

Electronic Supporting Information

Raman spectroscopy studies of the terahertz vibrational modes of DUT-8 (Ni) metal-organic framework

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1. Investigated materials

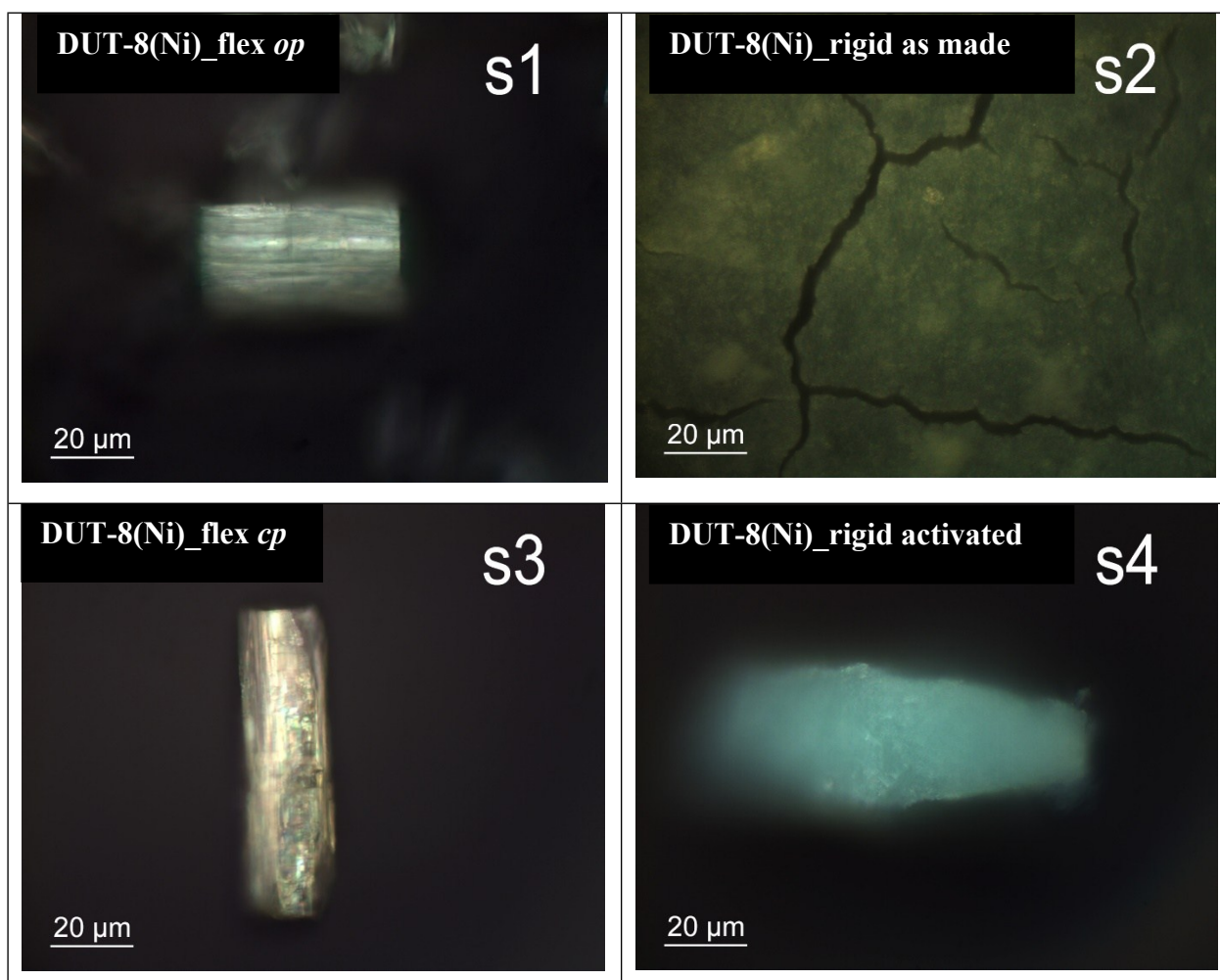


Figure S1. Images of samples investigated.

2. Group theoretical analysis and Raman spectra

2.1 Group theoretical analysis

DUT-8(Ni) (open phase) crystalizes in space group $P4/n$ (space group number 85).^[1] The atoms are located in the $8g$ Wyckoff position. The Raman mode representation in the hexagonal phase at Brillouin zone center is as follows: $\Gamma_R = 81A_g + 81B_g + 81^1E_g + 81^2E_g$. 1E_g , 2E_g are complex conjugate representations. Two peaks are observed in the spectrum because of the splitting of the longitudinal and transverse modes. Polarization selection rules are presented in the Table S1. The angular depending Raman spectra of open state should contain only A_g and B_g modes in our experimental geometry (shaded in gray in Table S1).

