Supporting Information: Structural phase transitions in flexible DUT-8(Ni) under high hydrostatic pressure

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This is the supplementary information for the manuscript entitled: "Structural phase transitions in flexible DUT-8(Ni) under high hydrostatic pressure" by Alexander Krylov, Irina Yushina, Evgenia Slyusareva, Svetlana Krylova, Alexander Vtyurin, Stefan Kaskel, and Irena Senkovska

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) measurements 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 (Figure S1).

Physisorption experiments

Belsorp Max volumetric adsorption instrument was used for physorption measurements. Before the measurements, the samples were activated in dynamic vacuum at 100 °C for at least 16 hours. Isopropanol physisorption isotherm at 298 K on DUT-8(Ni)_rigid and DUT-8(Ni)_flexible are presented in Figure S2.

Raman spectroscopy

DUT-8(Ni) (open pore phase) belongs to the space group $P4/n$ (symmetry international tables number 85).[S1] The Ni atoms are located in the 2c Wyckoff position. Other atoms are located in the 8g Wyckoff position. G_{IR} = Gacoustic = Au + ^{1}Eu + ^{2}Eu. The representation of Raman modes in the hexagonal phase at Brillouin zone center is: G_R= 73A_g + 69B_g + 73^1E_g + 73^2E_g. ^1E_g, ^2E_g are complex conjugate representations. If the longitudinal and transversal modes of the complex conjugated representations are allowed, this implies that two peaks will be observed in the spectrum due to the splitting. In other cases, only one peak is going to be observed.

DUT-8(Ni) (closed pore phase) belongs to the space group $P1$ (symmetry international tables number 1).[S2] The unit cell includes 132 atoms. The atoms are located in the 1a Wyckoff position. The Raman and infra-red (IR) mode representation (acoustic modes not included) in the hexagonal phase at Brillouin zone center is as follows: $G_{R,IR}$= 393A.

DFT simulations

The positions of vibration modes and corresponding atomic motions can be visualized using the CRYSPLOT webpage (http://crysplot.crystalsolutions.eu/web_pages_yves3/vibration.html) by uploading corresponding out-files for open and closed pore forms of DUT-8(Ni). The visualization of atomic motions during selected Raman active calculated modes has been provided in video format for modes 44, 67, 82 and 123 cm^{-1} for closed pore phase and 18, 23, 25 cm^{-1} for open pore phase. Selected bands deviations between experimental and calculated Raman shift in the open and close pore phases have been presented in Tables S1, S2.

Experimental details of *in situ* experiment

The sample was placed into a corresponding pressure transmitting medium, which contributes to the characteristic vibrational modes in the total spectrum recorded.

Figures S3 and S4 show the spectra of the silicone oil and spectra of the samples in the silicone oil at 0.5 GPa and at 6.5 GPa, respectively.

Figure S5 shows the spectra of DUT-8(Ni) op and DUT-8(Ni) cp in the isopropanol as pressure transmitting medium at 3.0 GPa.The lines belonging to IPA are marked.

Figure S6 includes dependencies of Raman shift and width of the 225-230 cm^{-1} lines for the open pore phase and closed pore phases of DUT-8(Ni) on pressure.

Pressure dependencies of Raman shift and width of the 1630 (in black), 1640 (in red) cm^{-1} lines for the closed pore phase in the isopropanol are presented in Figure S7.

Pressure dependencies of Raman shift and width of the 520–523 cm^{-1} line for the open pore phase (open circles and squares), closed pore phase (solid circles and squares) are presented in Figure S8.

The decompression run indicates that the pressure-driven changes in the spectra are reversible (Figs. S9 and S10). Raman shift of the 662 cm^{-1} line (in-plane δ of aromatic linkers without distortion of the pore shape) and 521 cm^{-1} line (in- and out-of-plane δ of

aromatic rings) in the open pore phase experiment in isopropanol as pressure transmitting medium. The colour indicates the running pressure: increasing pressure - in black, pressure release - in red.

Comparison of pressure-dependent Raman line shift in low wavenumbers region is presented in Figure S12. The behaviour of characteristic close pore phase line at 60 cm^{-1} is independent from initial pore state or pressure transmitting medium up to 2.2 GPa.

Raman spectra of DUT-8(Ni) op sample before and after experiment in the silicone oil are presented in Figure S13.

The comparison of initial Raman spectra (before pressure application) and resulting spectra after experiments in both pressure transmitting media are presented in Figure S14.

Pressure dependence of the silicone oil lines (Figure S15). This behaviour demonstrate no anomaly in pressure dependence. The lines at 1000 and 1030 cm^{-1} have a continuous shift and are approximated by solid black lines with increasing pressure. Thus, the silicone oil does not show any transitions in the investigated pressure region.

Figure S16 shows the samples in the high-pressure diamond anvil cell (DAC): a) DUT-8(Ni)_cp and high-pressure sensor (ruby) in silicone oil as a pressure transmitting medium; b) DUT-8(Ni)_op in the silicone oil as a pressure transmitting medium.

Figure S17 presents the comparison of Raman spectra of DUT-8(Ni) in different media under equal pressures.

In Figure S18, SEM images demonstrate comparison of sizes of DUT-8(Ni)_flex and DUT-8(Ni)_rigid.

References

(S1) N. Klein, C. Herzog, M. Sabo, I. Senkovska, J. Getzschmann, S. Paasch, M. R. Lohe, E. Brunner and S. Kaskel, *Phys. Chem. Chem. Phys.*, **2010**, 12, 11778–11784.

(S2) H. C. Hoffmann, B. Assfour, F. Epperlein, N. Klein, S. Paasch,I. Senkovska, S. Kaskel, G. Seifert and E. Brunner, *J. Am. Chem. Soc.*, **2011**, 133, 8681–8690.

Table S1: Selected bands deviations between experimental and calculated Raman shift in the open pore phase

Experimental band, cm^{-1}	Calculated mode, cm^{-1}	Delta	|Delta|
23	26	-3	3
122	131	-9	9
223	211	12	12
398	411	-13	13
521	528	-7	7
860	855	5	5
968	980	-12	12
1015	1028	-13	13
1147	1140	7	7
1230	1221	9	9
1390	1394	-4	4
1401	1409	-8	8
Average			8.5

Table S2: Selected bands deviations between experimental and calculated Raman shift in the closed pore phase

Experimental band,cm^{-1}	Calculated mode, cm^{-1}	Delta	|Delta|
59	68	-9	9
75	80	-5	5
93	103	-10	10
107	118	-11	11
216	218	-2	2
225	227	-2	2
272	267	5	5
393	381	12	12
402	401	1	1
517	530	-13	13
572	597	-25	25
660	655	5	5
773	783	-10	10
790	810	-20	20
967	988	-21	21
1015	1030	-15	15
1147	1149	-2	2
1234	1268	-34	34
1365	1360	5	5
1393	1393	0	0
1400	1427	-27	27
1426	1446	-20	20
1627	1617	10	10
Average			11.48

