Electronic supporting information

for the paper

Tailoring adsorption induced phase transitions in the pillared-layer type metal-organic framework DUT-8(Ni)

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1. Powder X-ray diffraction patterns and nitrogen adsorption isotherms for DUT-8(Ni) materials

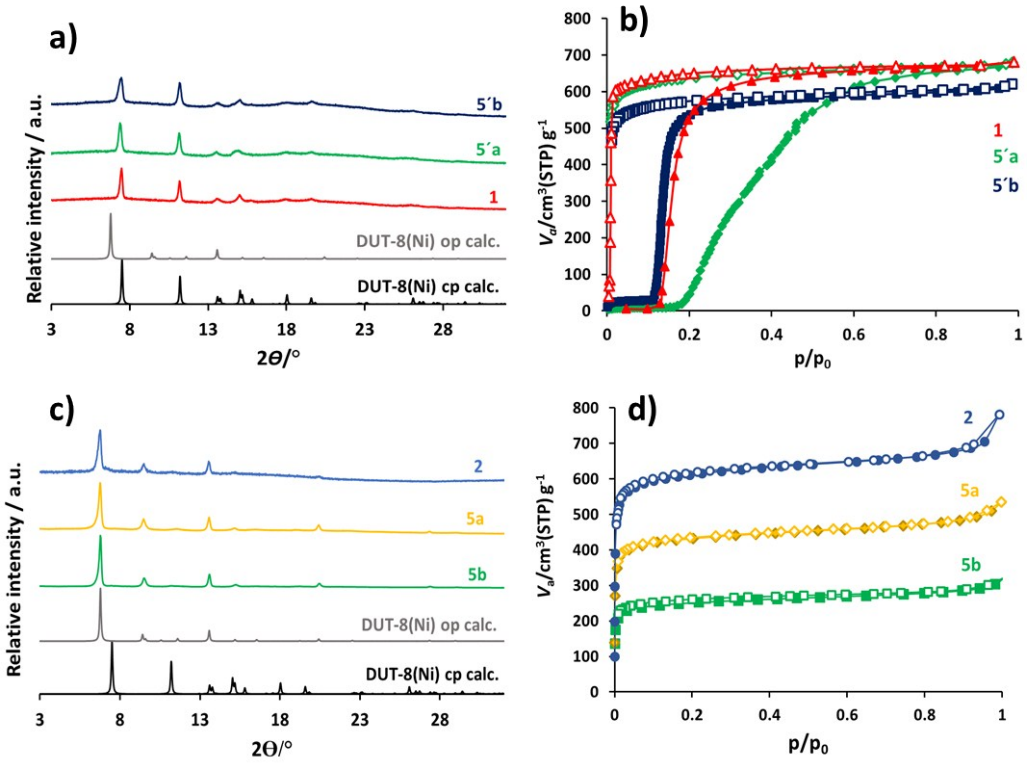
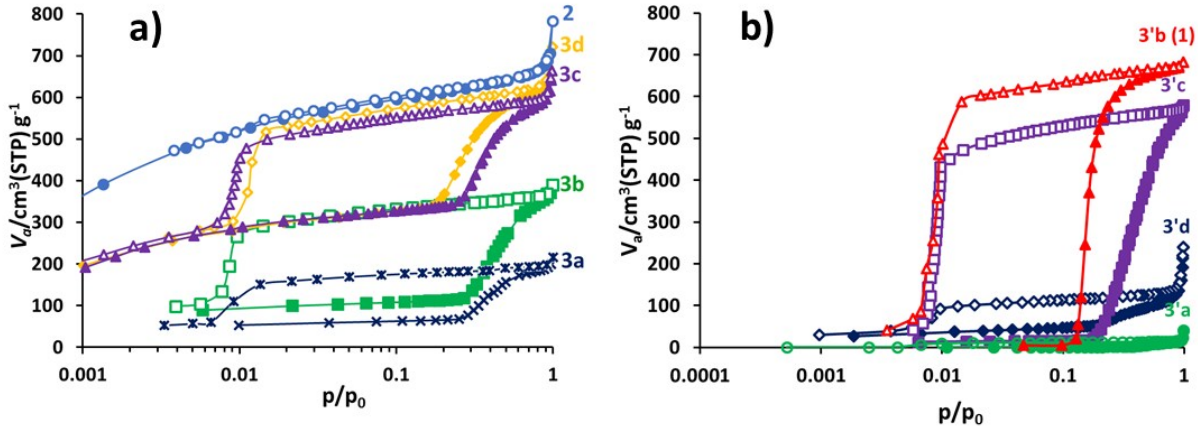


Figure S1. PXRD patterns (left) and nitrogen physisorption experiments at 77 K (right) for the series **5'** (a, b) and **5** (c, d) .