Table S1. Backscattering geometry DUT-8(Ni) (open phase)

	1E_g	2E_g	A_g	B_g
-X(YY)X	·	·	x	x
-X(YZ)X	x	x	·	·
-X(ZZ)X	·	·	x	·
-Y(XX)Y	·	·	x	x
-Y(XZ)Y	x	x	·	·
-Y(ZZ)Y	·	·	x	·
-Z(XX)Z	·	·	x	x
-Z(XY)Z	·	·	·	x
-Z(YY)Z	·	·	x	x

DUT-8(Ni) (closed phase) crystalizes in space group $P1$ (space group number 1)^[2] with 66 atoms in the unit cell. The atoms are located in the $1a$ Wyckoff position. The selection rules and Raman tensor were calculated for this case. The Raman and infra-red (IR) mode representation (acoustic modes are not included) in the hexagonal phase at Brillouin zone center is: $\Gamma_{R, IR} = 195A$. Polarization selection rules are presented in the Table S2. The number of observed modes (195) in Raman spectrum of the closed phase is expected to be larger in comparison with the open phase (162).

Table S2. Backscattering geometry DUT-8(Ni) (closed phase).

	A
-X(YY)X	x
-X(YZ)X	x
-X(ZZ)X	x
-Y(XX)Y	x
-Y(XZ)Y	x
-Y(ZZ)Y	x
-Z(XX)Z	x
-Z(XY)Z	x
-Z(YY)Z	x

2.2 polarized Raman spectroscopy

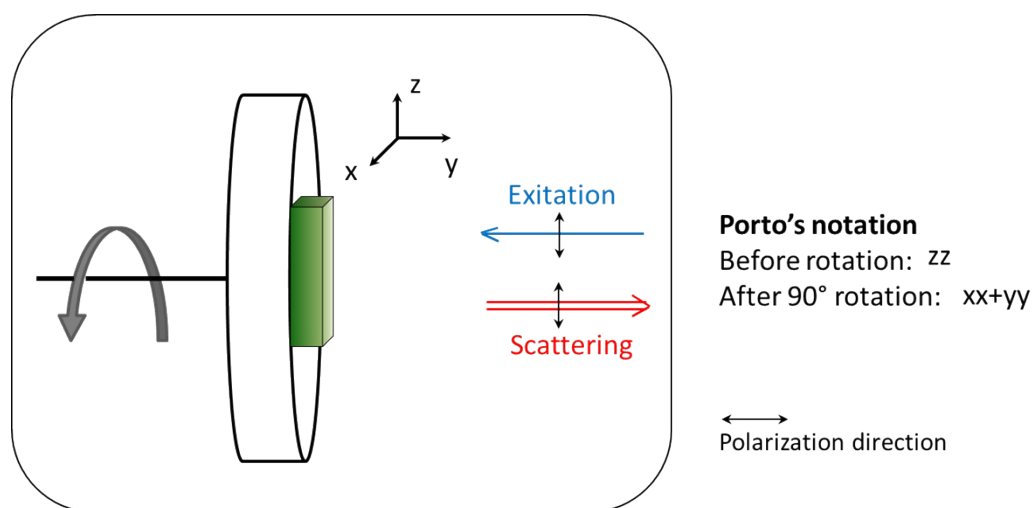


Figure S2. Schematic representation of the polarized Raman spectroscopy experiment.

DUT-8(Ni) op
 Space group $P4/n$
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$