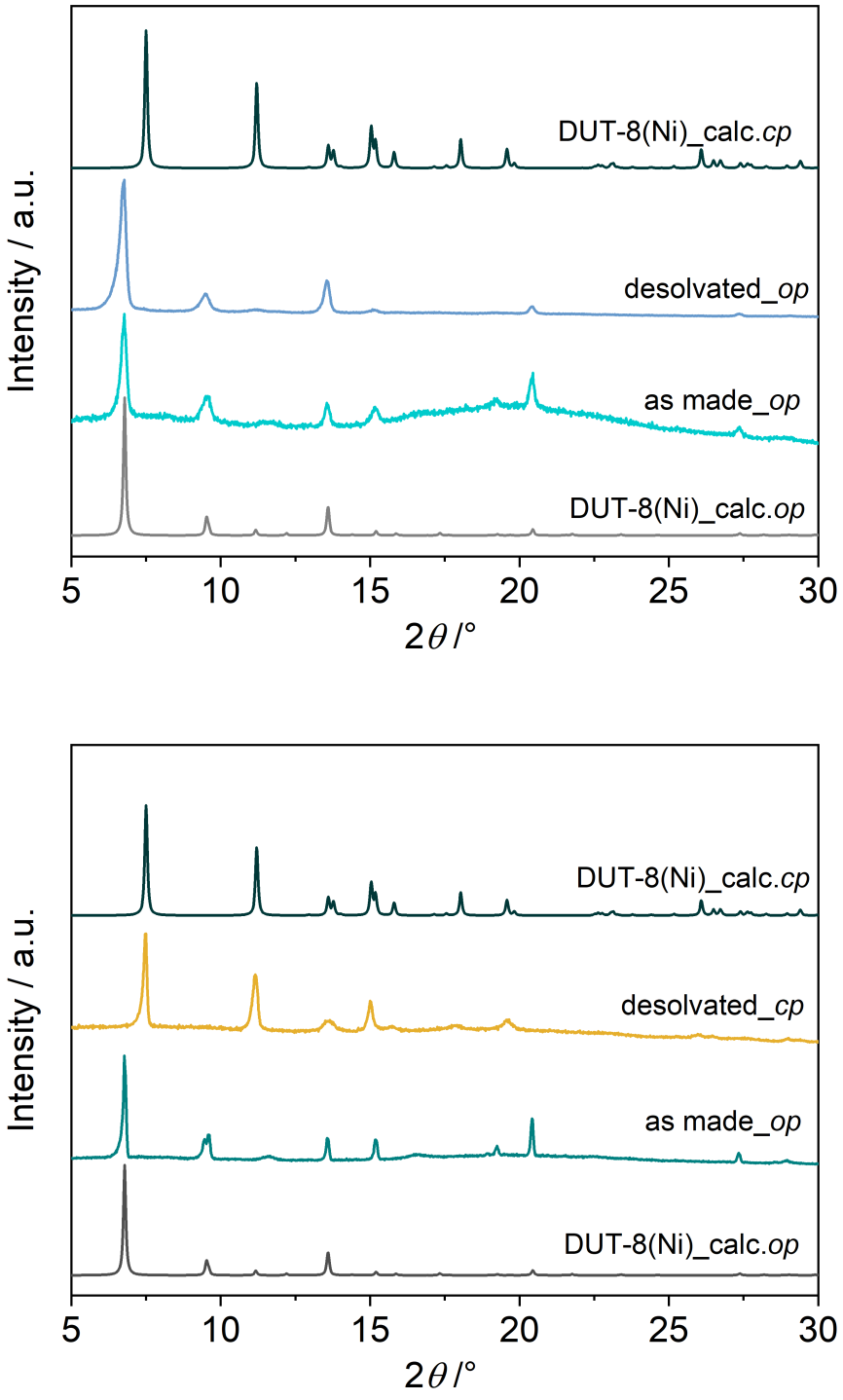

Figure S1: Calculated and experimental powder X-ray diffraction patterns for DUT-8(Ni) rigid (top) and DUT-8(Ni) flexible (bottom).

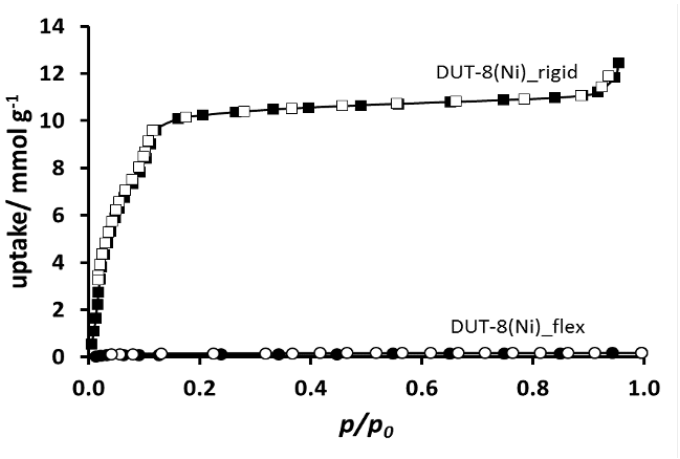

Figure S2: Isopropanol physisorption isotherms at 298 K on DUT-8(Ni)_rigid (squares) and DUT-8(Ni)_flexible (circles). Filled symbols – adsorption, open symbols – desorption.

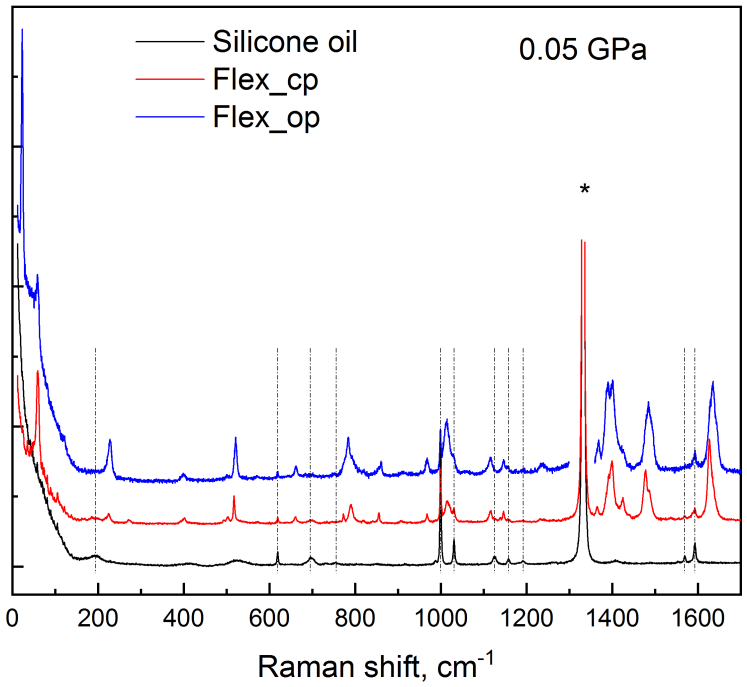

Figure S3: The spectra of the silicone oil and spectra of the samples in the silicone oil at 0.5 GPa. Dashed lines denote silicone oil bands, asterisk – band from diamond anvil.

