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. Semilogarithmic 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni$_2$(ndc)$_2$dabco Calculated content / %</th>
<th>Element content in 1 / %</th>
<th>Element content in 2 / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>54.35</td>
<td>53.92</td>
<td>53.37</td>
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<tr>
<td>H</td>
<td>3.62</td>
<td>3.57</td>
<td>3.53</td>
</tr>
<tr>
<td>N</td>
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<tr>
<td>Ni</td>
<td>17.7</td>
<td>17.6</td>
<td>17.1</td>
</tr>
</tbody>
</table>

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 3a-3d.
Figure S16. DRIFT spectra of DUT-8(Ni) derivatives 3′<sub>a</sub>-3′<sub>d</sub>.

Figure S17. DRIFT spectra of rigid DUT-8(Ni) 2 and its derivatives 4<sub>a</sub>-4<sub>c</sub>. 
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.