

Supporting Information for *Chemical Communications*

**A highly porous metal-organic framework, constructed from a cuboctahedral super-molecular building block, with exceptionally high methane uptake**

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- 1. General Information**
- 2. Synthetic procedures for H<sub>4</sub>BBCDC and DUT-49**
- 3. Crystal structure**
- 4. Powder X-ray diffraction**
- 5. Thermogravimetric analysis**
- 6. Additional physisorption data**

## 1. General Information

$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Sigma Aldrich), *N*-methyl-2-pyrrolidone (NMP) (AppliChem), and ethanol (abs.) (VWR Prolabo) were used as received. 4,4'-bis(9*H*-carbazol-9-yl)-1,1'-biphenyl was purchased from TCI Europe and 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  $\text{Cu-K}\alpha_1$  ( $\lambda = 0.15405$  nm) radiation and with a scan speed of 30 s/step and a step size of  $0.1^\circ$ .

The supercritical drying process was performed in the following manner: Prior to the supercritical drying process, samples were washed thoroughly with NMP and placed in EtOH (abs.). The ethanol was exchanged 10 times over 2 days. The samples were placed in a Jumbo Critical Point Dryer 13200J AB (SPI Supplies). The ethanol was exchanged with liquid carbon dioxide (purity: 99.995%) at  $\sim 15^\circ\text{C}$  for about 70 hours. After that period of time the temperature and pressure was raised beyond the critical point of  $\text{CO}_2$ . The resulting supercritical  $\text{CO}_2$  was released slowly within a time frame of 3h. The dried samples were transferred to a glove box.

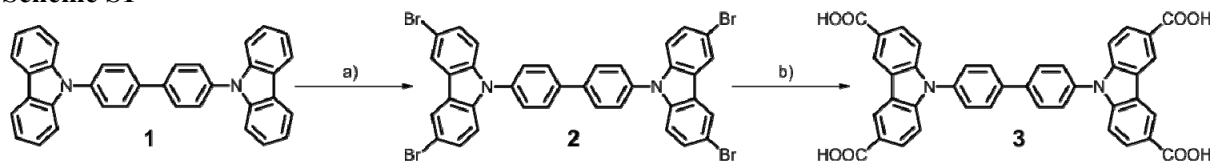
Prior to all physisorption measurements the samples were activated using supercritical  $\text{CO}_2$  and additionally evacuated at  $60^\circ\text{C}$  for 24h.  $\text{N}_2$  physisorption isotherm was measured up to 1 bar using a Quantachrome Autosorb 1C apparatus. High pressure  $\text{H}_2$  adsorption measurement at  $-196^\circ\text{C}$  up to 110 bar was performed using approximately 0.3 g sample on a volumetric BELSORP-HP apparatus. High pressure  $\text{CH}_4$  and  $\text{CO}_2$  adsorption was studied using a magnetic suspension balance (Rubotherm Co.). The total gas uptake was calculated by:  $N_{\text{total}} = N_{\text{excess}} + \rho_{\text{bulk}}V_{\text{pore}}$ , where  $\rho_{\text{bulk}}$  equals to the density of compressed gases at the measured temperature and pressure, and  $V_{\text{pore}}$  was obtained from the  $\text{N}_2$  sorption isotherm at 77K.

High purity gases were used ( $\text{N}_2$ : 99.999%,  $\text{H}_2$ : 99.999%,  $\text{CH}_4$ : 99.5%,  $\text{CO}_2$ : 99.995%).

Thermogravimetric analyses (TGA) were carried out under air atmosphere using a Netzsch STA 409 thermal analyzer. Elemental analysis (C, H, N) was performed with a Hekatech EA 3000 Euro Vector CHNS analyzer.

## Synthetic procedures for $\text{H}_4\text{BBCDC}$ and DUT-49

Scheme S1



Reagents & conditions: a) 4.3 eq NBS, THF,  $40^\circ\text{C}$ , 16h, 98% b) 10 eq, THF,  $0^\circ\text{C}$ , *t*-BuLi 10 h,  $\text{CO}_2$  73%.

### Synthesis of 4,4'-bis(3,6-dibromo-9H-carbazo-9-yl)-1,1'-biphenyl (2):

4,4'-bis(9H-carbazo-9-yl)-1,1-biphenyl (1) (10 g, 20.64 mmol) was dissolved in 200 ml of THF. The temperature of the solution was adjusted to 40 °C. After the addition of *N*-bromosuccinimide (15.8 g, 88.73 mmol) the temperature of the mixture was maintained for 16 h, during which a white precipitate is formed. The reaction mixture was filtered and the white precipitate was washed thoroughly with dichloromethane and ethanol. The resulting solid was virtually insoluble in any common organic solvent.<sup>[6]</sup> Because of that no NMR-analysis was performed. (Yield: 98%)

**Elemental analysis for C<sub>36</sub>H<sub>20</sub>Br<sub>4</sub>N<sub>2</sub>:** calculated: C: 54.04%, H: 2.52%, N: 3.5%; found: C: 54.71%, H: 2.62% N: 3.6%.

