Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Assembly of metal-organic polyhedra into highly porous frameworks for ethene delivery.

Ulrich Stoeck, Irena Senkovska, Volodymyr Bon, Simon Krause, and Stefan Kaskel*

Department of Inorganic Chemistry, Technische Universität Dresden, Bergstraße 66,
D-01062 Dresden, Germany.

Index

1. General remarks

$Cu(NO_3)_2 \cdot 3\ H_2O$ (Sigma Aldrich), *N,N*-dimethylformamide (Fisher Scientific), and ethanol (abs.) (VWR Prolabo) were used as received.

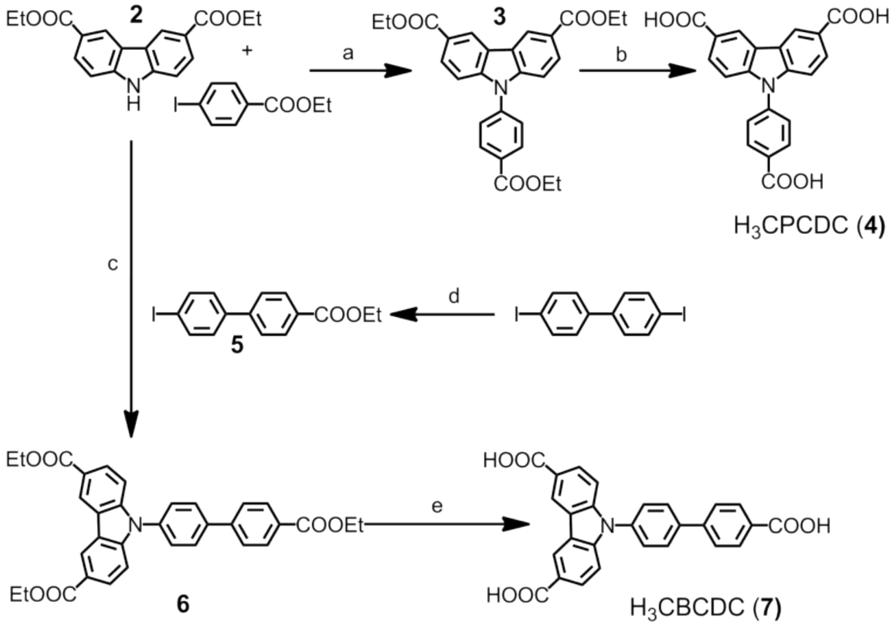
Powder X-ray diffraction (PXRD) patterns were collected in transmission geometry with a STOE STADI P diffractometer operated at 40 kV and 30 mA with monochromated Cu-Kα_1 ($\lambda = 0.15405$ nm) radiation and with a scan speed of 30 s/step and a step size of 0.1°.

The supercritical drying process was performed in the following manner: Prior to the supercritical drying, samples were washed thoroughly with DMF/EtOH (1:1) and placed in dry acetone. The acetone was exchanged 10 times over 2 days. The samples were placed in a Jumbo Critical Point Dryer 13200J AB (SPI Supplies) and purged 20 times with liquid carbon dioxide (purity: 99.995%) at ~ 15 °C over a time period of about 96 hours. After that period of time the temperature and pressure was raised beyond the critical point of CO_2. The resulting supercritical CO_2 was released slowly within a time frame of 3 h. The dried samples were transferred to a glove box.

Prior to all physisorption measurements the samples were activated using supercritical CO_2 and additionally evacuated at 50 °C for 24 h. N_2 physisorption isotherms were measured up to 1 bar using a Quantachrome Autosorb 1C apparatus. High pressure H_2 adsorption measurement at -196 °C up to 110 bar was performed using approximately 0.3 g sample on a volumetric BELSORP-HP apparatus. High pressure methane, ethene, and CO_2 adsorption was studied using a magnetic suspension balance (Rubotherm Co.). The total gas uptake was calculated by: $N_{\mathrm{total}} = N_{\mathrm{excess}} + \rho_{\mathrm{bulk}}V_{\mathrm{pore}}$, where ρ_{bulk} is equal to the density of compressed gas at the temperature and pressure of measurement, and V_{pore} was obtained from the N_2 sorption isotherm at 77 K.

High purity gases were used (N_2: 99.999 %, H_2: 99.999 %, CH_4: 99.5 %, CO_2: 99.995 %, C_2H_4 99.9 %). Thermogravimetric analyses (TGA) were carried out under air atmosphere using a Netzsch STA 409 thermal analyzer. Elemental analysis (C, H, N, O) was performed with a Hekatech EA 3000 Euro Vector CHNS analyzer. The metal content of the MOF compounds were determined with an Vista RL ICP-OES from Varian Inc.

2. Synthetic Procedures for H_3CPCDC, H_3CBCDC, DUT-75 and DUT-76



Scheme 1. a) CuI, K_2CO_3, L-proline, DMSO, 90 °C, 65 %; b) KOH, THF, MeOH, H_2O, 60 °C, 99 %; c) CuI, K_2CO_3, L-proline, DMSO, 90 °C, 67 %; d) 1. ^{i}PrMgCl, CO_2, THF; 2. EtOH, H_2SO_4, 73 %; e) KOH, THF, MeOH, H_2O, 60 °C, 99 %.

Synthesis of 3,6-dibromocarbazol (1)

9H-carbazol (150.0 g, 0.9 mol) was dissolved in 2 L of THF at 40 °C. After adding *N*-bromosuccinimide (351 g, 1,97 mol) the mixture was stirred maintaining the temperature. After 20 h the solution was concentrated in vacuum and reduced to one third of its initial volume. Following the addition of water (1.5 L) the raw product precipitated from the solution. The solid was filtered off and thoroughly washed with water. Subsequent re-crystallization from dichloromethane/*n*-hexane yielded the pure product.

Yield: 209.9 g (0.65 mol, 75 %).

Elemental analysis for $C_{12}H_7Br_2N$: calculated: C: 44.35 %, H: 2.17 %, N: 4.34 %, Br. 49.17 %; found: C: 44.27 %, H: 2.09 %, N: 4.41 %, Br. 51.12 %.

^{1}H-NMR (600MHz, d$_6$-DMSO):
δ (in ppm) = 7.47 (d, J = 8.7 Hz, 2H), 7.53 (dd, J = 8.7 Hz, J = 1.9 Hz, 2H), 8.43 (d, J = 1.9 Hz, 1H), 11.6(s, 1H).

^{13}C-NMR und DEPT (150MHz, d$_6$-DMSO):
δ (in ppm) = 111.02 (C_q), 113.22 (CH), 123.34 (CH), 123.41 (C_q), 128.74 (CH) 138.82 (C_q).