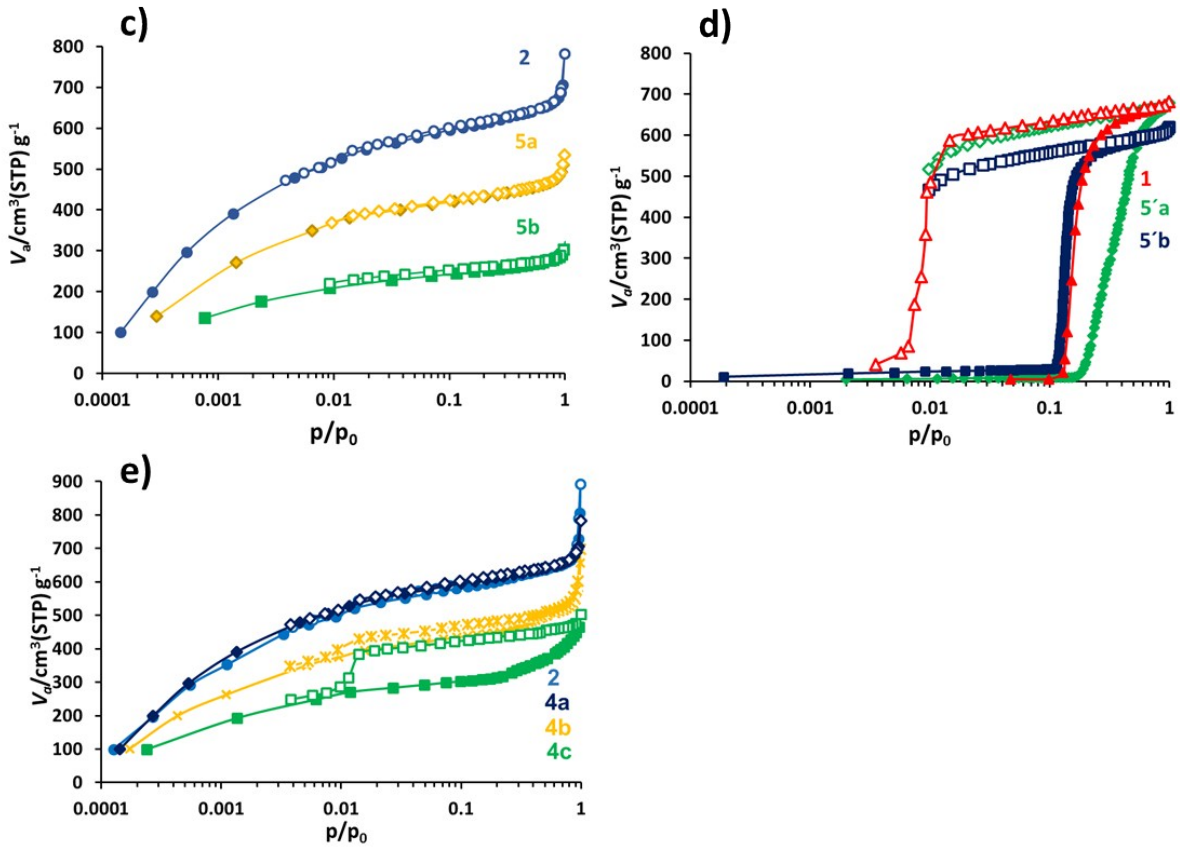


Figure S2. Semilogaritmic plots of nitrogen adsorption isotherms at 77 K for the series **3** (a), **3'** (b), **5** (c), **5'** (d), and **4** (e).

2. Argon adsorption at 87 K.

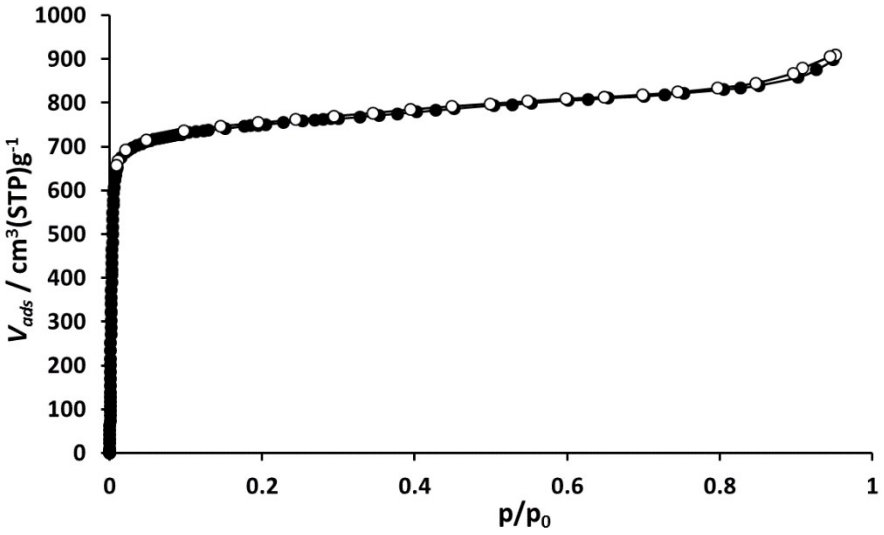


Figure S3. Argon physisorption isotherm for DUT-8(Ni) "rigid" (**2**) at 87 K.

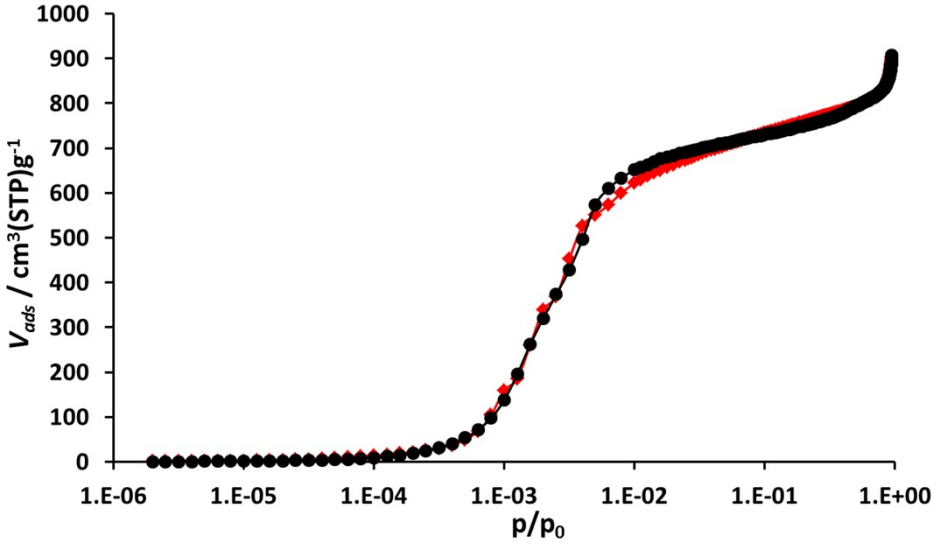


Figure S4. NLDFT fit of the argon adsorption isotherm of DUT-8(Ni) "rigid" (**2**) using zeolite/silica adsorption branch kernel based on a cylindrical pore model. Black line – measured adsorption isotherm, red line – isotherm fit.

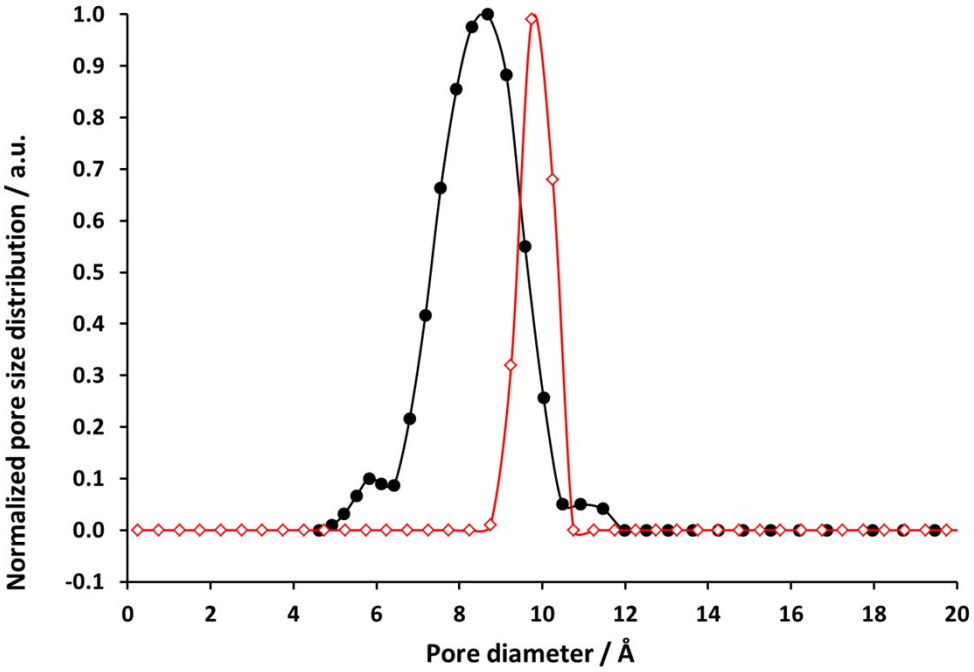


Figure S5. Pore size distribution of DUT-8(Ni) "rigid" (**2**), derived from the argon adsorption isotherm (black) and calculated geometrically using Poreblazer software (red).

