**Supplementary information**

**Amplification of Negative Gas Adsorption in a multivariate framework**

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**1. Materials**

All materials and gases used in the synthesis and analysis in this study were of high purity and summarized in Table S1.

*Table S1. List of chemicals used for the synthesis of ligands and MOFs.*

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS</th>
<th>purity</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>64-19-7</td>
<td>99.9%</td>
<td>Roth</td>
</tr>
<tr>
<td>Acetone extra dry</td>
<td>67-64-1</td>
<td>99.8%</td>
<td>Fischer Scientific</td>
</tr>
<tr>
<td>Copper(II) nitrate hemi(pentahydrate)</td>
<td>19004-19-4</td>
<td>99.9%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>N,N-Dimethylformamide (DMF)</td>
<td>68-12-2</td>
<td>99%</td>
<td>Fischer Scientific</td>
</tr>
</tbody>
</table>

**2. Synthesis and characterization**

The synthesis of all MOF’s was done in preheated Pyrex tubes. The tubes had been preheated in an oven to 80°C while solutions of the linkers and the Copper-(II)-nitrate were prepared. The prepared mixtures were stored at 80°C in an oven for 7 days until the MOF crystals precipitated. Yield was determined based on the resulting linker ratio built into the MOF.

**2.1. DUT-46 and DUT-49**

Both pure MOFs were prepared according to the procedure of Reference (1). Phase purity was confirmed by XRD.

**2.2. MTV-DUT-49-1**

66.6 mg of H$_4$BBCDC and 116.7 mg of H$_4$NBCDC were dissolved in 80 ml of DMF. After complete dissolution 10 ml of AcOH were added to the solution. After that 116 mg of Cu(NO$_3$)$_2$·3H$_2$O dissolved in 20 ml of DMF were added. The resulting reaction mixture was placed in an oven for 7 days for crystallization. After the crystallization was finished the resulting crystals were washed with warm DMF 3 times. The solvent was then changed to acetone to prepare the material for supercritical CO$_2$ drying. Phase Purity was verified by powder XRD. Composition was recalculated from NMR of digested MOF. After supercritical activation and the reaction yields 63.8 mg (34%) of MTV-DUT-49-1.

**2.3. MTV-DUT-49-2**

100 mg of H$_4$BBCDC and 88.3 mg of H$_4$NBCDC were dissolved in 80 ml of DMF. After complete dissolution 10 ml of AcOH have been added to the solution. After that 176 mg of Cu(NO$_3$)$_2$·3H$_2$O dissolved in 20 ml of DMF were added. The resulting reaction mixture was placed in an oven for 7 days.
for crystallization. After the crystallization the resulting crystals were washed with warm DMF 3 times. The solvent was then changed to acetone to prepare the material for supercritical CO$_2$ drying. Phase Purity was verified by powder XRD. Composition was recalculated from NMR of digested MOF. Supercritical activation yields 124.1 mg (49%) of MTV-DUT-49-2

2.4. MTV-DUT-49-3

133 mg of H$_4$BBCDC and 58.7 mg of H$_4$NBCDC were dissolved in 80 ml of DMF. After complete dissolution 10 ml of AcOH were added to the solution. After that 234 mg of Cu(NO$_3$)$_2$$\cdot$3H$_2$O dissolved in 20 ml of DMF were added. The resulting reaction mixture was placed in an oven for 7 days for crystallization. After the crystallization was finished the resulting crystals were washed with warm DMF 3 times. The solvent was then changed to acetone to prepare the material for supercritical CO$_2$ drying. Phase Purity was verified by powder XRD. Composition was recalculated from NMR of digested MOF. Activation with supercritical CO$_2$ yields 84.3 mg (39%).

3. Methods and instrumentation

Synchrotron single crystal X-ray diffraction

Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) patterns were collected on an X-ray powder diffractometer (STOE transmission diffractometer system) using Cu-K$_{\alpha1}$ radiation ($\lambda = 1.54059$ Å), operated at 40 kV and 30 mA and equipped with Mythen 100k detector (DECTRIS). PXRD patterns were collected in $2\theta$ range of 2-70° using a step mode with 6° steps and 120 s/step.