Synthesis of diethyl 9H-carbazole-3,6-dicarboxylate (2)

3,6-dibromocarbazole (**1**) (25.0 g, 80 mmol) was dissolved in 1 L of dry THF. The solution was cooled to -78 °C and *n*-BuLi (32 ml, 2.5 mol/l, 80 mmol) was added *via* a syringe pump. After stirring for 20 min chlorotrimethylsilane (10.2 ml, 80 mmol) was added. Afterwards the cooling bath was removed and the mixture was allowed to stir at room temperature for 1 h. The reaction mixture was re-cooled to -78 °C and *t*-BuLi (190 ml, 1.7 mol/l, 320 mmol) was added *via* a syringe pump. The cooling bath was removed and the mixture was stirred for 3 h during which it was allowed to warm up to 0 °C. Subsequent addition of dry CO_2 gas was followed by the precipitation of the raw carbazole acid with 2 M hydrochloric acid. The precipitate was filtered off and thoroughly washed with water. The solid was suspended in 1 l of ethanol. After the addition of 3 ml of concentrated H_2SO_4 the mixture was refluxed for 24 h. The solvent was removed and the resulting solid dissolved in ethylacetate. The solution was washed with saturated sodium bicarbonate solution until it displayed a neutral pH. After removing the solvent the raw product was purified using flash chromatography (dichloromethane/ethylacetate 15:1).

Yield: 16.7 g (54 mmol, 67 %).

Elemental analysis for $C_{18}H_{17}NO_4$: calculated: C: 69.44 %, H: 5.50 %, N: 4.50 %; found: C: 69.71 %, H: 5.63 %, N: 4.37 %.

^{1}H-NMR (600MHz, d$_6$-DMSO):
δ (in ppm) = 1.37 (tr, J = 7.2 Hz, 6H), 4.35 (q, J = 7.2 Hz, 4H), 7.61 (d, J = 8.7 Hz, 2H), 8,06 (dd, J = 8.7 Hz, J = 1.9 Hz, 2H), 8.89 (d, J = 1.9 Hz, 2H), 12.09 (s, 1H).

^{13}C-NMR und DEPT (150MHz, d$_6$-DMSO):
δ (in ppm) = 14.38 (CH_3), 60.39 (CH_2), 111.31 (CH), 121.24 (C_q), 122.29 (C_q), 122.77 (CH), 127.46 (CH), 143.25 (C_q), 166.33 (C_q).

Synthesis of diethyl 9-(4-(ethoxycarbonyl)phenyl)-9H-carbazole-3,6-dicarboxylate (3)

A Schlenk flask was charged with diethyl *9H*-carbazole-3,6-dicarboxylate (**2**) (6.0 g, 19.3 mmol), ethyl-4-iodobenzoate (6.4 g, 23.1 mmol), copper(I) iodide (375 mg, 1.9 mmol), L-proline (444 mg, 3.9 mmol) and K_2CO_3 (533 mg, 3.9 mmol). After adding 50 mL DMSO the resulting suspension was degassed in vacuum (10^{-3} mbar) for 30 min. The flask was backfilled with argon and heated to 90 °C for 3 d. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$ and the solvent was removed afterwards. The solid residue was purified using flash chromatography (*n*-hexane/ethylacetate 3:1).

Yield: 5.76 g (12.5 mmol, 65 %).

Elemental analysis for $C_{27}H_{25}NO_6$: calculated: C: 70.58 %, H: 5.48 %, N: 3.05 %; found: C: 70.71 %, H: 5.42 %, N: 3.02 %.

^{1}H-NMR (600MHz, $CDCl_3$):
δ (in ppm) = 1.45 (tr, J = 7.3 Hz, 3H), 1.47 (tr, J = 7.3 Hz, 6H), 4.45 (q, J = 7.3 Hz, 4H), 4.46 (q, J = 7.3 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 8.16 (dd, J = 8.5 Hz, 1.6 Hz, 2H), 8.33 (d, J = 8.5 Hz, 2H), 8.92 (d, J = 1.6 Hz, 2H).

^{13}C-NMR und DEPT (150MHz, $CDCl_3$):
δ (in ppm) = 14.37 (CH_3), 14.48 (CH_3), 61.00 (CH_2), 61.45 (CH_2), 109.67 (CH), 123.06 (CH), 123.43 (C_q), 123.58 (C_q), 126.62 (CH), 128.36 (CH), 130.27 (C_q), 131.59 (CH), 140.51 (C_q), 143.64 (C_q), 165.62 (C_q), 166.85 (C_q).

Synthesis of 9-(4-carboxyphenyl)-9H-carbazole-3,6-dicarboxylic acid (4)

Diethyl 9-(4-(ethoxycarbonyl)phenyl)-*9H*-carbazole-3,6-dicarboxylate (**3**) (5 g, 10.9 mmol) was dissolved in 100 mL THF. After the addition of 100 mL methanol and 50 mL of 2 M KOH solution the resulting mixture was stirred at a temperature of 60 °C for 24 h. The organic solvents were removed and the remaining basic solution was neutralized. The precipitated solid was filtered off and was washed thoroughly with water.

Yield: 4.06 g (10.8 mmol, 99 %)

Elemental analysis for $C_{21}H_{13}NO_6$: calculated: C: 67.20 %, H: 3.49 %, N: 3.73 %; found: C: 67.22 %, H: 3.37 %, N: 3.60 %.

^{1}H-NMR (600MHz, d_6-DMSO):
δ (in ppm) = 7,51 (d, J = 8,3 Hz, 2H), 7,81 (dd, J = 8,3 Hz, 2H), 8,08 (dd, J = 8,7 Hz, J = 1,5 Hz, 2H), 8,25 (d, J = 8,7 Hz, 2H), 8,95 (d, J = 1,5 Hz, 2H)

^{13}C-NMR und DEPT (150MHz, d_6-DMSO):
δ (in ppm) = 110,11 (CH), 122,91 (C_q), 123,13 (CH), 123,89 (C_q), 126,89 (CH), 128,49 (CH), 130,55 (C_q), 131,53 (CH), 139,80 (C_q), 143,09 (C_q), 166,74 (C_q), 167,69 (C_q).

Synthesis of ethyl 4'-iodo-(1,1'-biphenyl)-4-carboxylate (5)

An oven-dryed flask was charged with 4,4‘-diiodobiphenyl (20 g, 49.26 mmol) under argon atmosphere. The solid was dissolved in 500 mL of dry THF and the resulting solution was cooled down to 0 °C. Commercial isopropyl magnesium chloride solution (2M, 25 mL, 50 mmol) was slowly added using syringe pump. While stirring the reaction for an hour, the mixture was allowed to warm up to room temperature. Subsequent addition of dry CO_2 gas was followed by the precipitation of the raw acid with hydrochloric acid (2 M, 500 mL). The solid was filtered off and washed thoroughly with water. Subsequently the raw acid was suspended in 500 mL of ethanol and 3 mL of concentrated H_2SO_4 were added. The mixture was refluxed for 24 h. After completion of the reaction the solvent was removed and the solid residue was taken up dichloromethane and was washed with aqueous $NaHCO_3$ solution to remove the sulfuric acid. After drying of the organic phase the solvent was removed. The resulting raw product was purified by flash chromatography (DCM/*n*-hexane 1:1).

Yield: 12.66 g (36 mmol, 73 %).