3. ^{1}H-NMR

The ratio between the integral intensities of ndc^{2-} and dabco protons, calculated from ^{1}H-NMR spectra amounts to 2.0:0.995 for flexible DUT-8(Ni) and 2.0:1.013 for rigid DUT-8(Ni), which is in good agreement with theoretical composition.

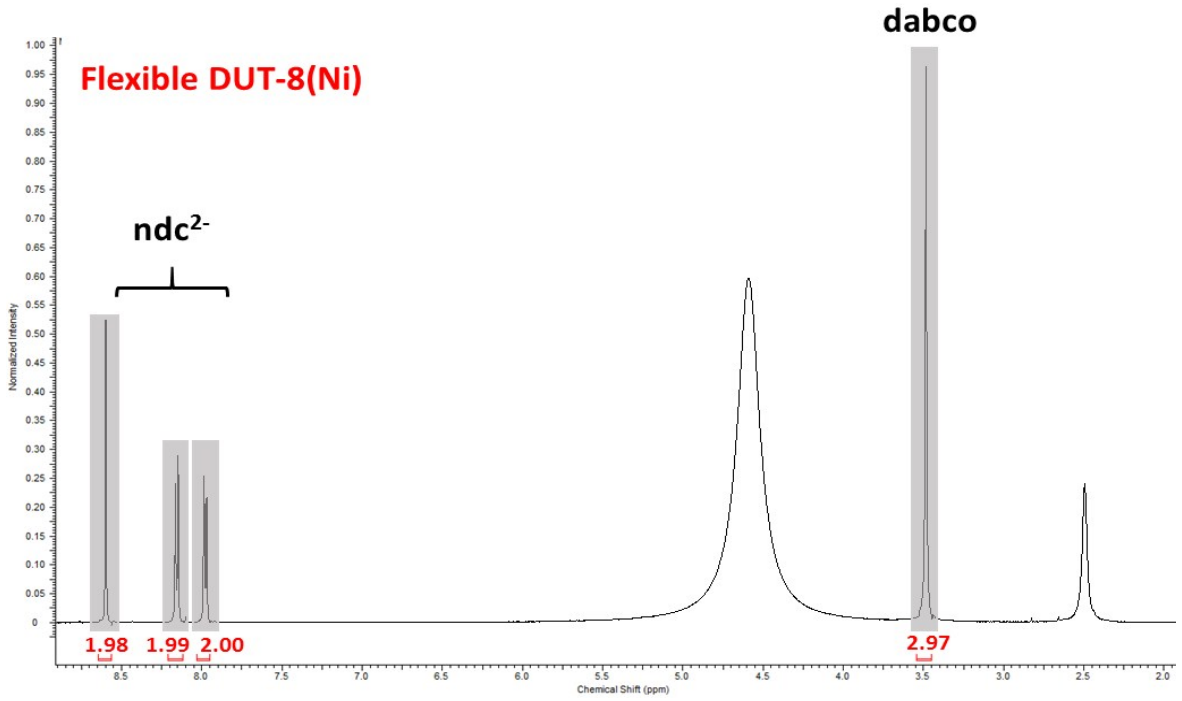


Figure S6. ^{1}H NMR of **1** dissolved in a mixture of dimethyl sulfoxide-d6 and DCl.

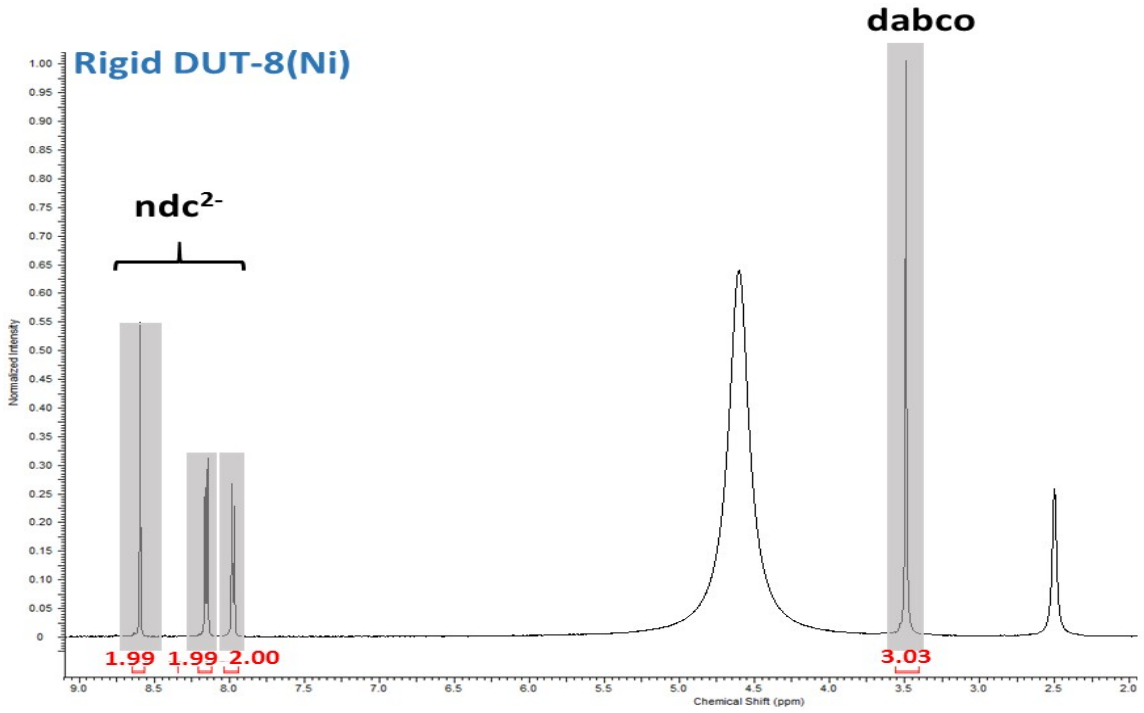


Figure S7. ^{1}H NMR of **2**, dissolved in mixture of dimethyl sulfoxide-d6 and DCl.

