 8.20443(74)
		c = 12.12632(96)
		α = 90.90965(1933)
		β = 103.41308(1483)
		γ = 105.02245(1497)
2θ range / °	5 - 53	5 – 35
Final R indices:		
Rp; Rwp	6.28; 9.00	2.80; 3.54
Profile function:	Thompson-Cox-Hastings	Thompson-Cox-Hastings
Final profile parameters:		
FWHM		
U:	0.03016	0.28143
V:	-0.01160	0.02273
W:	0.00169	0.00920 ± 0.00088
X:	0.10732	0.03271
Y:	0.13539	0.10199 ± 0.00273

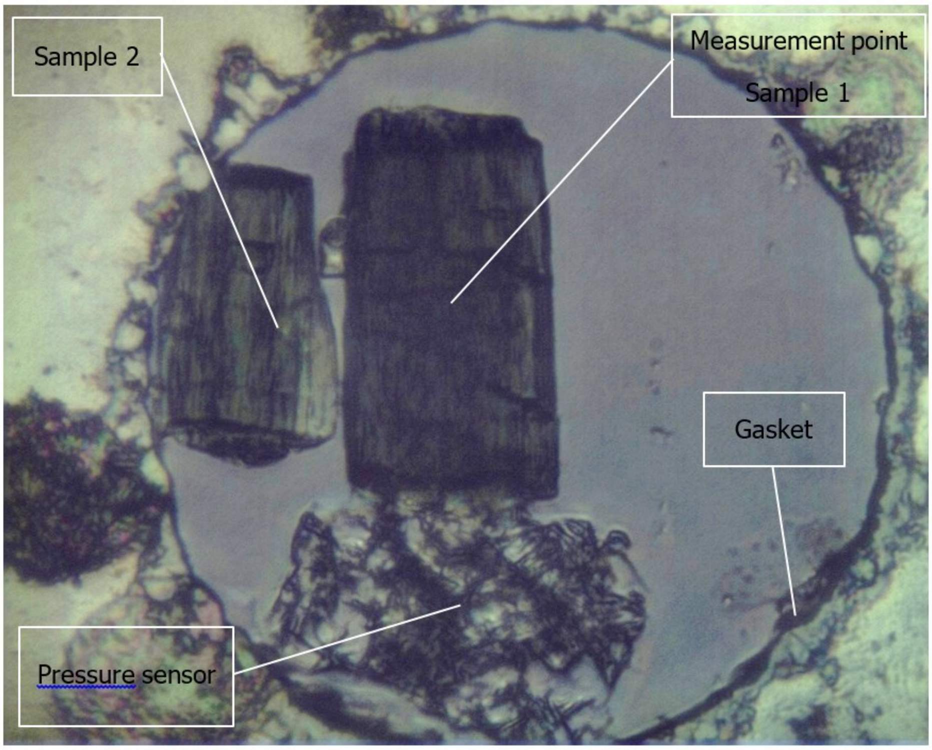

Figure S2. Two crystals and pressure sensor in Diamond Anvil Cell (DAC) in silicon oil (0.53 GPa).