Elemental analysis for $C_{15}H_{13}IO_2$: calculated: C: 51.16 %, H: 3.72 %; found: C: 51.12 %, H: 3.68 %.

^{1}H-NMR (600MHz, d_6-DMSO):
δ (in ppm) = 1,33 (tr, J = 7,2 Hz, 3H), 4,33 (q, J = 7,2 Hz, 2H), 7,53 (d, J = 8,7 Hz, 2H), 7,80 (d, J = 8,7 Hz, 2H), 7,85 (d, J = 8,7 Hz, 2H), 8,02 (d, J = 8,7 Hz, 2H)

^{13}C-NMR und DEPT (150MHz, d_6-DMSO):
δ (in ppm) = 14,21 (CH_3), 60,83 (CH_2), 95,16 (C_q), 126,79 (CH), 126,89 (CH), 129,07 (C_q), 129,12 (CH), 129,86 (CH), 137,89 (CH), 138,33 (C_q), 143,50 (C_q), 165,49 (C_q).

Synthesis of diethyl 9-(4'-(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)-9H-carbazole-3,6-dicarboxylate (6)

A Schlenk flask was charged with diethyl *9H*-carbazole-3,6-dicarboxylate (**2**) (6.0 g, 19.3 mmol), ethyl 4'-iodo-(1,1'-biphenyl)-4-carboxylate (**5**) (8.14 g, 23.1 mmol), copper(I) iodide (375 mg, 1.9 mmol), L-proline (444 mg, 3.9 mmol) and K_2CO_3 (533 mg, 3.9 mmol). After adding 70 mL DMSO the resulting suspension is degassed in vacuum (10^{-3} mbar) for 30 min. The flask was backfilled with argon and heated to 90 °C for 3 d. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$ and the solvent was removed afterwards. The solid residue was purified using flash chromatography (toluene/ethylacetate 7:1).

Yield: 6.92 g (12.9 mmol, 67 %)

Elemental analysis for $C_{33}H_{29}NO_6$: calculated: C: 74.00 %, H: 5.46 %, N: 2.62 %; found: C: 74.02 %, H: 5.67 %, N: 2.48 %.

^{1}H-NMR (600MHz, d_6-DMSO):
δ (in ppm) = 1,43 (tr, J = 7,1 Hz, 3H), 1,47 (tr, 7,1 Hz, 6H), 4,43 (q, J = 7,1 Hz, 2H), 4,46 (q, J = 7,1 Hz, 4H), 7,44 (d, J = 8,7 Hz, 2H), 7,65 (d, J = 8,7 Hz, 2H), 7,76 (d, J = 8,7 Hz, 2H), 7,89 (d, J = 8,7 Hz, 2H), 8,17 (dd, J=8,7 Hz, J=1,6 Hz; 2H), 8,18 (d, J=8,7 Hz, 2H), 8,93 (d, J = 1,6 Hz, 2H)

^{13}C-NMR und DEPT (150MHz, d_6-DMSO):
δ (in ppm) = 14,36 (CH_3), 14,49 (CH_3), 60,94 (CH_2), 61,12 (CH_2), 109,74 (CH), 123,02 (CH), 123,22 (C_q), 123,26 (C_q), 127,06 (CH), 127,46 (CH), 128,24 (CH), 129,01 (CH), 129,89 (C_q), 130,29 (CH), 136,34 (C_q), 140,22 (C_q), 144,07 (C_q), 144,11 (C_q), 166,35 (C_q), 166,96 (C_q).

Synthesis of diethyl 9-(4'-carboxy-[1,1'-biphenyl]-4-yl)-9H-carbazole-3,6-dicarboxylic acid (7)

Diethyl 9-(4'-(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)-*9H*-carbazole-3,6-dicarboxylate (**6**) (5 g, 9.3 mmol) was dissolved in 150 mL THF. After the addition of 150 mL methanol and 100 mL of 2 M KOH solution the resulting mixture was stirred at a temperature of 60 °C for 24 h. The organic solvents were removed and the remaining basic solution was neutralized. The precipitated solid was filtered off and was washed thoroughly with water.

Yield: 4.19 g (9.3 mmol, 99 %).

Elemental analysis for $C_{27}H_{14}NO_6$: calculated: C: 71.84 %, H: 3.80 %, N: 3.1 %; found: C: 71.49 %, H: 3.72 %, N: 2.96 %.

^{1}H-NMR (600MHz, d_6-DMSO):

δ (in ppm) = 7,51 (d, J = 8,7 Hz, 2H), 7,77 (d, J = 7,9 Hz, 2H), 7,94 (d, J = 7,9 Hz, 2H), 8,04 (d, J = 8.3 Hz, 2H), 8,07 (d, J = 8,3 Hz, 2H), 8,10 (dd, J = 8,7 Hz, J = 1,9 Hz, 2H), 8,98 (d, J = 1,9 Hz, 2H), 12,90 (s, 3H).

^{13}C-NMR und DEPT (150MHz, d_6-DMSO):

δ (in ppm) = 110,06 (CH), 122,68 (C_q), 123,11 (CH), 123,57 (C_q), 127,11 (CH), 127,57 (CH), 128,41 (CH), 128,96 (CH), 130,13 (C_q), 130,18 (CH), 135,87 (C_q), 139,12 (C_q), 143,26 (C_q), 143,46 (C_q), 167,17 (C_q), 167,70(C_q).

Synthesis of $Cu_3(CPCDC)_2$ (DUT-75)

9-(4-carboxyphenyl)-*9H*-carbazole-3,6-dicarboxylic acid (**4**) (1.0 g, 2.66 mmol) $Cu(NO_3)_2 \cdot 3\ H_2O$ (1.03, 2.66 mmol) were dissolved in 90 mL of a mixture of DMF and ethanol (1:1). After the addition of 10 mL (175 mmol) glacial acetic acid the resulting solution was divided in portion of 10 mL each the are and transfered into Pyrex® tubes and heated to 80 °C for 2 d. After cooling the reaction mixtures the crystals were collected in a single vessel. The combined solid was washed thoroughly with fresh solvent and afterwards exchanged with dry acetone. The exchanged crystals were dryed using supercritical carbon dioxide. For the determination of the yield, dryed DUT-75 was heated to 180 °C in vacuum for two days.

Yield: 709 mg (0.76 mmol, 57 %).

Elemental analysis for $Cu_3C_{42}H_{20}N_2O_{12}$: calculated: C: 53.94 %, H: 2.16 %, N: 3.00 %, O: 20.53 %, Cu: 20.38 %; found: C: 53.78 %, H: 2.49 %, N: 2.93 %, O: 21.17 %, Cu: 19.57 %.