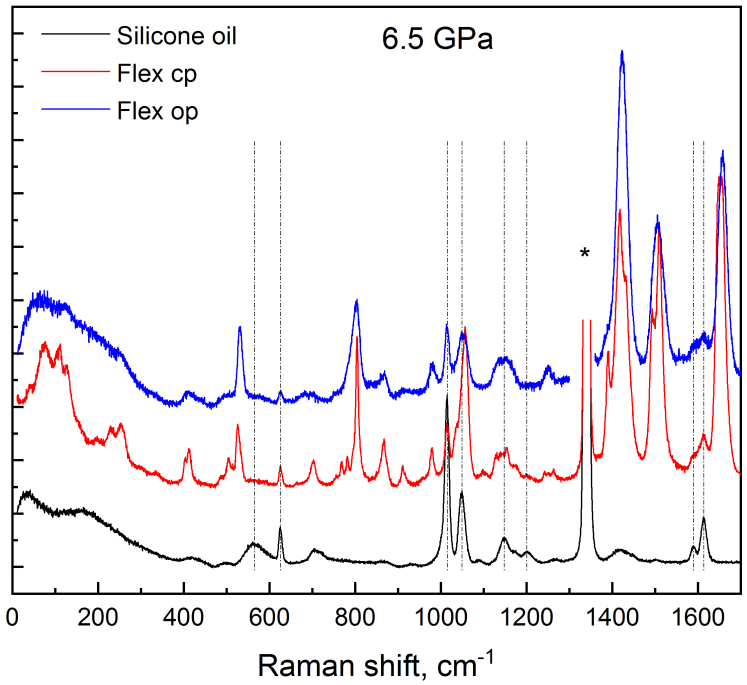

Figure S4: The spectra of the silicone oil and spectra of the samples in the silicone oil at 6.5 GPa. Dashed lines denote silicone oil bands, asterisk – band from diamond anvil.

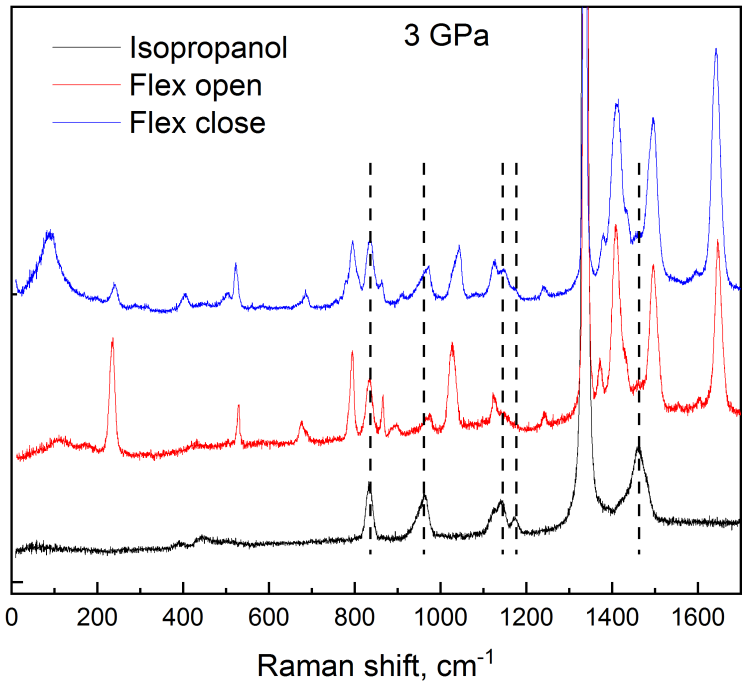

Figure S5: Raman spectra of isopropanol and DUT-8(Ni)_op, DUT-8(Ni)_cp in isopropanol as pressure transmitting medium at 3.0 GPa. Dashed lines denote isopropanol bands.