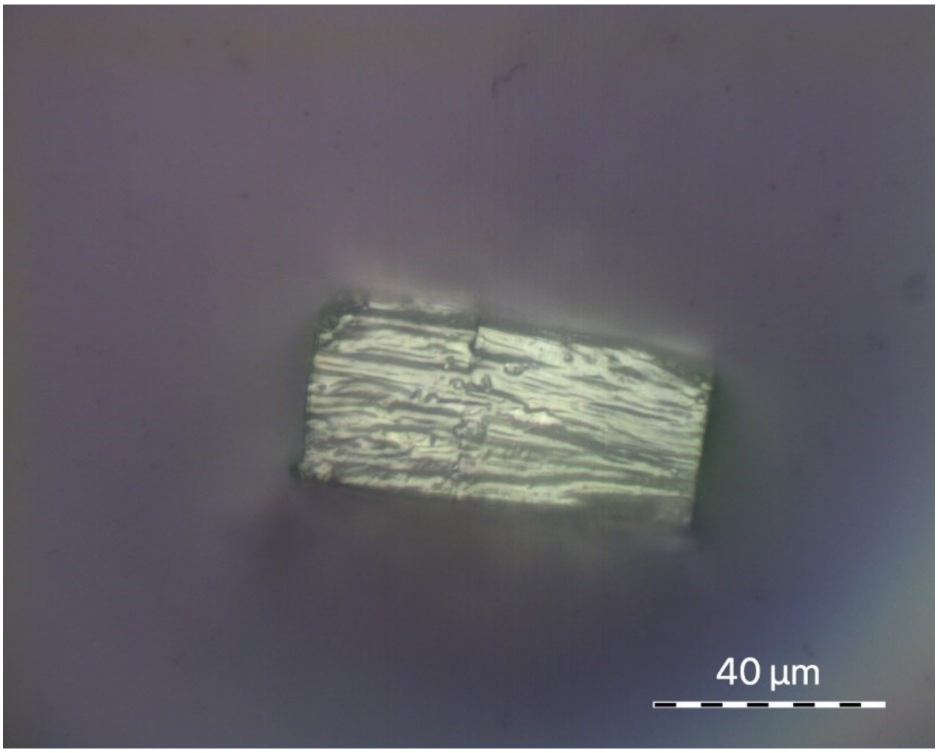

Figure S3. Image of the sample after the high pressure experiment in silicon oil.

Prior to *in situ* experiments, the sample was placed into a corresponding pressure transmitting medium, which contributes to the characteristic vibrational modes in the total spectrum recorded. Figure S4 shows the spectra of the silicone oil and all samples in the silicone oil at 0.05 GPa. The medium lines and the diamond line are marked.

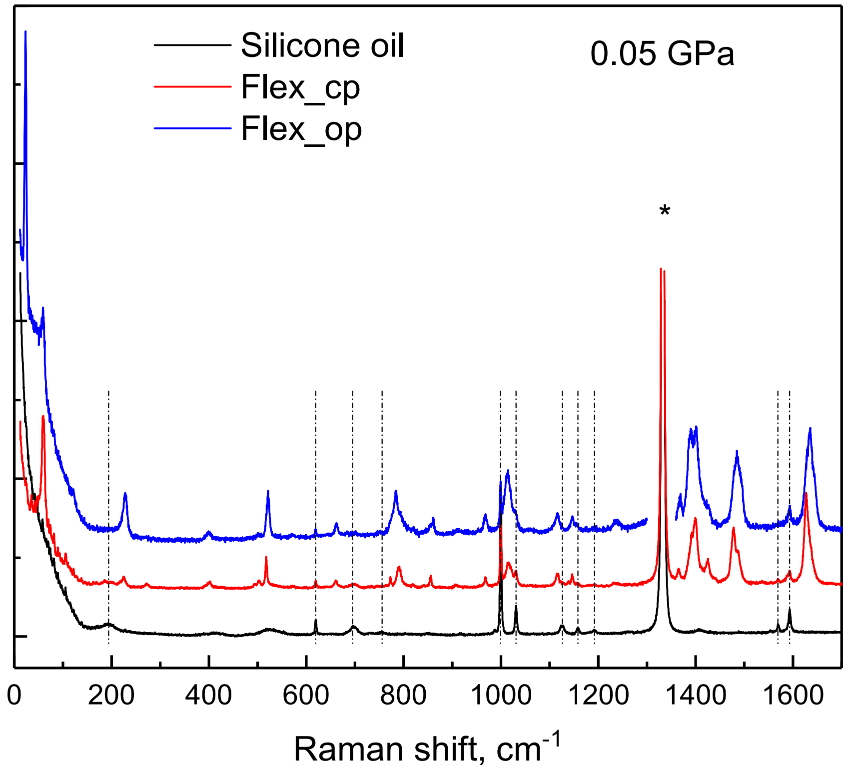

Figure S4. Raman spectra of DUT-8(Ni)_*op*, DUT-8(Ni)_*cp* and silicone oil as pressure transmittance media at 0.05 GPa. Dashed lines denote silicone oil bands, asterisk – band from diamond anvil.