Synthesis of $Cu_3(CBCDC)_2$ (DUT-76)

9-(4'-carboxy-[1,1'-biphenyl]-4-yl)-9H-carbazole-3,6-dicarboxylic acid (7) (1.0 g, 2.21 mmol)$Cu(NO_3)_2 \cdot 3\ H_2O$ (0.92 g, 3.54 mmol) were dissolved in 190 ml of a mixture of DMF and ethanol (1:1). After the addition of 10 mL (175 mmol) glacial acetic acid the resulting solution is divided in portion of 10 mL each the are and transfered into Pyrex® tubes and heated to 80 °C for 2 d. After cooling the reaction mixtures the crystals were collected in a single vessel. The combined solids were washed thoroughly with fresh solvent and afterwards exchanged with dry acetone. The exchanged crystals were dryed using supercritical carbon dioxide. For the determination of the yield dryed DUT-76 was heated to 180 °C in vacuum for two days.

Yield: 664 mg (0.66 mmol, 55 %)

Elemental analysis for $Cu_3C_{54}H_{28}N_2O_{12}$: calculated: C: 59.64 %, H: 2.60 %, N: 2.58 %, O: 17.66 %, Cu: 17.53 %; found: C: 58.78 %, H: 2.29 %, N: 2.86 %, O: 17.91 %, Cu: 16.98 %.

3. Crystal Structure

The single crystals of DUT-75 and DUT-76 were transferred in a glass capillary (0.3 mm) with some amount of solvent. The capillaries were sealed with melted wax. The datasets were collected at BESSY MX BL14.2 beamline of Helmholtz Zentrum Berlin für Materialien und Energie.[1] All diffraction experiments were performed at room temperature using the radiation with energy of 14 kEv (λ = 0.88561 Å). The φ-scans with oscillation range of 1° were used for data collection. The datasets were processed using CCP4 software.[2] Both crystal structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL program package.[3] All non hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using "riding model" with $U_{iso}(H)=1.2U_{iso}(C)$. In the crystal structure of DUT-76, the C7 and C8 atoms are disordered over two equally occupied positions. Because of the high symmetry of the crystal system, it was not possible to localize the lattice solvent molecules in the pores. Therefore, the SQUEEZE procedure was used to correct reflection intensities corresponding to disordered solvent molecules.[4] This results in 1363 electrons per unit cell for DUT-75 and 2541 electrons per unit cell for DUT-76. CCDC-982441 and CCDC-982442 contain the supplementary crystallographic data for DUT-75 and DUT-76, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Single crystal data for DUT-75 and DUT-76.

	DUT-75	**DUT-76**
Empirical formula	$C_{42}H_{20}Cu_3N_2O_{15}$	$C_{54}H_{28}Cu_3N_2O_{15}$·
Formula weight, *g/mol*	983.22	1135.40
Crystal system, space group	Cubic, *Pm*-3*m*	Cubic, *Pm*-3*m*
Unit cell dimensions, *Å, deg.*	$a = 27.860(3)$	$a = 33.970(4)$
Volume, *Å³*	21624(4)	39200(8)
Z, Calc. density, *g/cm³*	6, 0.453	6, 0.289
μ, *mm⁻¹*	0.832	0.462
F(000)	2958	3438
Limiting indices	$0 \leq h \leq 20$ $-35 \leq k \leq -1$ $-35 \leq l \leq 0$	$0 \leq h \leq 24$ $1 \leq k \leq 41$ $0 \leq l \leq 41$
Reflections collected / unique	8156 / 4428 ($R_{int} = 0.0304$)	13443 / 7208 ($R_{int} = 0.0265$)
Data / parameters	4428 / 107	7208 / 133
Refinement data before SQUEEZE		
GooF on F^2	1.750	2.058
R [I>2σ(I)]*	0.0913	0.0722
wR (all data)*	0.3082	0.2507
Largest diff. peak / hole, e/Å³	0.472 / -0.561	0.491 / -0.535
Refinement data after SQUEEZE		
SQUEEZEd electrons count	1363	2541
GooF on F^2	0.911	1.060
R [I>2σ(I)]*	0.0555	0.0453
wR (all data)*	0.1817	0.1572
Largest diff. peak / hole, e/Å³	0.272 / -0.502	0.390 / -0.329

$^*R1 = \Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

4. X-ray Powder Diffraction Data

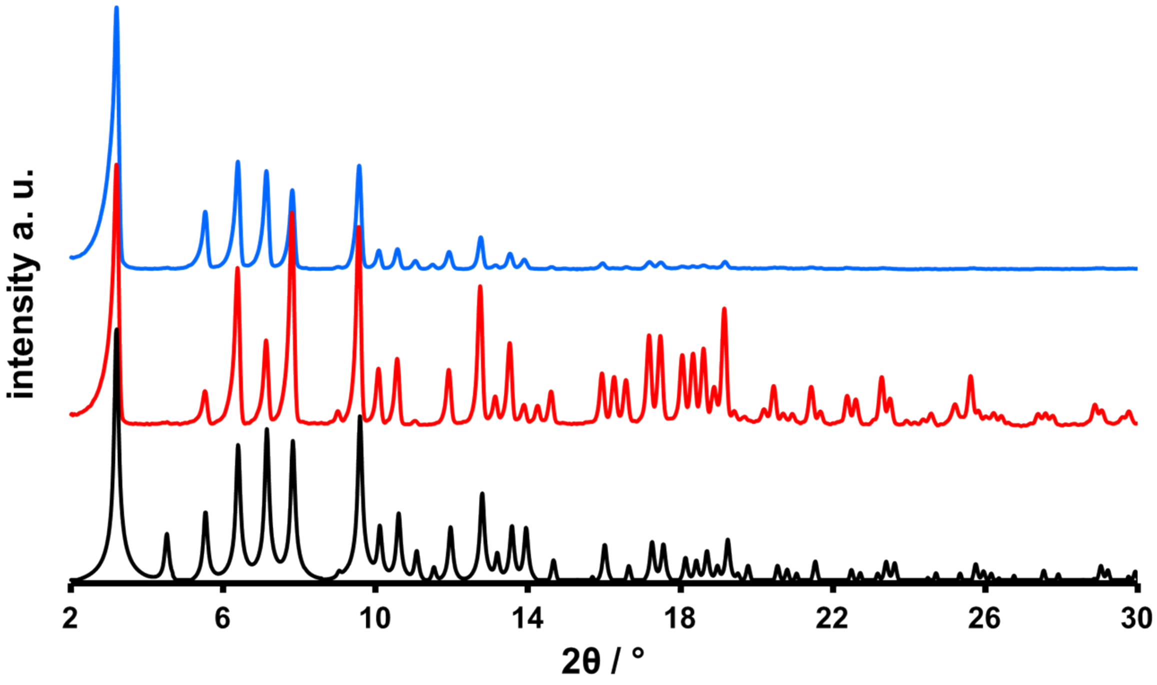


Figure S1. Comparison of powder X-ray diffraction patterns of DUT-75: theoretical pattern (black), as made material (red), supercritically dried material (blue).