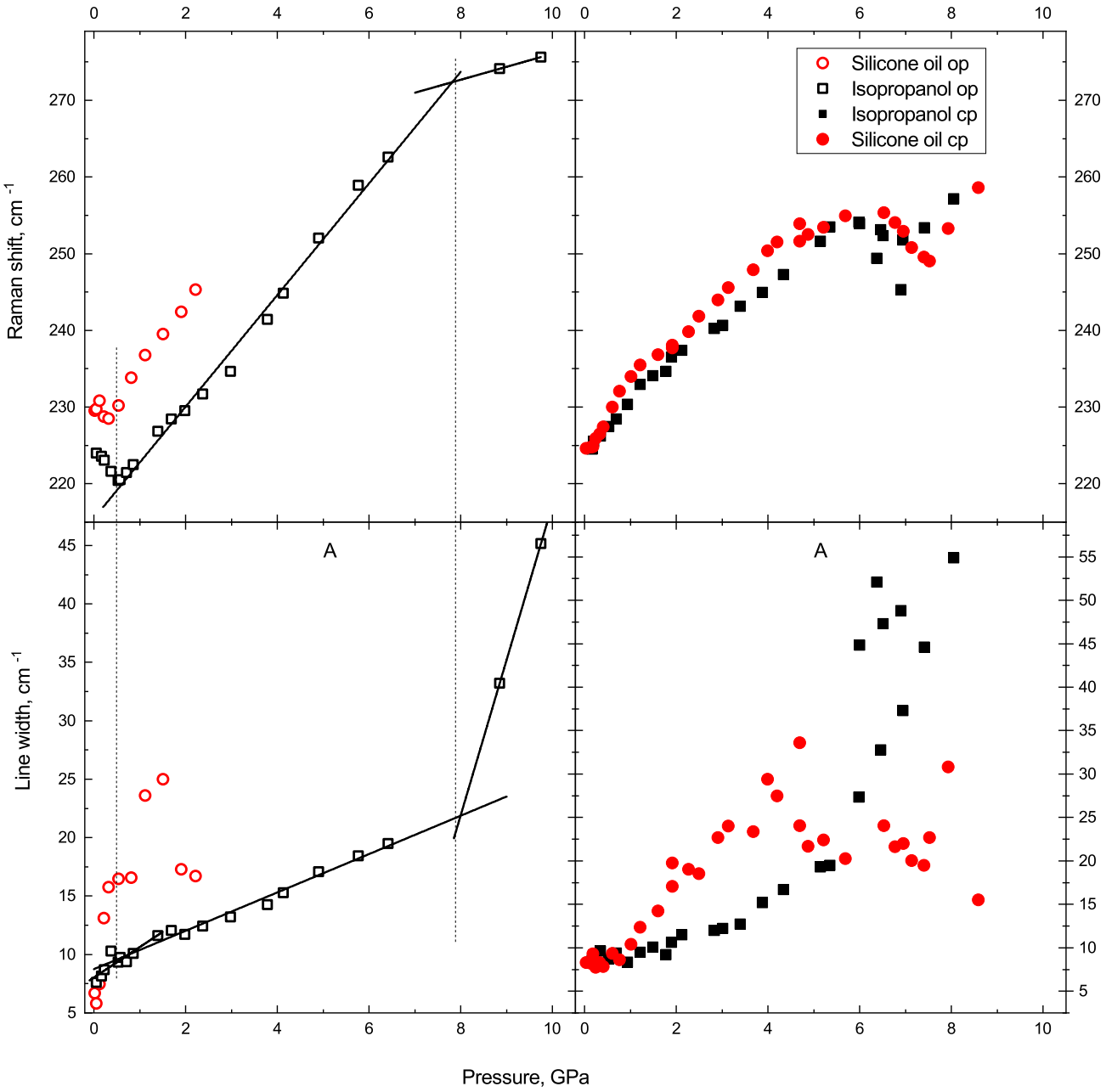

Figure S6: Raman shift and width of the 223 and 230 cm^{-1} lines (Ni-O and Ni-N bending) for the open pore phase (open circles and squares) and closed pore phase (dabco rotation, δ O-Ni(O)-O) (solid circles and squares). The colour denotes transmitting medium: silicone oil - in red, isopropanol - in blue. Dashed lines denote the pressure of phase transitions: 0.5 GPa in silicone oil op and isopropanol op; 8 GPa in isopraponol op.

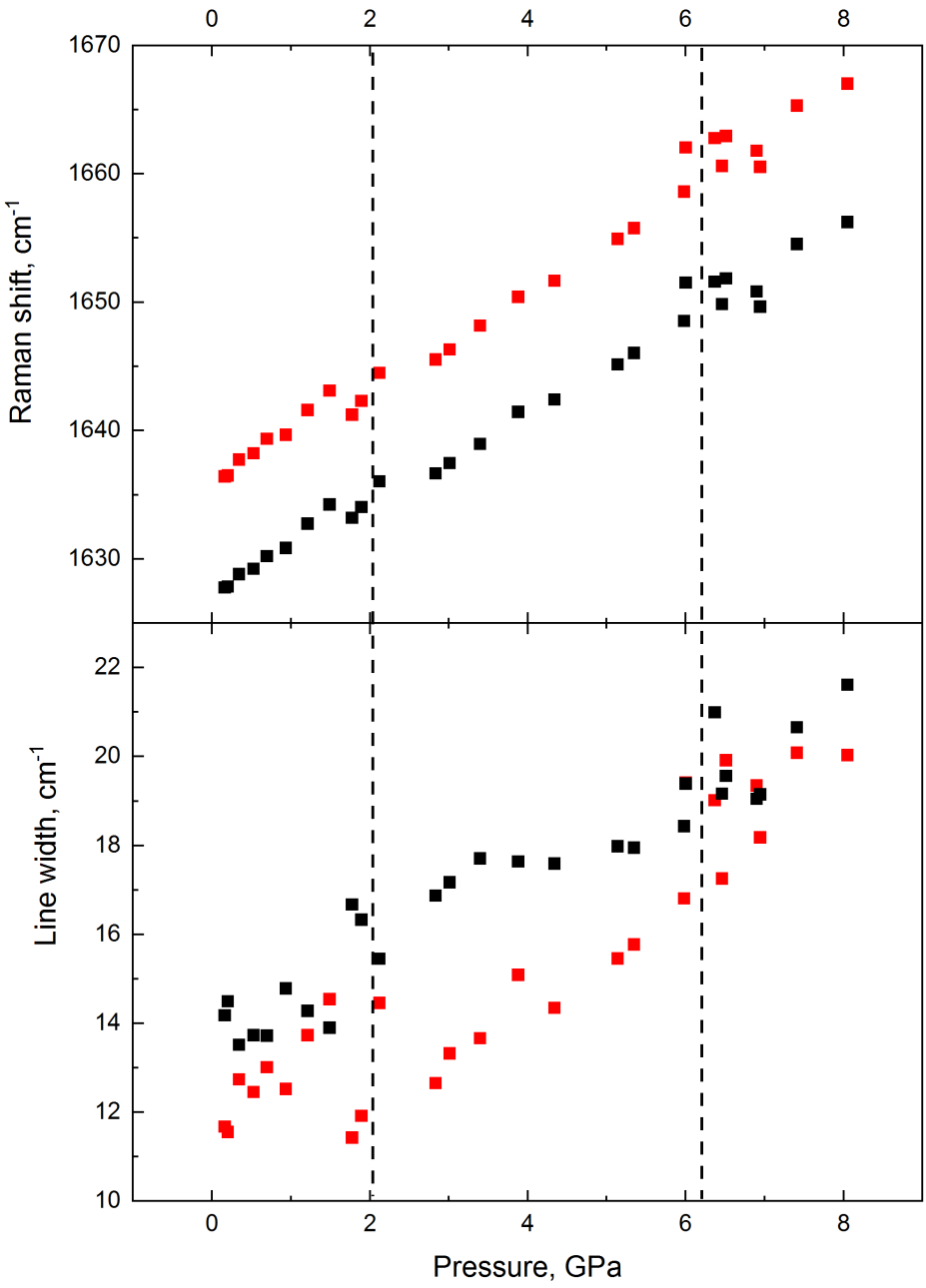

Figure S7: Raman shift and width of the 1630 (in black), 1640 (in red) cm^{-1} lines (ν C=C and ν C=O of ndc) for the closed pore phase in the isopropanol. Dashed lines denote pressure of phase transitions: 2 GPa in isopropanol cp; 6 GPa in isopropanol cp.