4. Elemental analyses

Table S1. Elemental analysis for “flexible” and “rigid” DUT-8(Ni) samples

Element	$Ni_2(ndc)_2dabco$ Calculated content / %	Element content in **1** / %	Element content in **2** / **%**
C	54.35	53.92	53.37
H	3.62	3.57	3.53
N	4.23	4.21	4.33
Ni	17.7	17.6	17.1

5. Thermogravimetric analysis

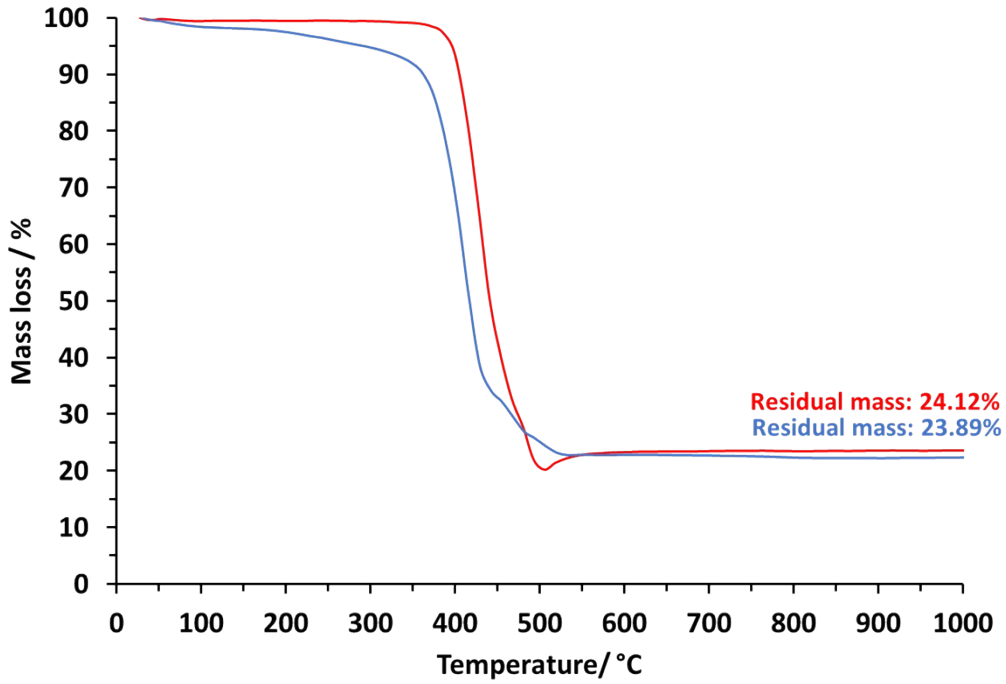


Figure S8. TG analysis performed in synthetic air atmosphere on samples **1** (red) and **2** (blue).

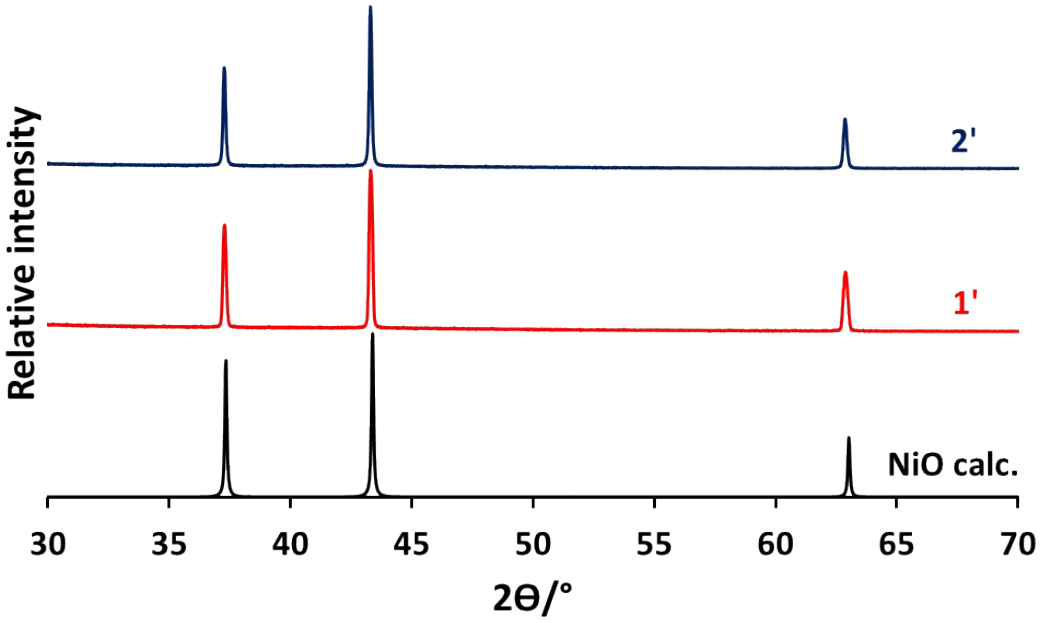


Figure S9. PXRD patterns of the residuals obtained after TG-analysis of **1** and **2**.