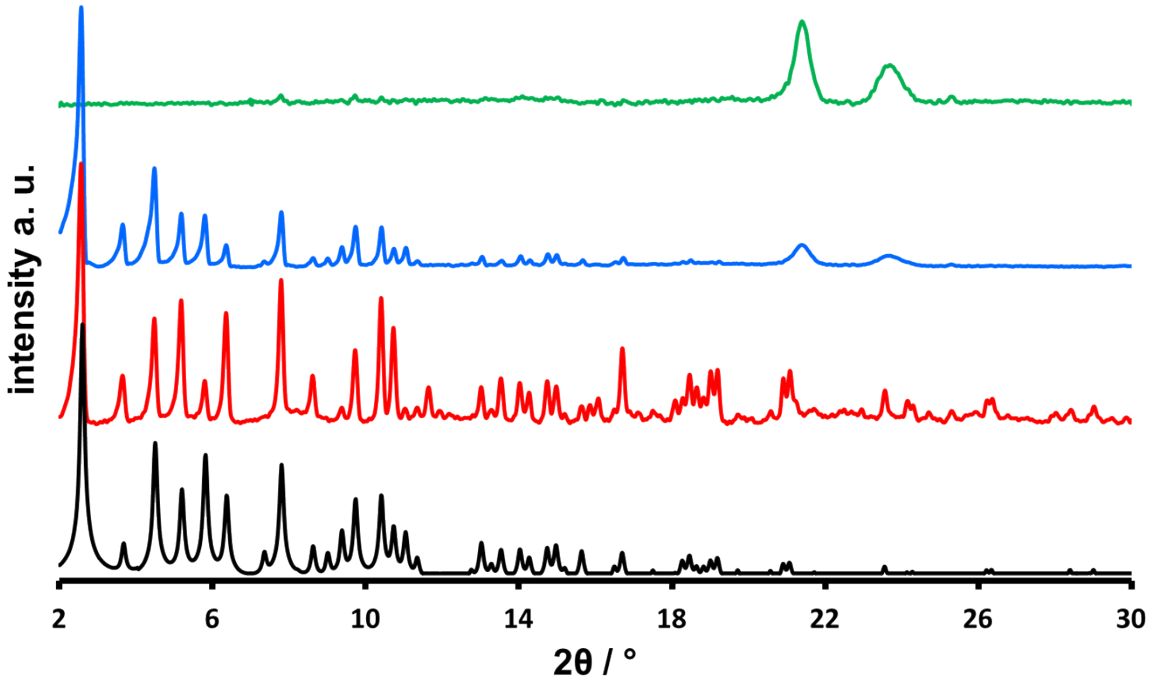


Figure S2. Comparison of powder X-ray diffraction patterns of DUT-76: theoretical pattern (black), as made material (red), supercritically dried material (blue), background for the sample holder of the activated material (green).

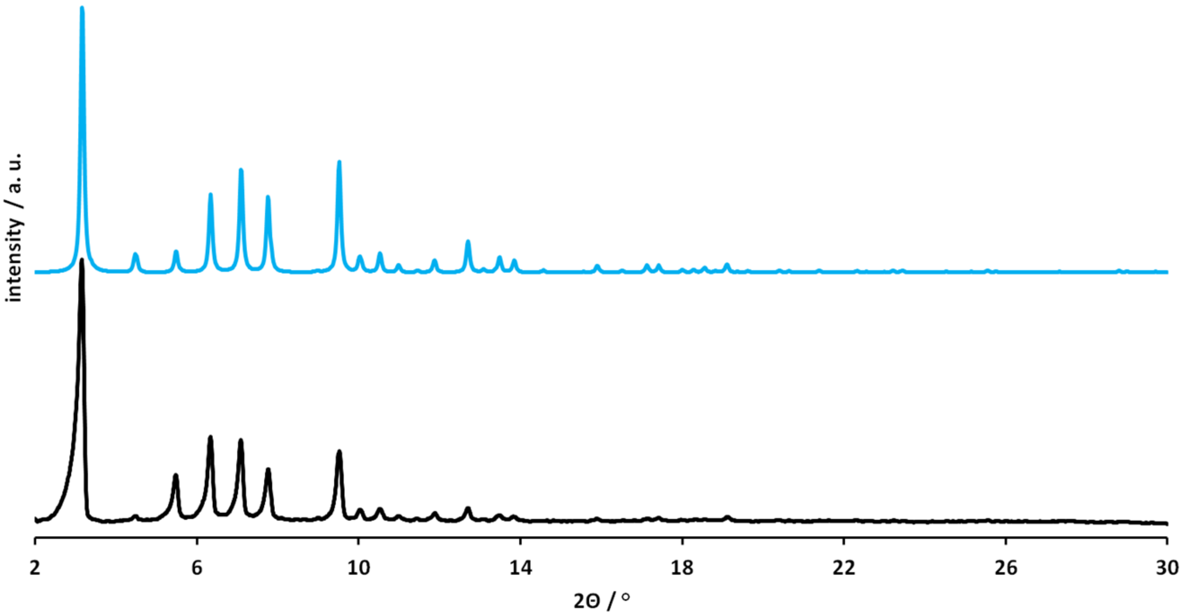


Figure S3. Powder X-ray diffraction patterns of DUT-75: theoretical pattern (black), measured after nitrogen adsorption experiment (blue).

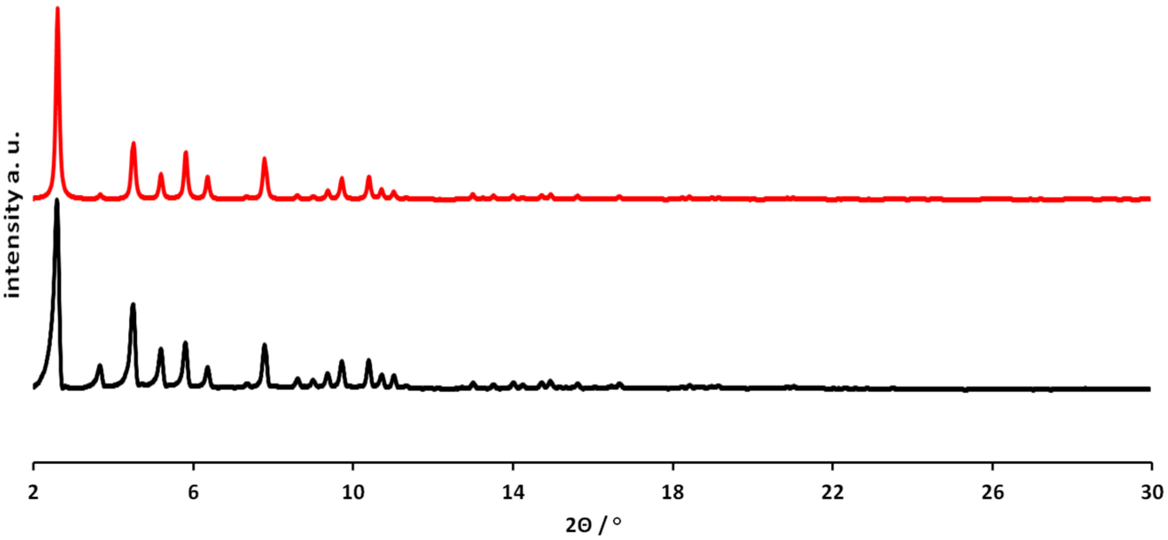


Figure S4. Powder X-ray diffraction patterns of DUT-76: theoretical pattern (black), measured after nitrogen adsorption experiment (red).