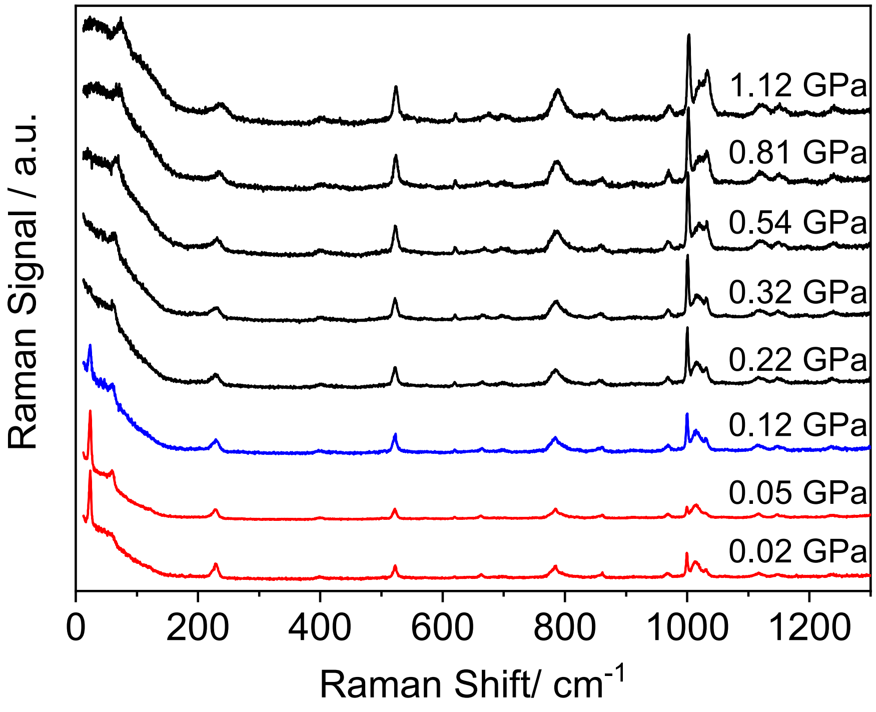

Figure S5. Raman spectra of DUT-8(Ni)_*op* under hydrostatic pressure in silicone oil.

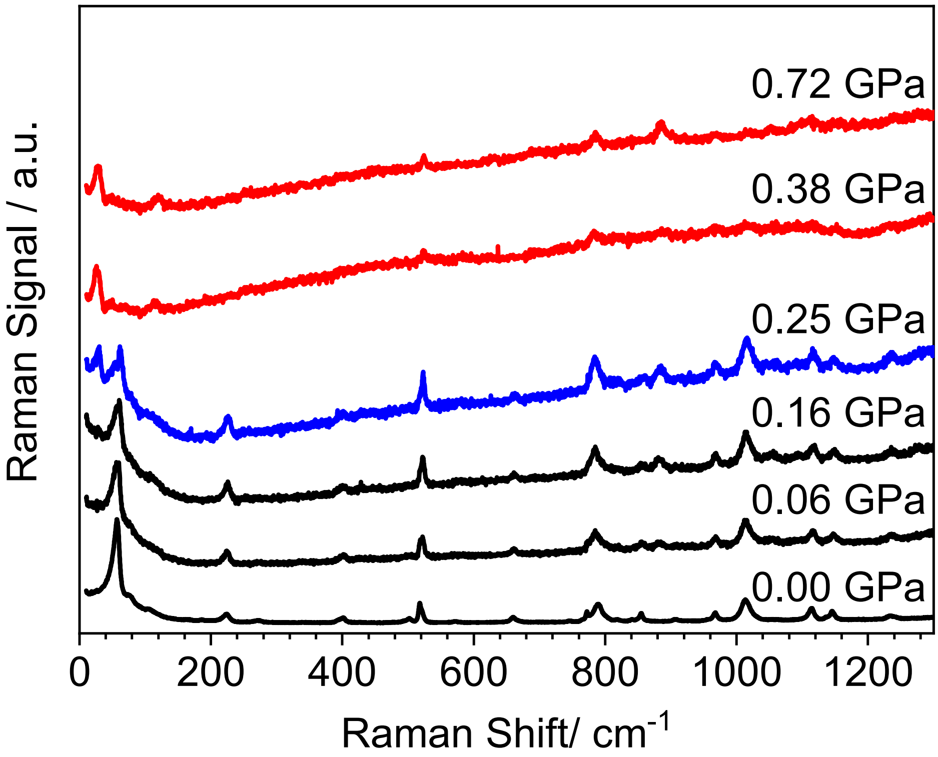

Figure S6. Raman spectra of DUT-8(Ni)_*cp* under hydrostatic pressure in methanol.

References:

1. J. Rodriguez-Carvajal, *Physica B.,* 1993, **192**, 55-69.
2. J. Rodríguez-Carvajal, *Newsletter of Commission on Powder Diffraction of the IUCr,* 2001, **26**, 12-19.
3. N. Kavoosi, V. Bon, I. Senkovska, S. Krause, C. Atzori, F. Bonino, J. Pallmann, S. Paasch, E. Brunner and S. Kaskel, *Dalton Trans.*, 2017, **46**, 4685-4695.
4. https://systatsoftware.com/products/peakfit/
5. G. L. Squires, *Practical Physics*, Cambridge University Press, Cambridge, 4 edn., 2001.