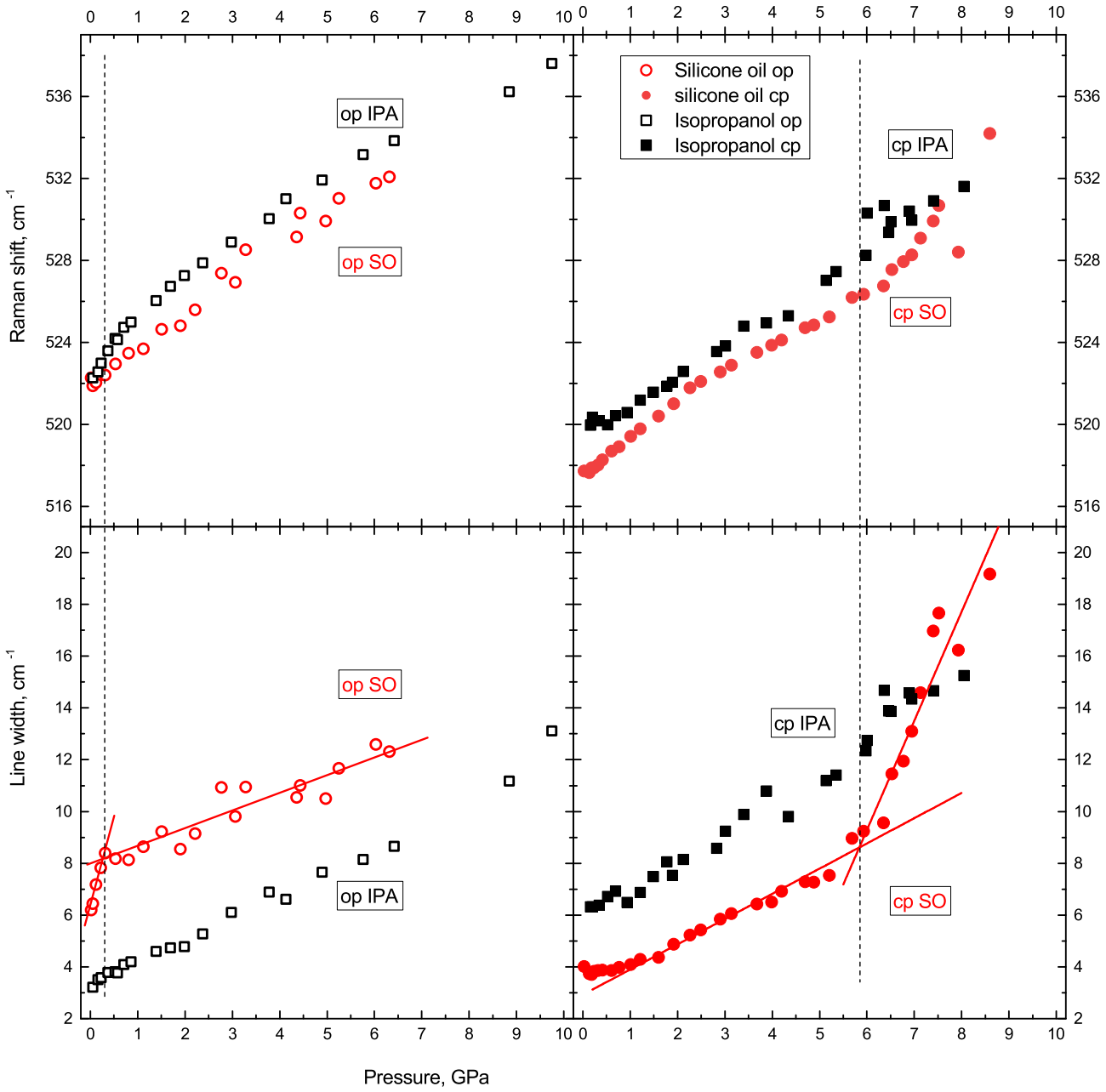

Figure S8: Raman shift and linewidth (FWHM) of the 520-523 cm^{-1} line (δ of aromatic rings) for the open pore phase (open circles and squares), and of the 517 cm^{-1} line (δ of aromatic rings) of the closed pore phase (solid circles and squares). The color denotes pressure transmitting medium: silicone oil (SO) – in red, isopropanol (IPA) – in blue. Dashed lines denote regions of phase transitions.

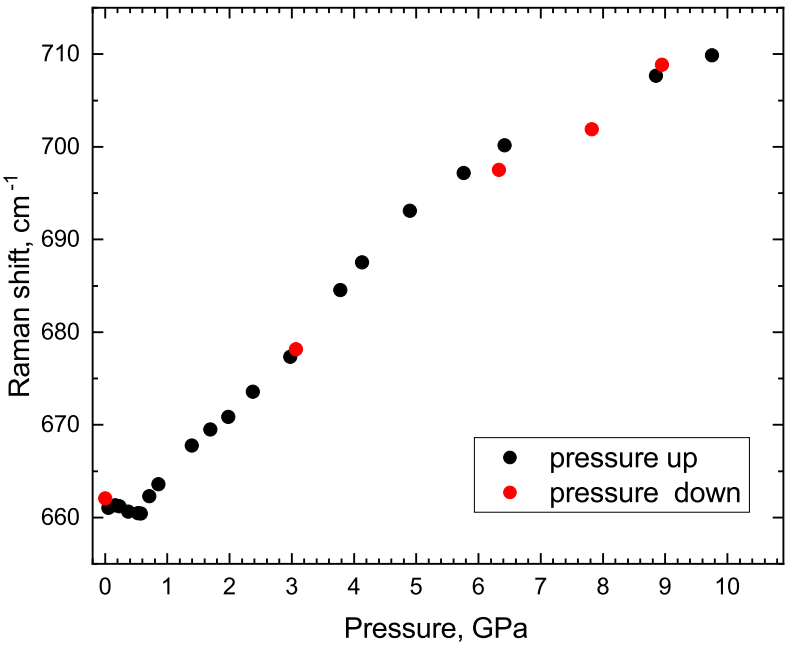

Figure S9: Reversibility of the structural changes under pressure. Raman shift of the 662 cm^{-1} line (in-plane δ of aromatic linkers without distortion of the pore shape) of the open pore phase in experiment with isopropanol as pressure transmitting medium. Increasing pressure is indicated in black, pressure release - in red.

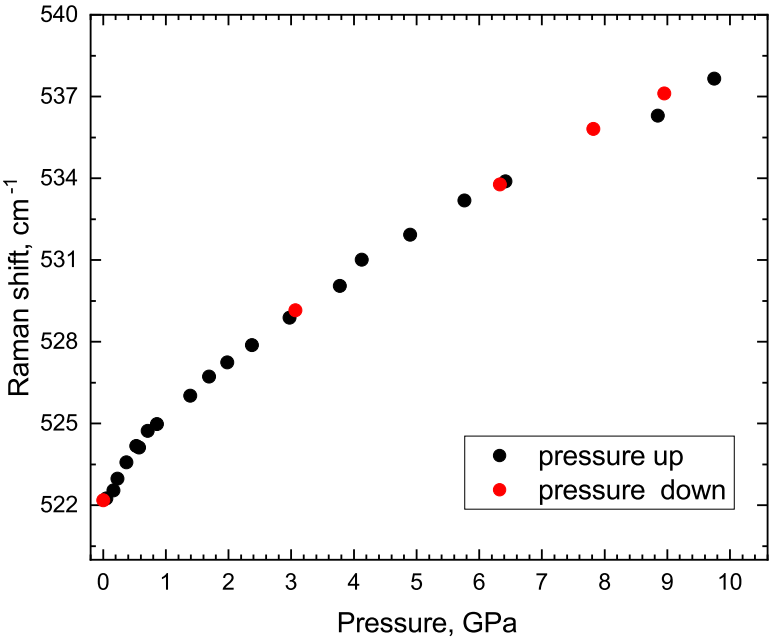

Figure S10: Reversibility of the structure changes under pressure. Raman shift of the 521 cm^{-1} line (in- and out-of-plane δ of aromatic rings) of the open pore phase in experiment with isopropanol as pressure transmitting medium. Increasing pressure is indicated in black, pressure release - in red.