5. Physisorption Data

The course of action suggested by Rouquerol and Llewellyn for analyzing sorption data to obtain the apparent surface area from application of the BET-theory goes as follows. Starting from the linearized form of the BET-equation the term $n_a(p_0\text{-}p)$ is plotted against the relative pressure p/p_0.

$$\frac{p}{n_a(p_0 - p)} = \frac{1}{n_m C} + \frac{C - 1\, p}{n_m C p_0}$$

n_a - adsorbed volume; n_m - adsorbed volume equivalent to a monolayer; C - BET-constant

The data analysis should be limited to the pressure range were the term $n_a(p_0\text{-}p)$ increases with increasing p/p_0, because in this range the isotherm has not yet reached saturation. For DUT-75 this range ends at p/p_0=0.113 (Figure S3).

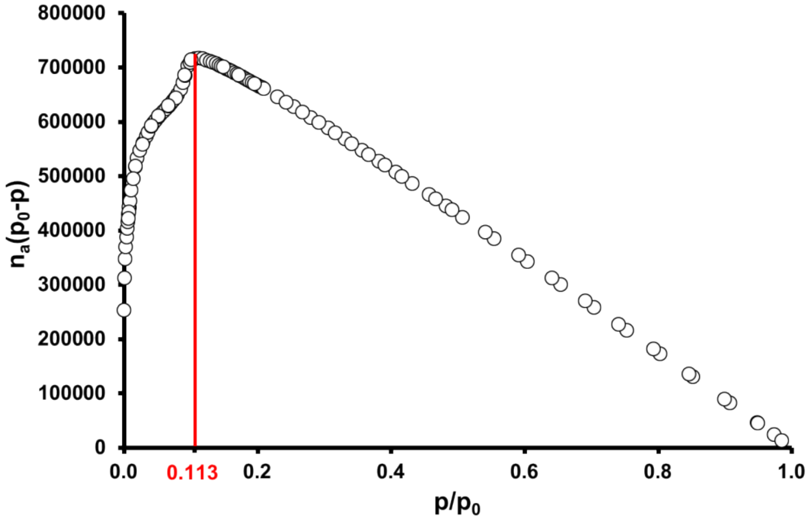


Figure S5. Self-consistency plot of the nitrogen physisorption isotherm of DUT-75.

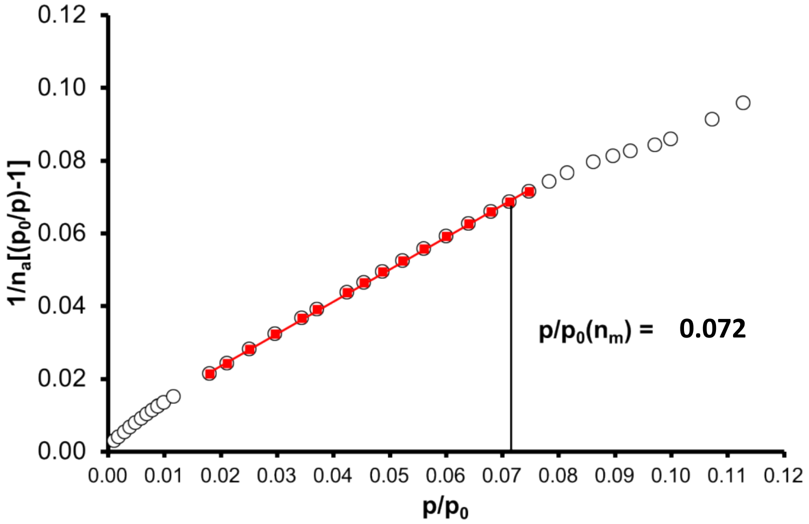


Figure S6. BET plot of the nitrogen physisorption isotherm of DUT-75 up to p/p_0 = 0.113, linear range (red).

Afterwards the term $1/n_a[(p_0/p)\text{-}1]$ (this term is accessible by expanding the fraction on the left of the BET equation with 1/p) is plotted against p/p_0. In this BET plot there should be a linear range corresponding to the monolayer capacity of the given compound which than in turn can be transformed into the apparent surface area. According to Rouquerol and Llewellyn the linear region in the BET plot should fulfill two last criteria. The C constant of the linear fitting should be positive (or the linear fitting should intersect the ordinate at a positive value) and the relative pressure corresponding to the monolayer capacity should be within the chosen linear range. Taking these considerations into account a wide linear region with a C value of 150 and a correlation coefficient of r = 0.9998 was found for DUT-75. The resulting monolayer capacity was translated into a relative pressure of $p/p_0(n_m) = 0.072$ (Figure S4). This value lies well within the chosen linear range. Thus the resulting apparent specific surface area of DUT-75 is 4081 m^2/g. The plots for DUT-76 are shown below (Figures S5, S6). The resulting values for the linear range are: C = 11, r = 0.9997, $p/p_0(n_m) = 0.159$. The apparent specific surface area of DUT-76 amounts to 6344 m^2/g.

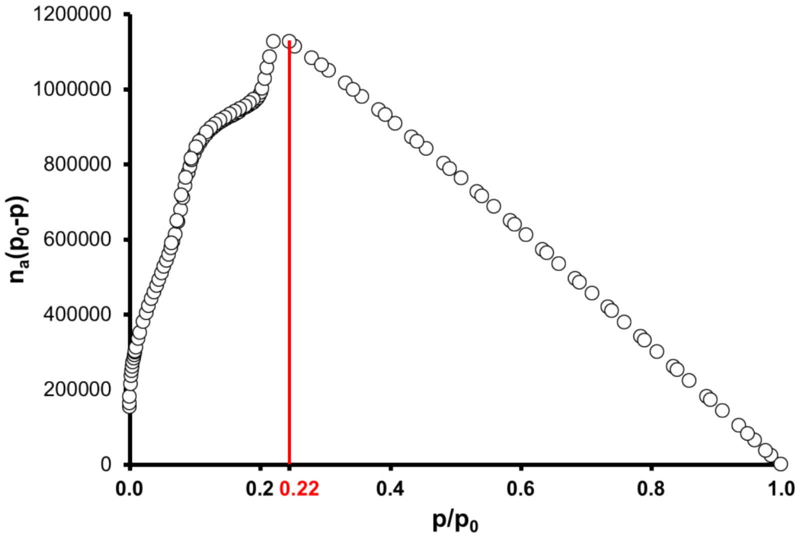


Figure S7. Self-consistency plot of the nitrogen physisorption isotherm of DUT-76.