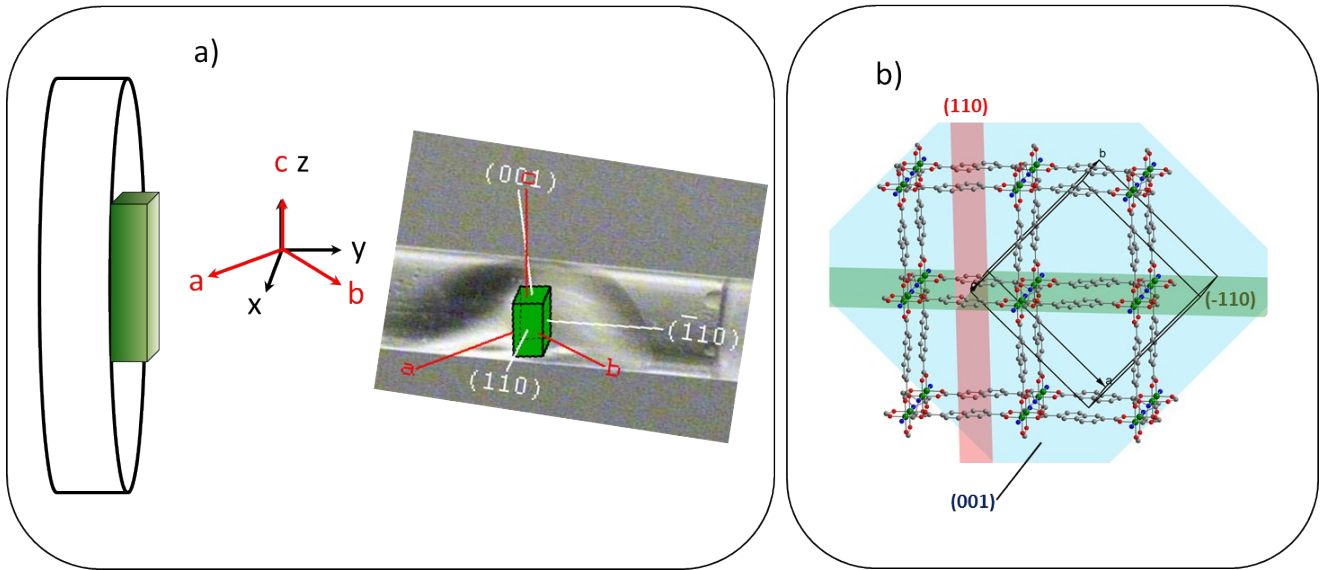


Figure 3. a) Left: Assignment of the axis defined for Raman experiment to the crystallographic axis of DUT-8(Ni)_op crystal. Right: The photograph of the single crystal and indexing of crystal faces performed on the single crystal X-ray diffractometer.

Only the z axis in Raman experiment can be unambiguously assigned to the crystallographic c axis. Because the a and b axis are equivalent in the tetragonal space group, they accurate assignment is less important. b) Position of (001), (-110), and (110) planes in the crystal structure, corresponding to the crystal faces.

2.3 Peak fitting of the spectral lines

The peak fitting of the spectral lines was performed using different functions (Lorentz, Voigt and dumping harmonic oscillator (DHO)). The values obtained for lines with intensity higher than 3% of the strongest line, are very similar. Deviations obtained are less than pixel spectral size of the detector and also much less than spectral resolution of the experiment.

Lorentz function used:

$$I(\omega) = \frac{2}{\pi} \frac{A\Gamma}{4(\omega - \omega_0) + \Gamma^2} \quad (1)$$

3. Powder X-ray diffraction patterns

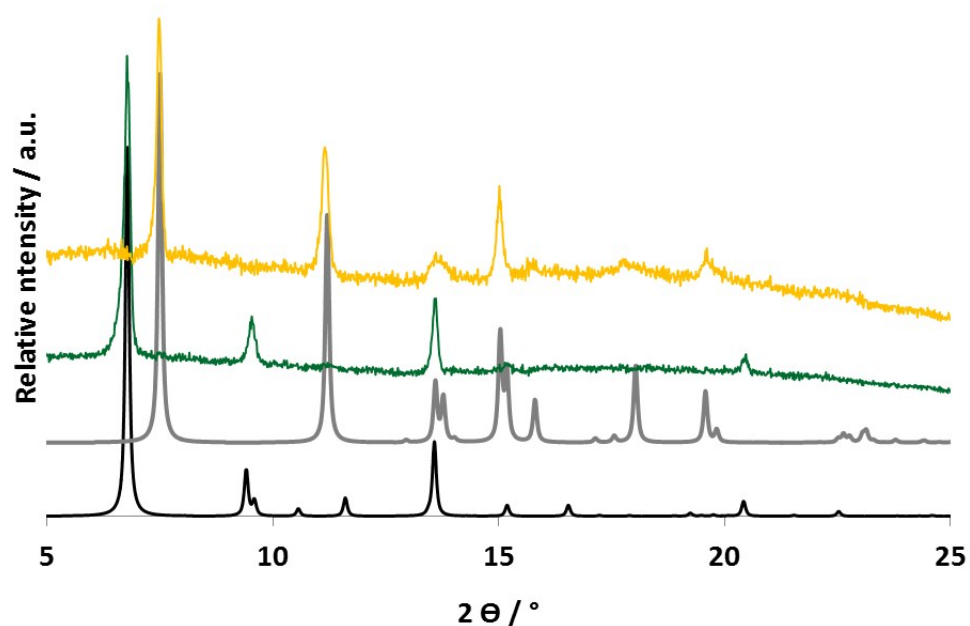


Figure S4. Powder X-ray diffraction patterns of DUT-8(Ni): calculated from the crystal structure of DUT-8(Ni)_flex *op* (black) and DUT-8(Ni)_flex *cp* (grey); as made DUT-8(Ni)_flex (green) and desolvated DUT-8(Ni)_flex (yellow).

4. References

- [1] N. Klein, C. Herzog, M. Sabo, I. Senkowska, J. Getzschmann, S. Paasch, M. R. Lohe, E. Brunner, S. Kaskel, *Phys. Chem. Chem. Phys.* 2010, **12**, 11778.
- [2] V. Bon, N. Klein, I. Senkowska, A. Heerwig, J. Getzschmann, D. Wallacher, I. Zizak, M. Brzhezinskaya, U. Mueller, and S. Kaskel, *Phys. Chem. Chem. Phys.* 2015, **17**, 17471.