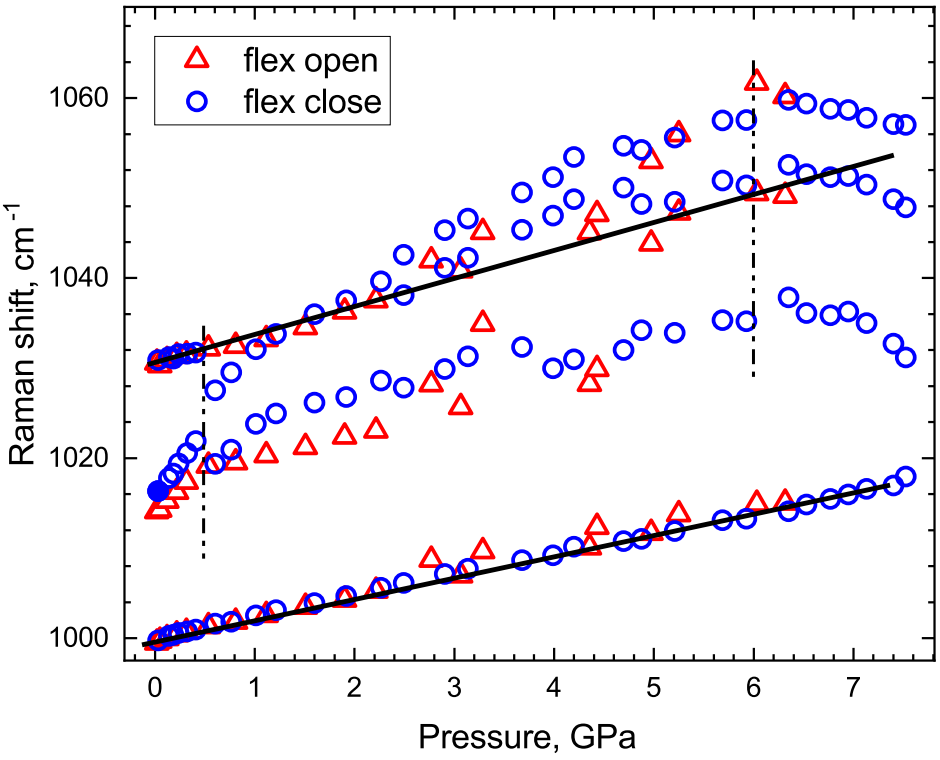

Figure S11: Comparison of pressure-dependent Raman line shift at 1015 cm^{-1}: as made DUT-8(Ni)_op flexible (red), desolvated DUT-8(Ni)_cp flexible (blue) in silicone oil as pressure transmitting medium. The lines at 1000 cm^{-1} and 1030 cm^{-1}, showing a continuous shift (solid black lines) with increasing pressure, belong to the silicone oil. Vertical dashed lines denote the pressures of structural changes.

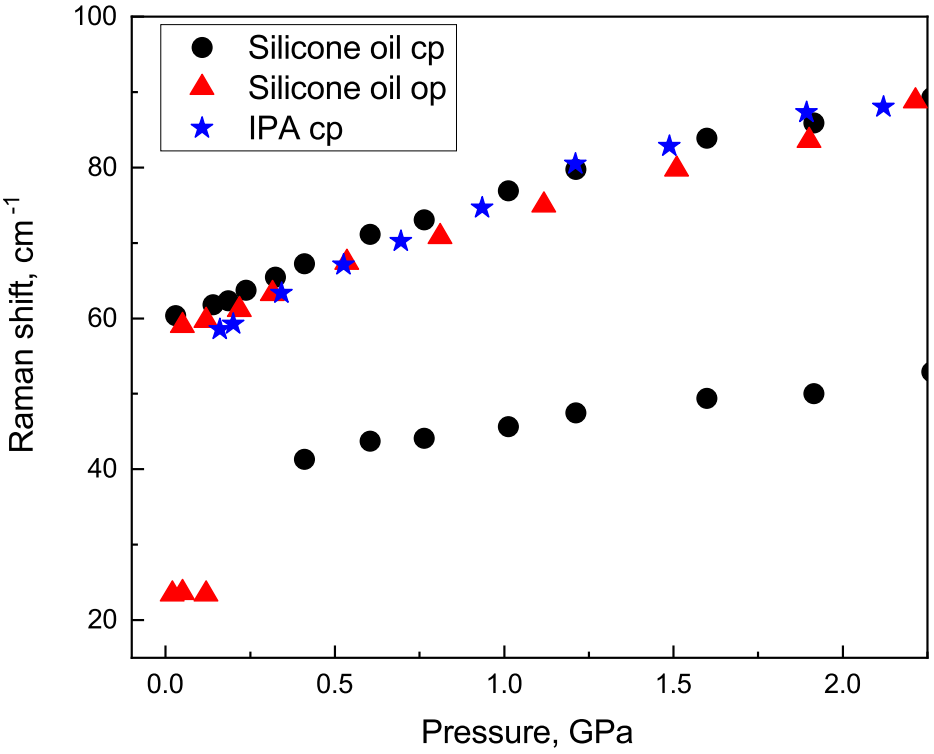

Figure S12: Comparison of pressure-dependent Raman line shifts in low wavenumbers region. The behaviour of characteristic close pore phase line at 60 cm^{-1} is independent from initial pore state or pressure transmitting medium up to 2.2 GPa.

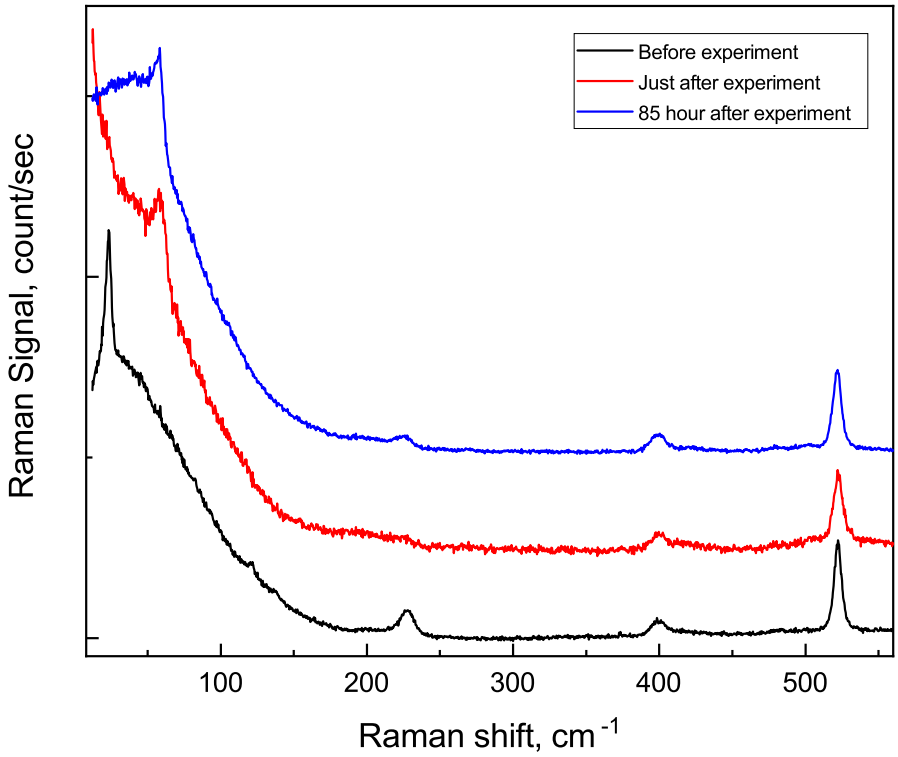

Figure S13: Raman spectra of DUT-8(Ni) before and after *in situ* experiment in silicone oil.