6. Scanning electron microscopy

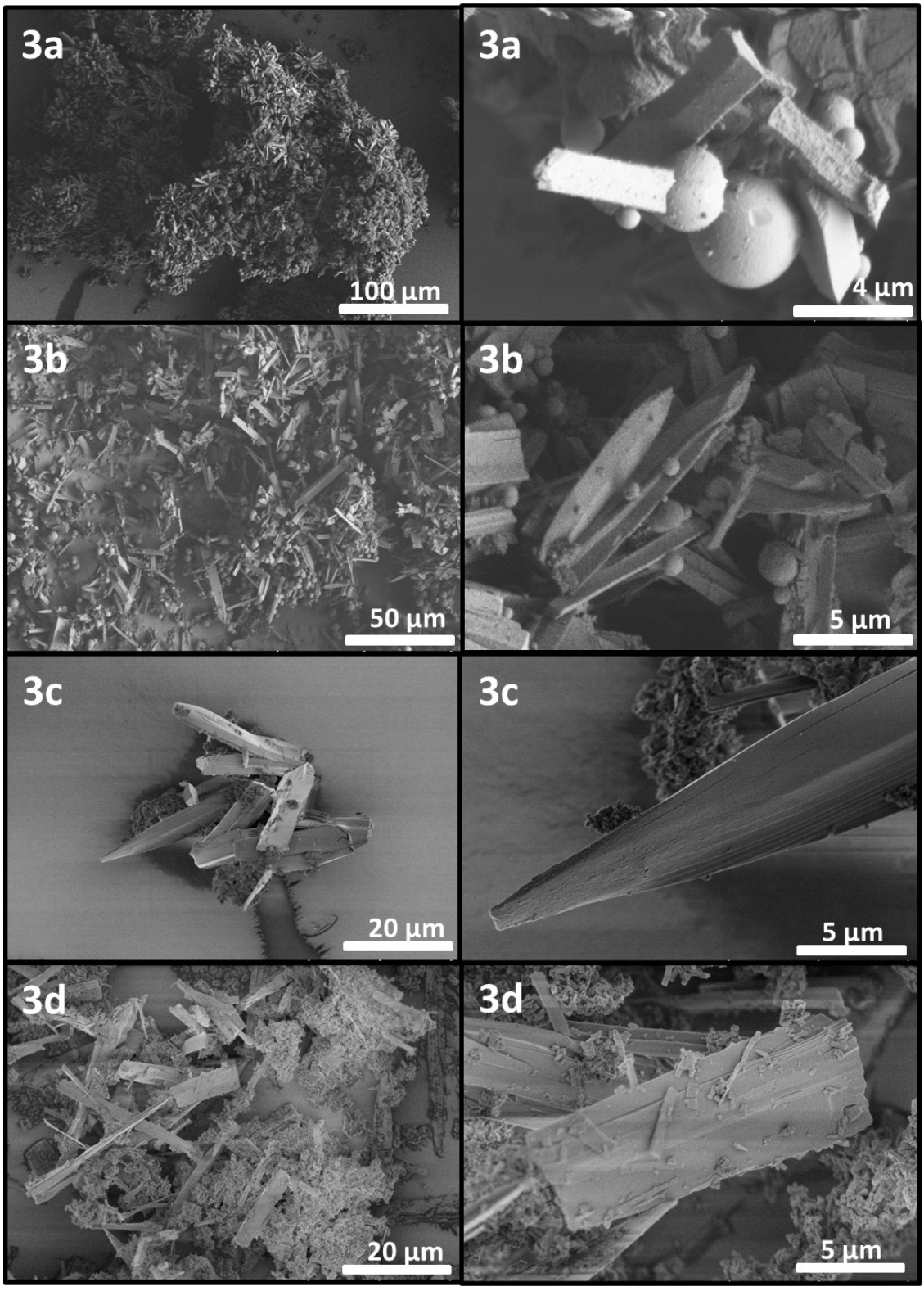


Figure S10. SEM images for the sample series **3**.

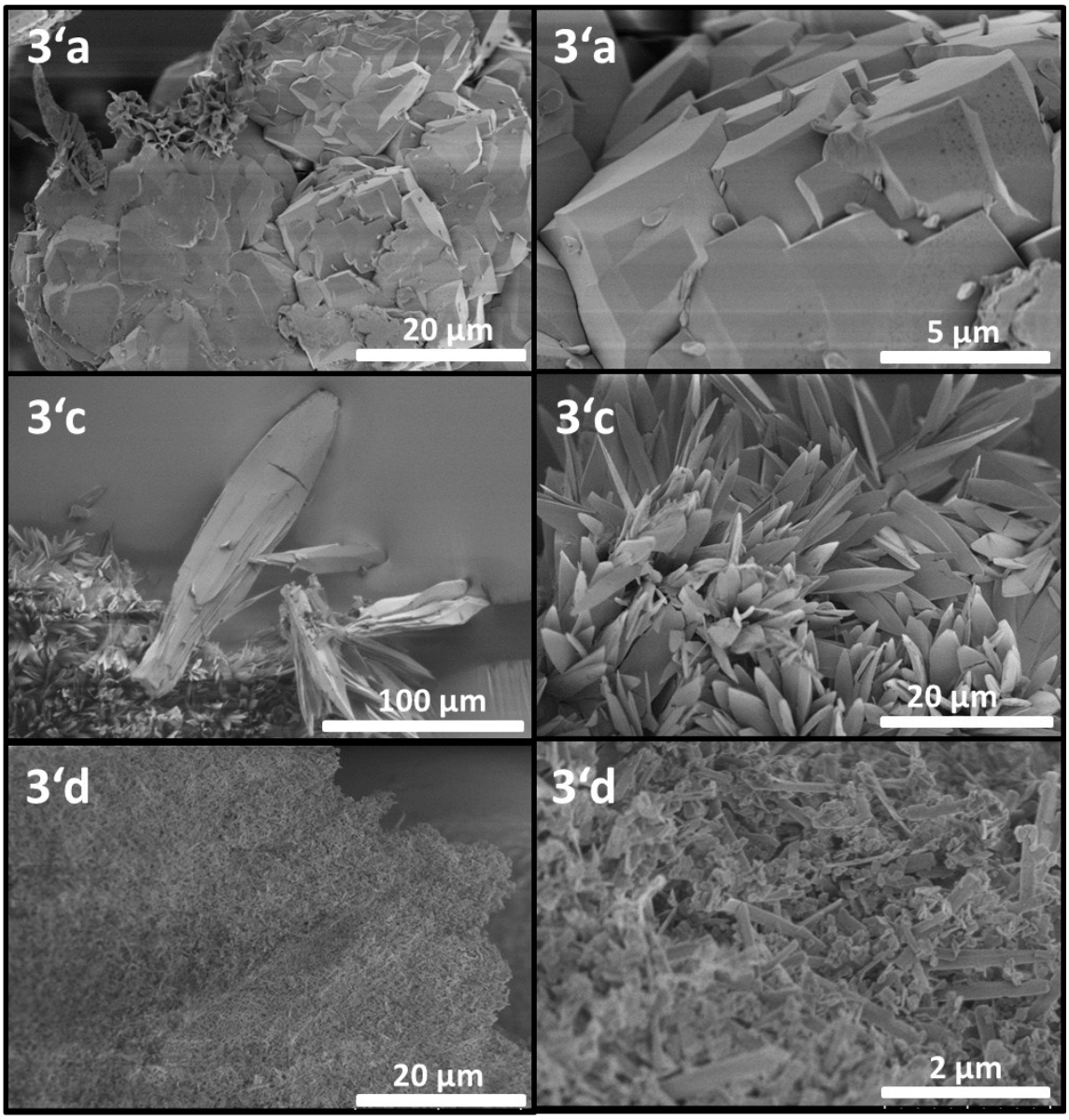


Figure S11. SEM images for sample series **3’**.