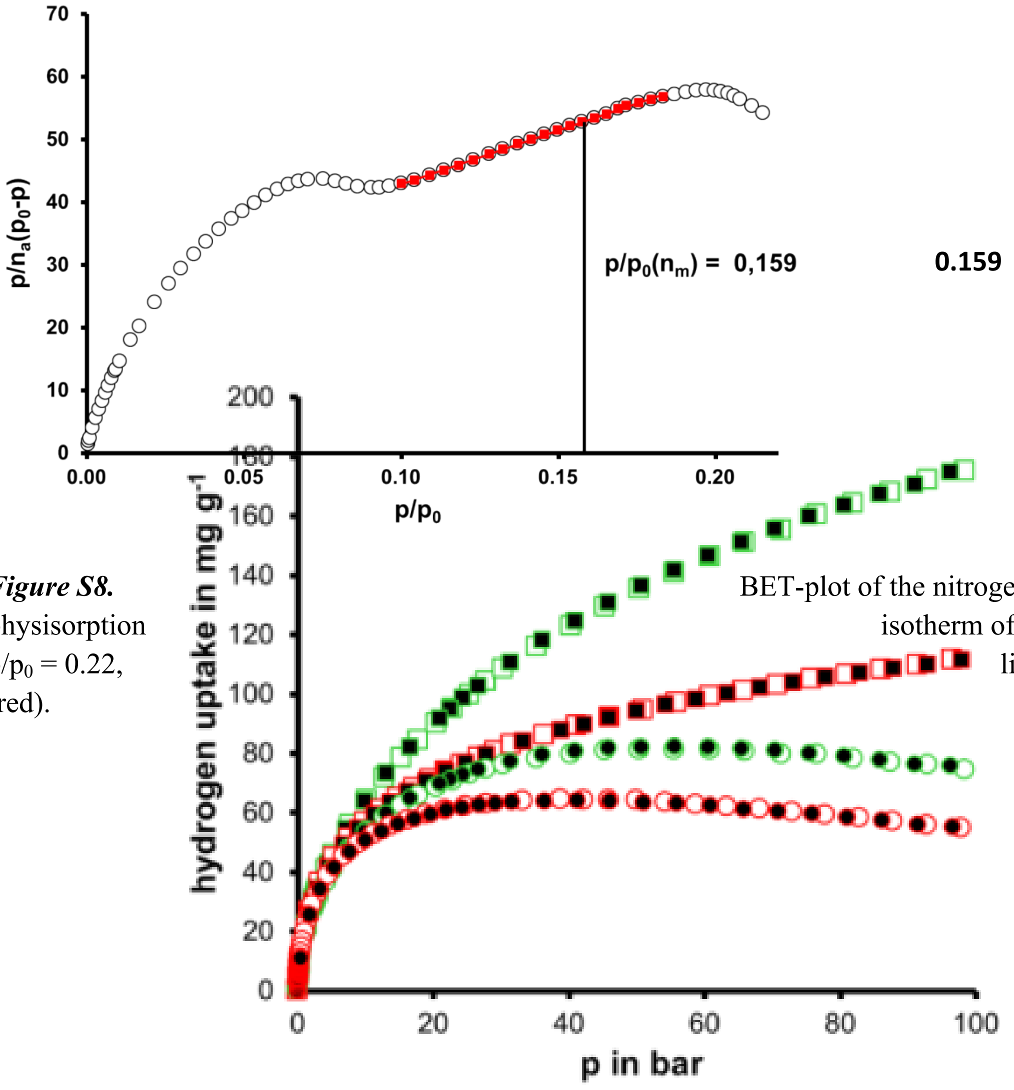


Figure S8. BET-plot of the nitrogen physisorption isotherm of DUT-76 up to $p/p_0 = 0.22$, linear range (red).

Figure S9. Hydrogen physisorption isotherms of DUT-75 (red) and DUT-76 (green) at 77 K. Excess: circles, total: squares; adsorption – open symbols, desorption – filled symbols.

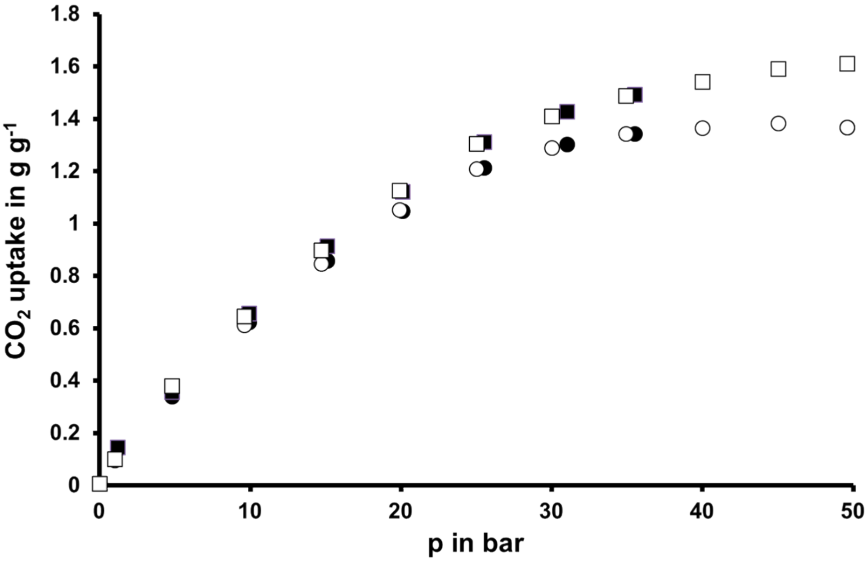


Figure S10. Carbon dioxide physisorption isotherms of DUT-75 at 298 K. Excess: circles, total: squares; adsorption – open symbols, desorption – filled symbols.

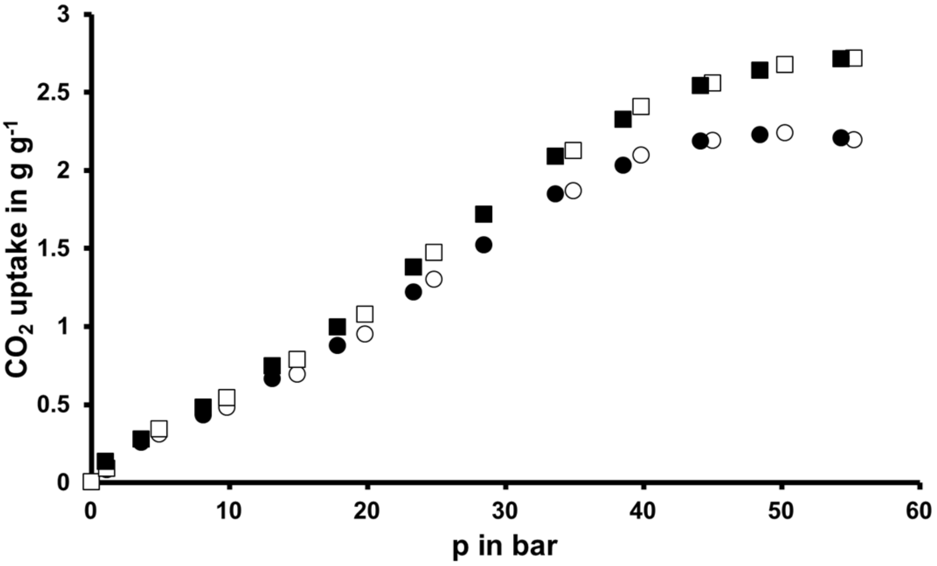


Figure S11. Carbon dioxide physisorption isotherms of DUT-76 at 298 K. Excess: circles, total: squares; adsorption – open symbols, desorption – filled symbols.