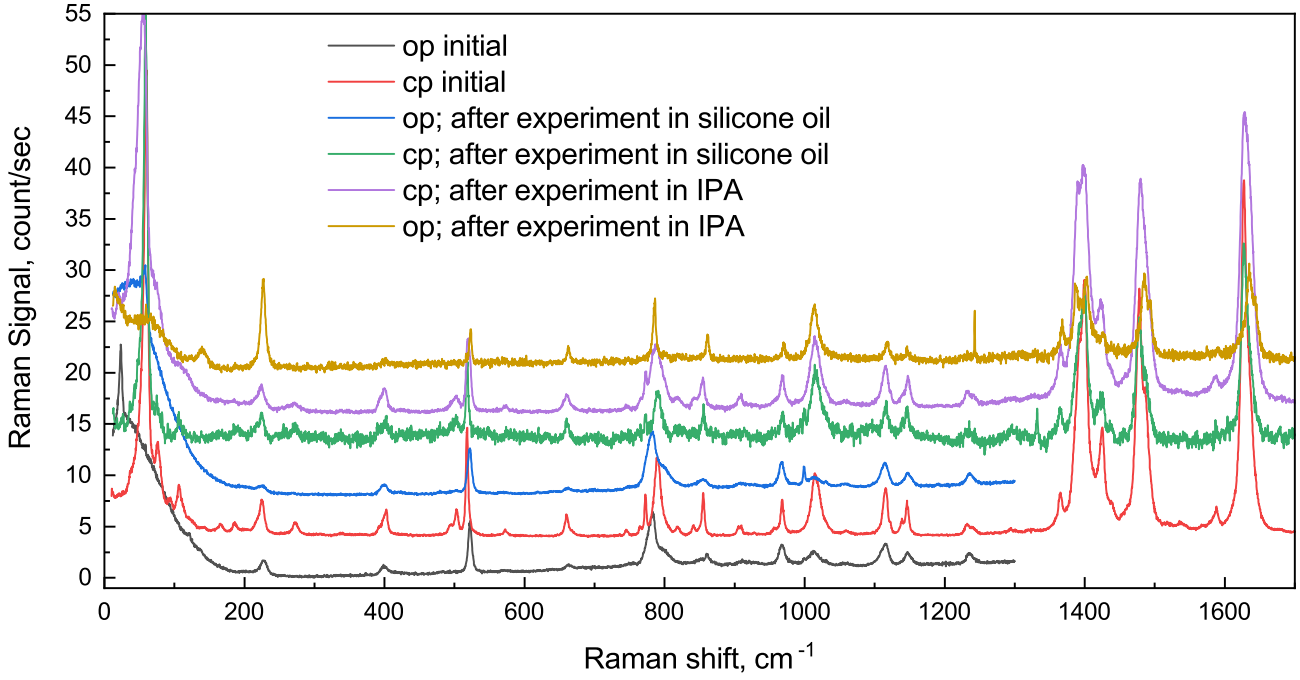

Figure S14: Raman spectra of DUT-8(Ni) after experiments in silicone oil and IPA (isopropyl alcohol). Labels op and cp denote the initial state of samples before experiment.

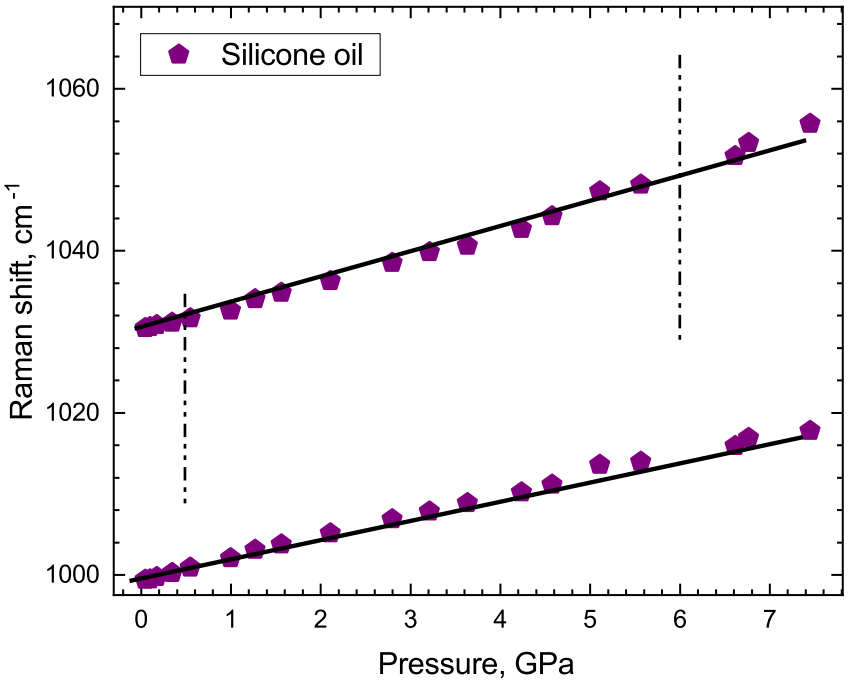

Figure S15: Pressure dependence of the silicone oil lines. The lines at 1000 and 1030 cm^{-1} have a continuous shift with increasing pressure and are approximated by solid black lines. Vertical dashed lines denote pressures of structural changes in the DUT-8(Ni).

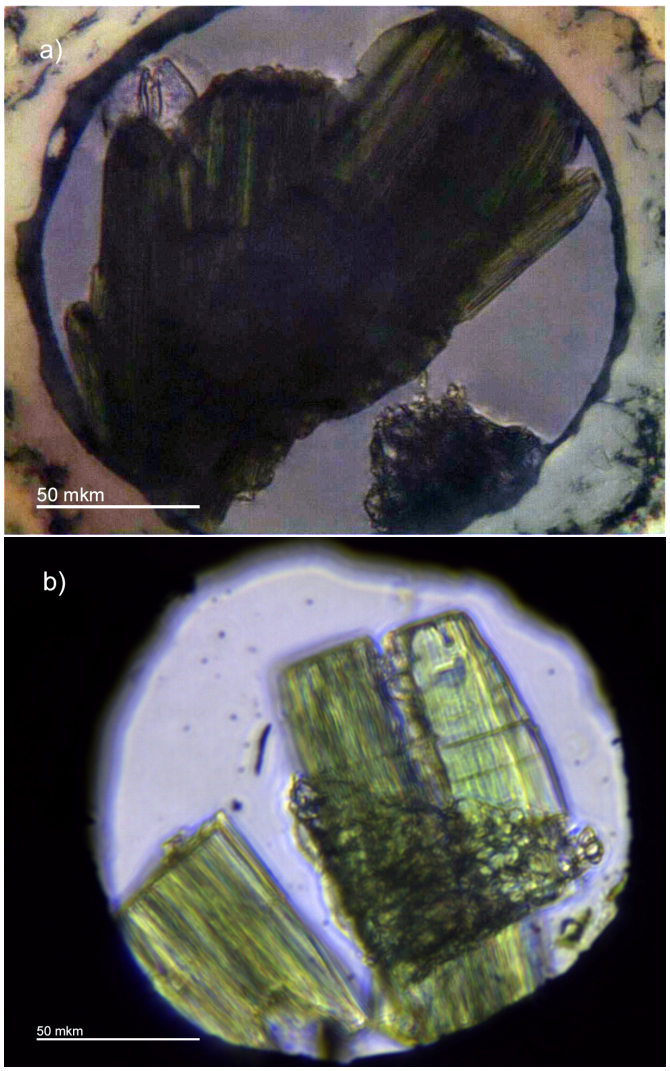

Figure S16: Samples in the high-pressure diamond anvil cell (DAC): a) DUT-8(Ni)_cp and high-pressure sensor (ruby) in silicone oil as a pressure transmitting media; b) DUT-8(Ni)_op in the silicone oil as a pressure transmitting media.