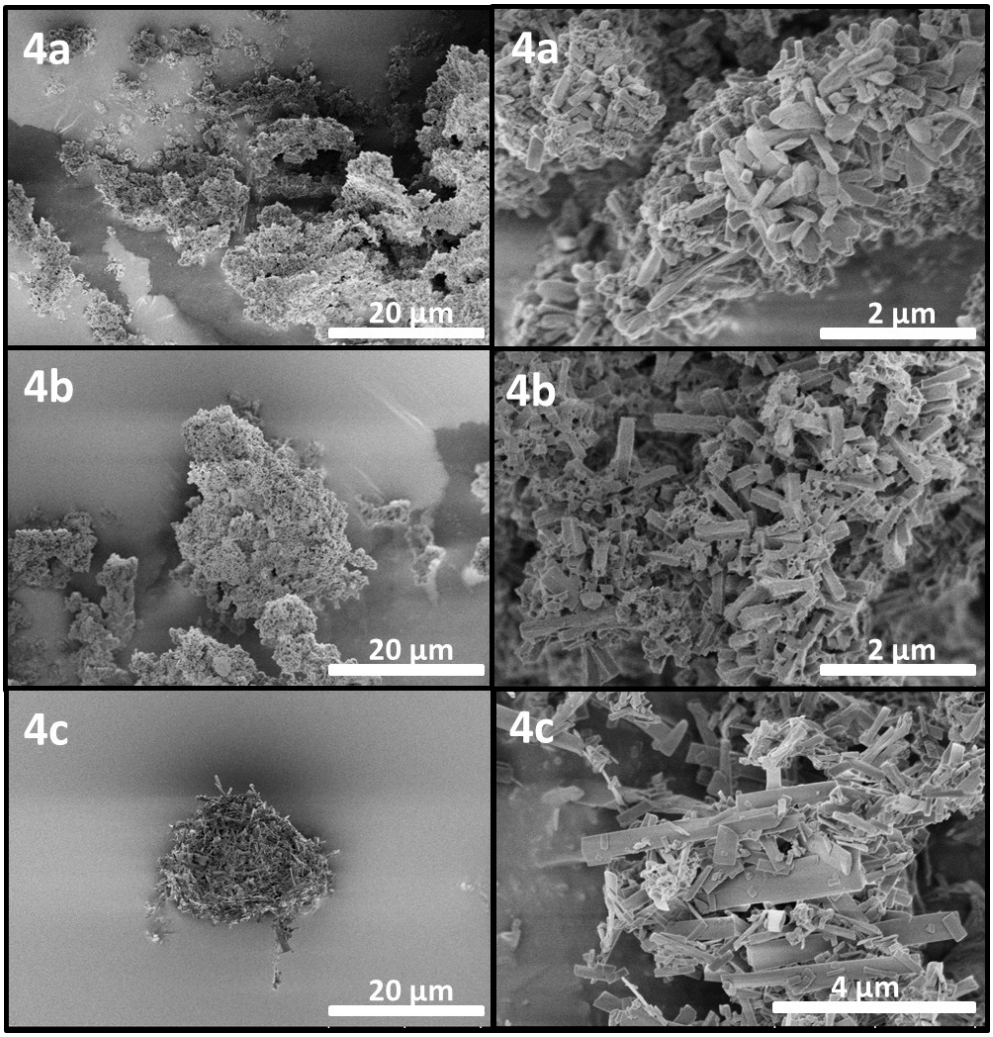


Figure S12. SEM images for the sample series **4**.

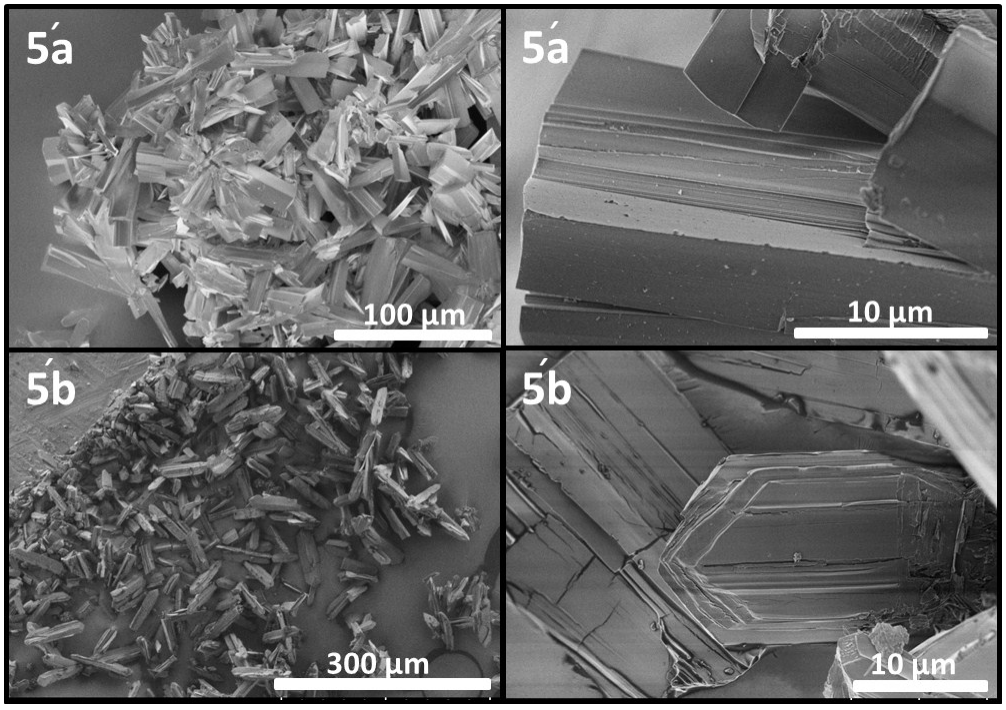


Figure S13. SEM images for the sample series **5´**.