SEM

Scanning electron microscope (SEM) images were taken with a HITACHI SU8020 microscope at an acceleration voltage of 2.0 kV and a working distance of 8.1 mm. The samples were placed on a carbon sample holder and coated with Au to enhance the conductivity.

Gas adsorption isotherms

Nitrogen physisorption was measured using a Quadrasorb (SI, 3P instruments) instrument in a pressure range of 10$^{-3}$ to 1 bar at 77 K. MIL-53(Cr) desolvated samples (around 40-60 mg) were previously activated at 120 °C under vacuum (up to 10$^{-3}$ bar) for 24 h. MIL-53(Cr)-np sample with H$_2$O adsorbed was measured directly without activation. Brunauer-Emmett-Teller (BET) surface areas were calculated using AsiqWin software from the linearized BET plot within the $p/p_0$ pressure range of 0.05–0.25 so that the linear model fit had an R2 value greater than 0.999.

NMR

$^1$H nuclear magnetic resonance (NMR) and $^{13}$C NMR spectra of the reaction solutions were acquired on a Bruker Avance III HD 300 MHz spectrometer and a Bruker DRX-500, 500 MHz spectrometer using 1% DCl in DMSO-$d_6$ as the solvent at 25 °C. The data was processed with the software 1D NMR Processor from the Software package ACDLabs 12.0.

Le Bail refinement

PXRD patterns, measured on DUT-46, DUT-49, and MTV-DUT-49 structures were analysed by Le Bail method. The unit cell parameters for PXRD patterns containing single phase were obtained using indexing procedure in DICVOL91 followed by Le Bail fit using FullProf software using pseudo Voigt profile function including axial divergence asymmetry. The resulted plots and unit cell parameters are given in Figures S1-S5.
Crystal engineering

Structural models were generated using Materials Studio 5.0 software. The crystal structures were simulated in using visualization module and optimized using Forcite Geometry optimization algorithm using Universal Force Field (UFF). PXRD patterns were simulated using Mercury 2023.3.0 software.

Pore size distribution

The pore size distribution was calculated using Zeo++ software. The structural models, obtained from the PXRD analysis were used for the calculations. For calculation of pore size distribution, the hypothetical spherical probe molecule with atomic radius of 1.2 Å (equivalent of helium atom) was used. Default parameters with 100 bins each 0.1 Å in size were used for calculation in the range between 0 and 100 Å.

In situ-PXRD in parallel to gas physisorption

In situ PXRD patterns on MTV-DUT-49-3 in parallel to methane physisorption at 111 K were measured using home-built dedicated instrumentation (DYNADIFF®), based on Empyrean-2 powder X-ray diffractometer (ω–2θ goniometer, alpha1 system) using a customized setup based on ARS DE-102 closed cycle helium cryostat (T = 30–300 ± 0.1 K) and adsorption cell, built of 1.33” CF-flange and Beryllium dome. The cell was connected to the low-pressure port of the BELSORP-max (Microtrac MRB) volumetric adsorption instrument. The TTL-trigger was used for establishing the communication between BELSORP-max and Data Collector software and ensure the measurement of adsorption isotherm and PXRD patterns in automated mode. The diffraction experiments were performed using ω–2θ scans in transmission geometry in the range of 2θ = 2–50°. Parallel beam optics (W/Si mirror, hybrid 2xGe(220) monochromator, 4 mm mask, primary divergence and secondary antiscatter slits with ¼° opening) was used for the data collection. Pixcel-3D detector in 1D scanning mode (255 active channels) was used for recording of the scattered intensities. Selected pressures of methane were dosed in the cell and equilibrated for at least 15 minutes before measurements of PXRD patterns. PXRD patterns and selected points on the isotherm are shown in the Figs. S13 – S18.
Supplementary Figures

**Figure S1.** Le Bail fit of PXRD measured on desolvated DUT-46 ($Fm\overline{3}m$, $a = 43.4910(16)$ Å, $V = 82262(5)$ Å³, $R_{wp} = 0.139$, $R_p = 0.0993$)