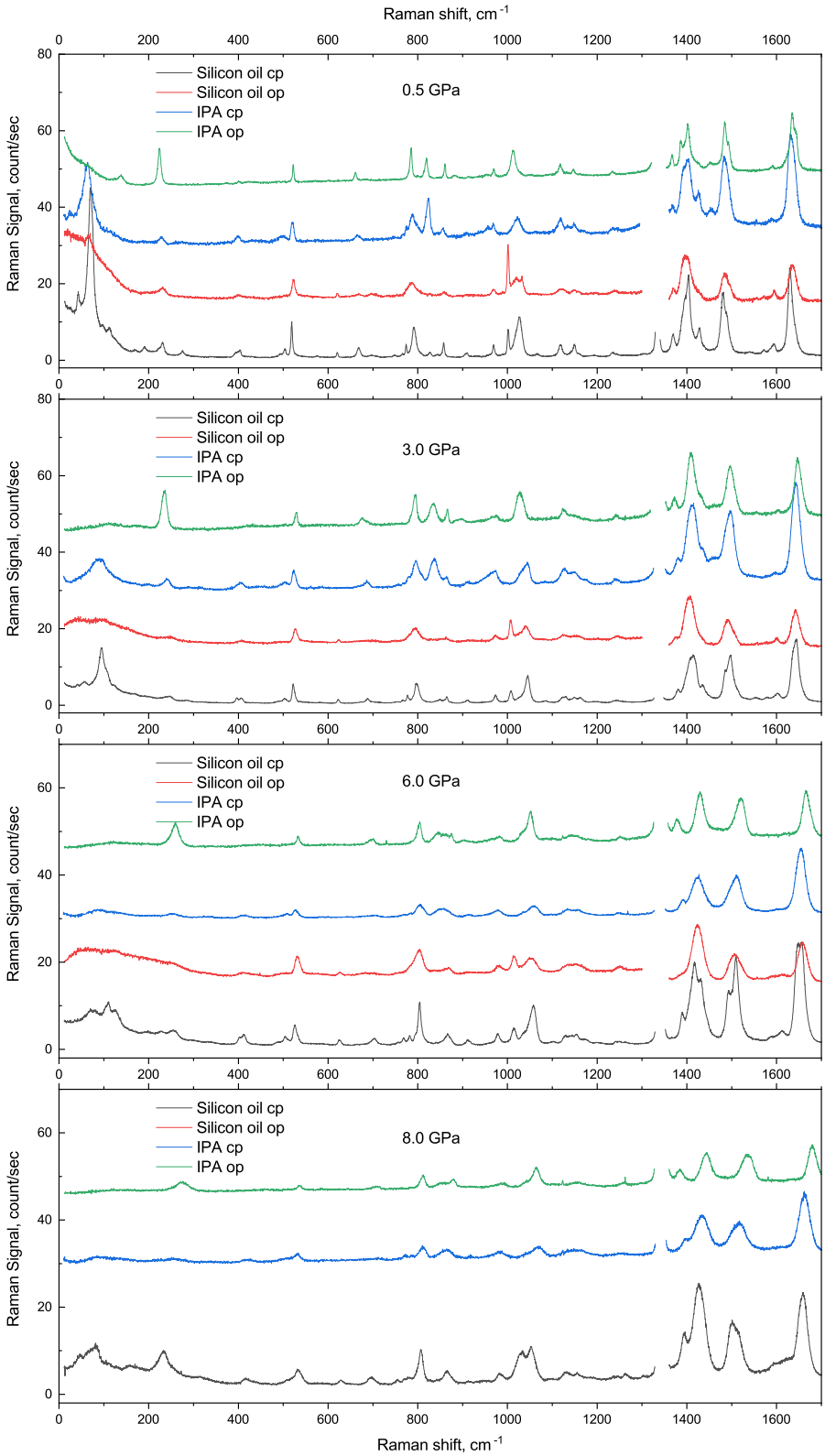

Figure S17: Comparison of Raman spectra of DUT-8(Ni) in different media under equal pressure.

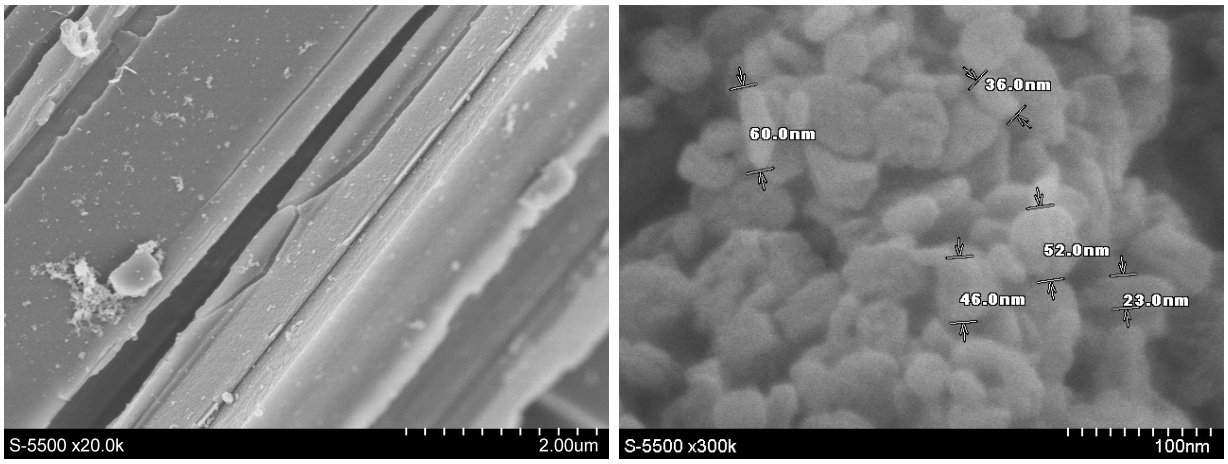

Figure S18: SEM images demonstrating the crystal size of DUT-8(Ni)_flex (left) and DUT-8(Ni)_rigid (right).