7. IR spectroscopy

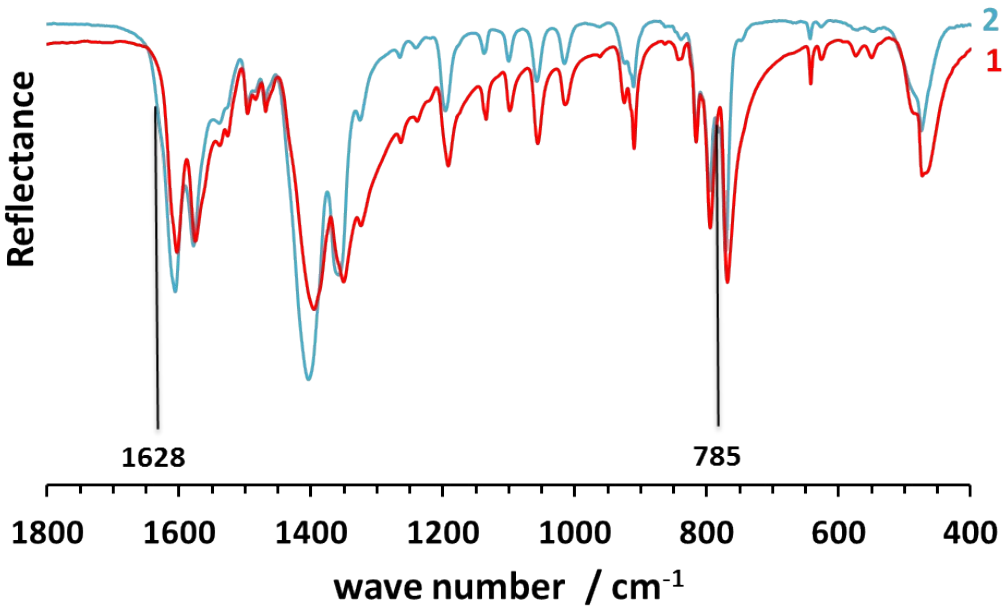


Figure S14. ATR spectra of DUT-8(Ni) “flexible” (1), “rigid” (2).

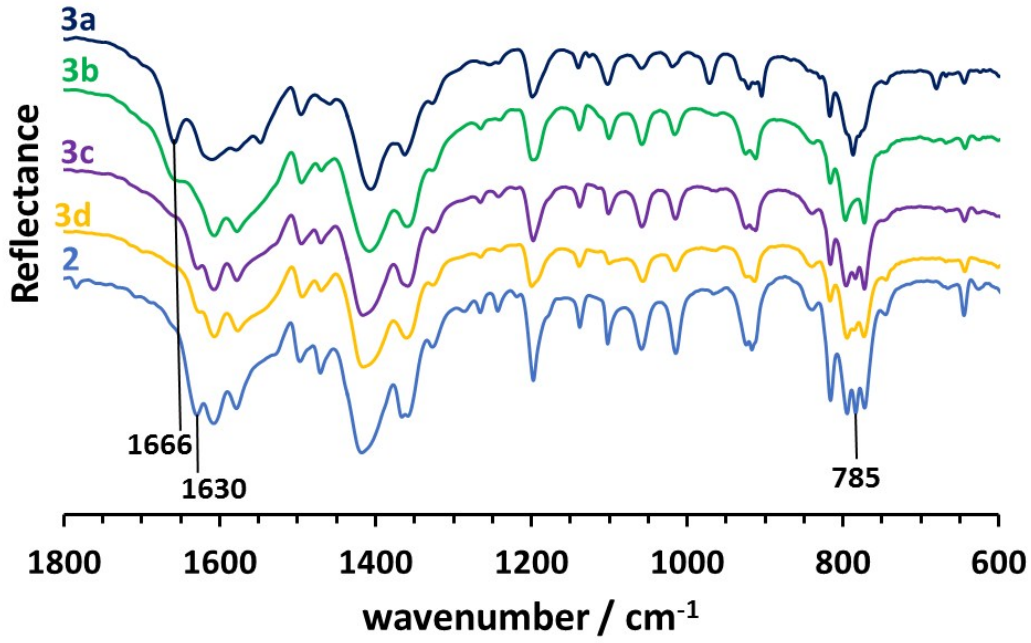


Figure S15. DRIFT spectra of rigid DUT-8(Ni) **2** and derivatives $\mathbf{3}_a$-$\mathbf{3}_d$.

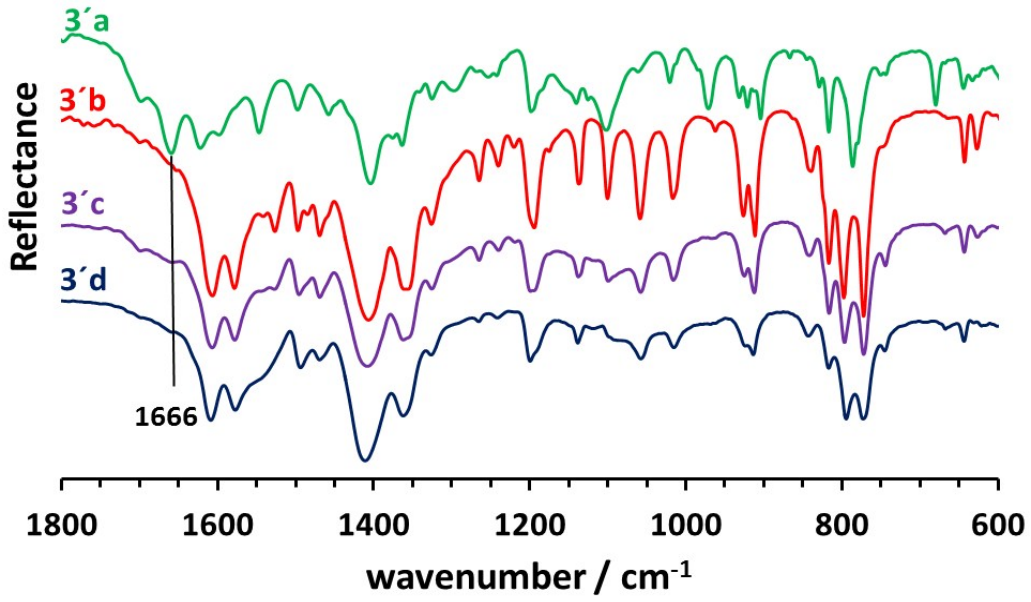


Figure S16. DRIFT spectra of DUT-8(Ni) derivatives **3'$_a$-3'$_d$**.