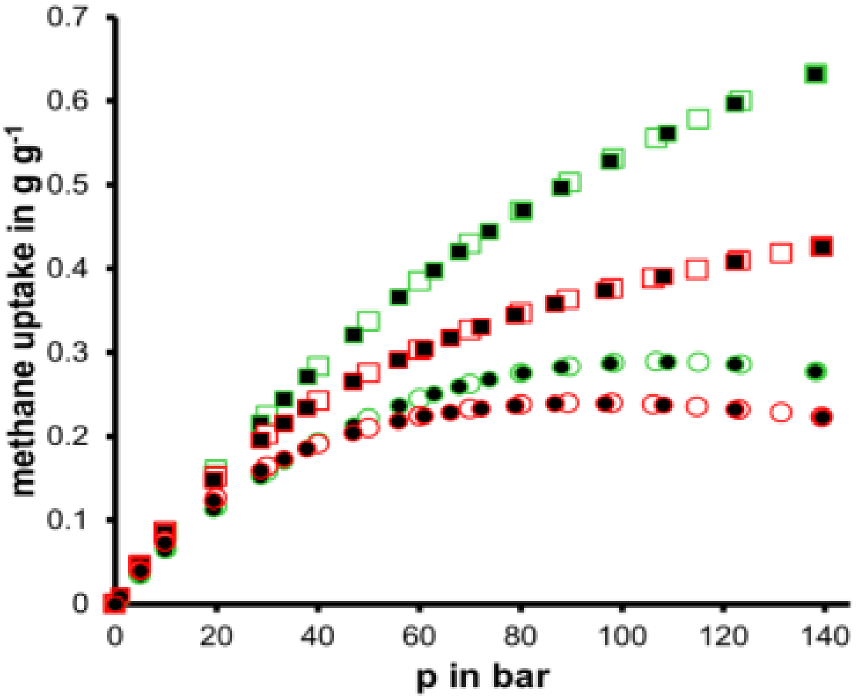


Figure S 12. Methane physisorption isotherms of DUT-75 (red) and DUT-76 (green) at 298 K. Excess: circles, total: squares; adsorption – open symbols, desorption – filled symbols.

6. Thermogravimetric Data

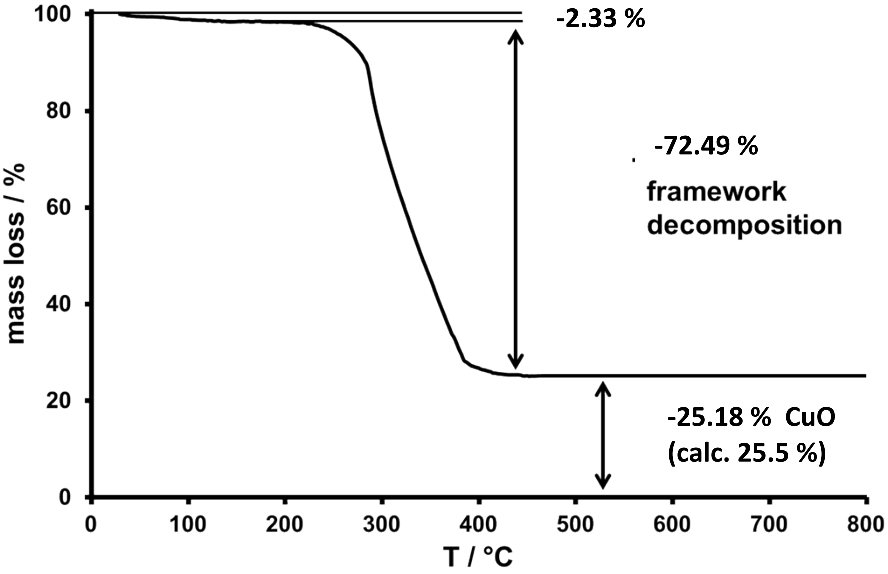


Figure S13. Thermogravimetric analysis of DUT-75.

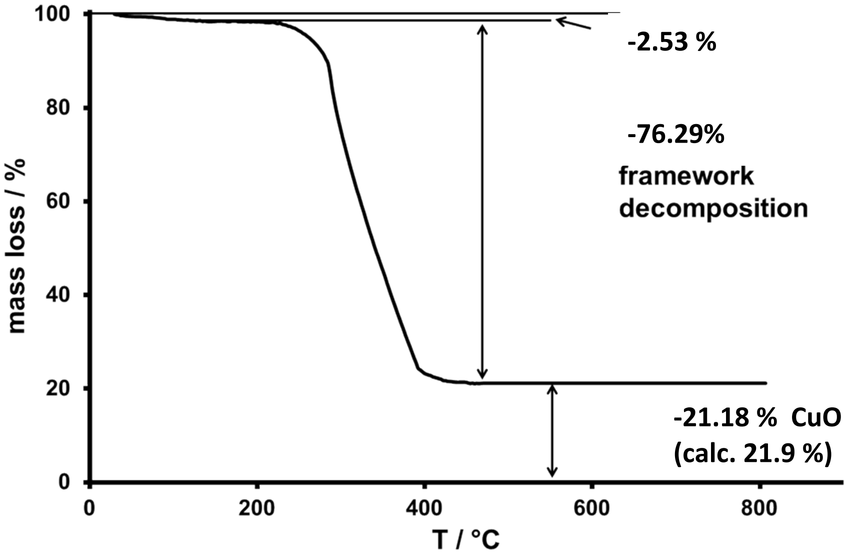


Figure S14. Thermogravimetric analysis of DUT-76.

The first step in both TG curves is due to adsorbed moisture from ambient air because the samples have to be transferred from the glove box to thermal analyzer in ambient conditions.

References

1 U. Mueller, N. Darowski, M. R. Fuchs, R. Forster, M. Hellmig, K. S. Paithankar, S. Puhringer, M. Steffien, G. Zocher, M. S. Weiss, *J. Synchrotron Rad.* 2012, **19**, 442-449.

2 M. D. Winn, C. C. Ballard, K. D. Cowtan, E. J. Dodson, P. Emsley, P. R. Evans, R. M. Keegan, E. B. Krissinel, A. G. W. Leslie, A. McCoy, S. J. McNicholas, G. N. Murshudov, N. S. Pannu, E. A. Potterton, H. R. Powell, R. J. Read, A. Vagin, K. S. Wilson, *Acta Cryst. D* 2011, **67**, 235-242.

3 G. Sheldrick, *Acta Cryst. A* 2008, **64**, 112-122.

4 A. Spek, *Acta Cryst. D* 2009, **65**, 148-155.