**Figure S2.** Le Bail fit of PXRD measured on desolvated DUT-49 ($Fm\overline{3}m$, $a = 46.4378(10)$ Å, $V = 100139(4)$ Å³, $R_{wp} = 0.0522$, $R_p = 0.0394$)
Figure S3. Le Bail fit of PXRD measured on desolvated MTV-DUT-49-1 (*Fm*3̅*m*, *a* = 44.1756(10) Å, *V* = 86208(4) Å³, *R_w* = 0.0459, *R_p* = 0.0347)

Figure S4. Le Bail fit of PXRD measured on desolvated MTV-DUT-49-2 (*Fm*3̅*m*, *a* = 44.7868 (14) Å, *V* = 89836(5) Å³, *R_w* = 0.0443, *R_p* = 0.0350)
**Figure S5.** Le Bail fit of PXRD measured on desolvated MTV-DUT-49-3 ($Fm\overline{3}m$, $a = 45.4619(10)$ Å, $V = 93960(4)$ Å$^3$, $R_{wp} = 0.0449$, $R_p = 0.0342$)

**Figure S6.** SEM images of DUT-46 (a), MTV-DUT-49-1 (b), MTV-DUT-49-2 (c), MTV-DUT-49-3 (d) and DUT-49 (e).
Figure S7. $^1$H NMR of digested DUT-46

Figure S8. $^1$H NMR of digested MTV-DUT-49-1

Figure S9. $^1$H NMR of digested MTV-DUT-49-2
Figure S10. $^1$H NMR of digested MTV-DUT-49-3

Figure S11. $^1$H NMR of digested DUT-49
Figure S12. Simulated ordered crystal structures containing different ratio of NBCDC and BBCDC linkers: a) $I4/m$, $a = 32.55$ Å, $c = 40.78$ Å; NBCDC:BBCDC = 2:1; b) $R\bar{3}m$, $a = 32.95$ Å, $c = 71.78$ Å; NBCDC:BBCDC = 1:1; c) $Pbca$, $a = 43.38$ Å, $b = 43.77$ Å, $c = 48.64$ Å; NBCDC:BBCDC = 1:2.
Figure S13. Le Bail fit of PXRD measured on MTV-DUT-49-3 at 111 K in vacuum ($Fm\bar{3}m$, $a = 45.348(2)$ Å, $V = 93255(5)$ Å$^3$, $R_{wp} = 0.1141$, $R_p = 0.0909$)

Figure S14. Le Bail fit of PXRD measured on MTV-DUT-49-3 at 111 K loaded at $p_{eq} = 12 $ kPa of methane in adsorption ($Pa\bar{3}$, $a = 35.877(1)$ Å, $V = 46179(7)$ Å$^3$, $R_{wp} = 0.0665$, $R_p = 0.0519$)
**Figure S15.** Le Bail fit of PXRD measured on MTV-DUT-49-3 at 111 K loaded at $p_{eq} = 95$ kPa of methane upon adsorption ($Fm\overline{3}m$, $a = 45.412(2)$ Å, $V = 93651(8)$ Å$^3$, $R_{wp} = 0.0843$, $R_p = 0.0657$)

**Figure S16.** Le Bail fit of PXRD measured on MTV-DUT-49-3 at 111 K loaded at $p_{eq} = 25$ kPa of methane in desorption ($Fm\overline{3}m$, $a = 45.255(2)$ Å, $V = 92683(7)$ Å$^3$, $R_{wp} = 0.0763$, $R_p = 0.0600$)
Figure S17. Le Bail fit of PXRD measured on MTV-DUT-49-3 at 111 K loaded at $p_{eq} = 5$ kPa of methane in desorption ($Pa\bar{3}$, $a = 35.722(2)$ Å, $V = 45583(6)$ Å$^3$, $R_{wp} = 0.0690$, $R_p = 0.0545$)

Figure S18. Le Bail fit of PXRD measured on MTV-DUT-49-3 at 111 K loaded at $p_{eq} = 0.1$ kPa of methane in desorption ($Pa\bar{3}$, $a = 35.721(2)$ Å, $V = 45580(6)$ Å$^3$, $R_{wp} = 0.0688$, $R_p = 0.0543$)
References