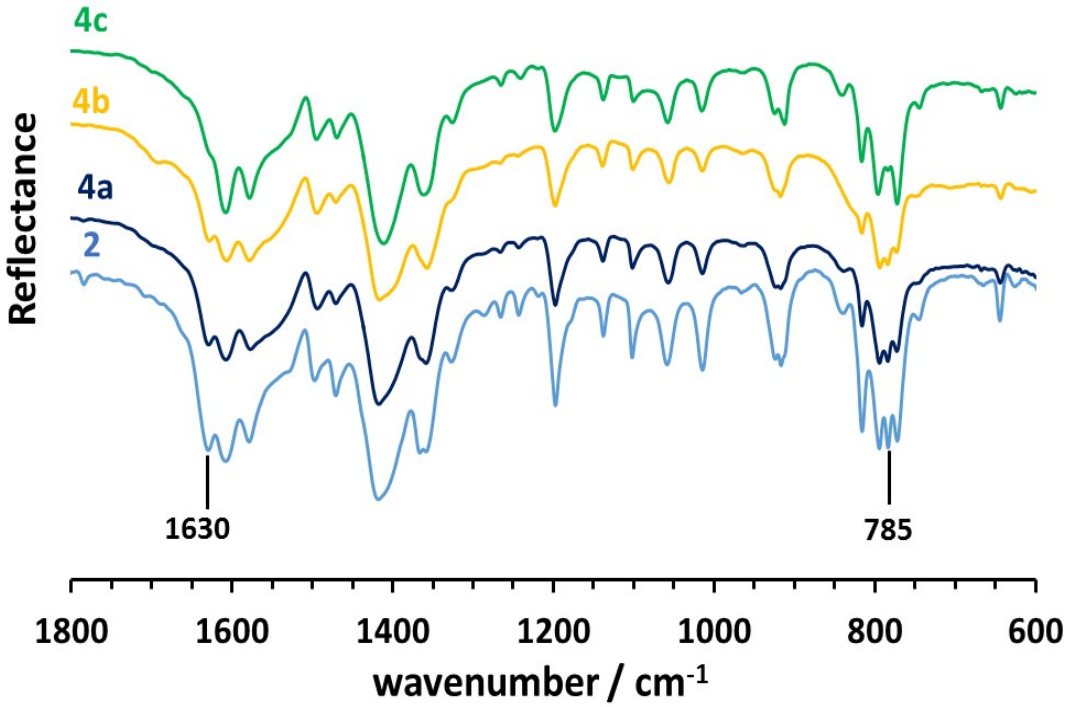


Figure S17. DRIFT spectra of rigid DUT-8(Ni) **2** and its derivatives **4$_a$-4$_c$**.

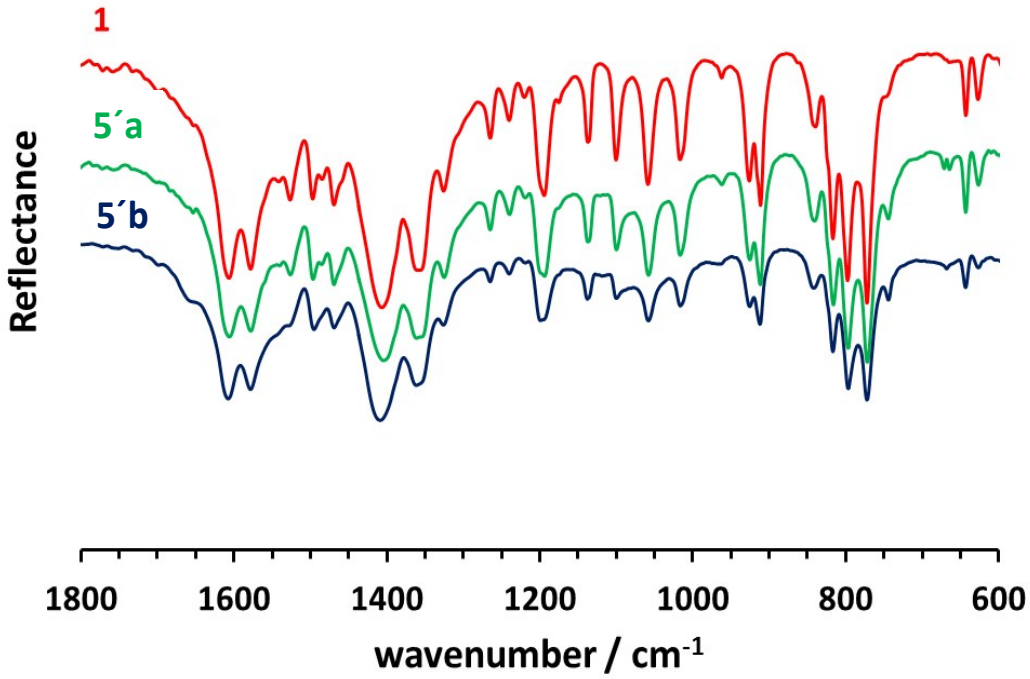


Figure S18. DRIFT spectra of DUT-8(Ni) "flexible" and its derivatives **5´$_a$-5´$_b$**.

8. ***Temperature dependent X-ray diffraction study***

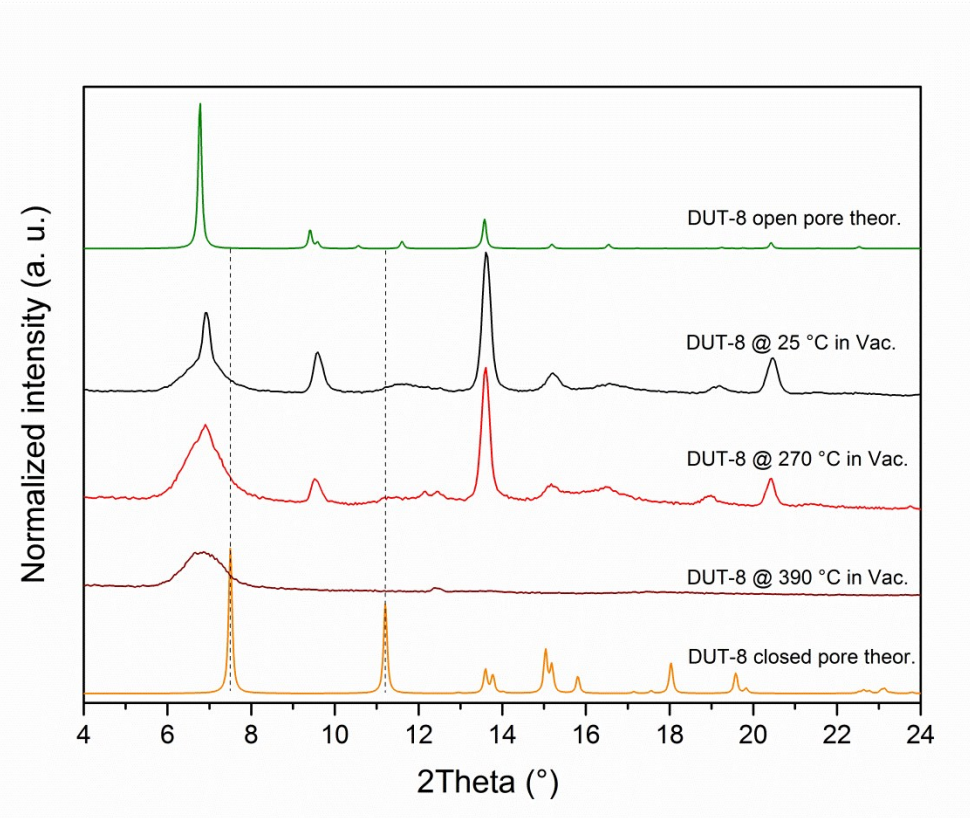


Figure S19. Temperature dependent X-ray diffraction patterns of **2**.