**DTA/TG-measurements** under argon shows no phase transition, hence no melting. The compound begins to decompose at 400 °C.

**IR wavenumber** (in cm<sup>-1</sup>) = 3059, 3043, 1910, 1850, 1718, 1606, 1502, 1466, 1436, 1364, 1317, 1278, 1228, 1052, 1020, 938, 865, 814, 793, 743, 718, 634, 577, 561.

### Synthesis of 9,9'-([1,1'-biphenyl]-4,4'-diyl)bis(9H-carbazole-3,6-dicarboxylic acid) (3):

4,4'-bis(3,6-dibromo-9H-carbazo-9-yl)-1,1'-biphenyl (2) (18 g, 22.5 mmol) was suspended under inert atmosphere in dry THF (1.8 L). The suspension was cooled down to -15 °C and 106 ml (0.18 mol) of a *t*-BuLi solution (1.7 mol L<sup>-1</sup>) were added. The reaction was stirred for 3 h. During that time the temperature was allowed to rise to 0 °C. Subsequent additional 13.5 mL (23 mmol) of *t*-BuLi were added. The mixture was stirred for another 2 h maintaining the temperature. After 2 h another 13.5 ml of *t*-BuLi were added. After 3 h maintaining the reaction temperature, dry gaseous CO<sub>2</sub> was bubbled through the reaction mixture. The resulting white precipitate was filtered off and refluxed with 2 L of sodium hydroxide solution. The solution was filtered and neutralized using hydrochloric acid. The raw acid was filtered and recrystallized from *N*-methyl-2-pyrrolidinone. (Yield: 73 %)

**<sup>1</sup>H-NMR (600MHz, d<sub>6</sub>-DMSO):**

δ (in ppm) = 7.55 (d, J = 8.3 Hz, 4H), 7.85 (d, J = 8.3 Hz, 4H), 8.14 (m, 8H), 9.1(s, 4H), 12.8 (s, 4H).

**<sup>13</sup>C-NMR and DEPT (150 MHz, d<sub>6</sub>-DMSO )**

δ (in ppm) = 101.07 (4 CH), 122.67 (4 C), 123.12 4(4 CH), 123.56 (4 C), 127.60 (4 CH), 128.40 (4 CH), 128.84 (4 CH), 135.56(2 C), 139.22(2 C), 143.49(4 C), 167.69(4 C).

**Elemental analysis of C<sub>40</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>:** Calculated: C: 72.72%, H: 3.66%, N: 4.24; Found: C: 72.91, H: 3.87%, N: 4.29%

### Synthesis of DUT-49

H<sub>4</sub>BBCDC (1.25 g, 1.89 mmol) was dissolved in a mixture of 17.6 ml (227 mmol) of glacial acetic acid and 232.4 ml of NMP. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.15 g, 4.73 mmol) was added and dissolved by sonication. Afterwards the clear solution was divided and filled in pyrex tubes, 10 ml each. The pyrex tubes were heated to 80°C for 24 h. The resulting solids were combined and washed several times with fresh NMP until the solvent appeared colourless. The combined solids were exchanged with ethanol and dried using supercritical CO<sub>2</sub>. Subsequent to the supercritical drying the DUT-49 compound was subjected to additional evacuation at a temperature of 60 °C for 24 h. Yield: 56% (823 mg)

**Elemental analysis  $C_{40}H_{20}N_2O_8Cu_2$ :** Calculated: C: 61.3%, H: 2.57%, N: 3.57% Found: C: 59.84 %, H: 2.53%, N: 3.50%. Phase purity was also confirmed by powder X-ray diffraction.

## Crystal structure

Cubic shaped single crystal of DUT-49(Cu), DUT-49(Zn) or DUT-49(Co) was inserted into the glass capillary ( $d = 0.3$  mm) with some amount of mother liquor. The capillary was sealed using wax. The data collection was performed at Berlin Helmholtz Centre for Materials and Energy (MX beamline BL-14.2).<sup>2</sup> Image frames were collected at room temperature using  $\phi$ -scan technique ( $\Delta\phi = 1^\circ$ ). Image frames were integrated using the Mosflm 1.0.5 software.<sup>3</sup> Obtained intensities were scaled with the help of Scala program.<sup>4</sup> The crystal structures were solved by direct methods and refined by full matrix least-squares on  $F^2$  using SHELXTL program package.<sup>5</sup> All non hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using “riding model” with  $U_{\text{iso}}(\text{H})=1.2U_{\text{iso}}(\text{C})$ . Due to the high space group symmetry as well as strong positional disorder it was impossible to locate lattice solvent molecules from the difference Fourier map in all three cases. On this ground, the SQUEEZE procedure, implemented in PLATON<sup>6</sup>, was performed to correct reflection intensities, corresponding to disordered solvent molecules. Count of SQUEEZEd electrons as well as values of formula weight, calculated density and absorption coefficient involving disordered solvent are given in table S1. The residual parameters before and after performing the procedure are also presented. The positional disorder near the mirror plane of C10 and C11 atoms of the phenyl ring was resolved with equal occupancies (50%) for each position. As expected, all three compounds are isomorphous and crystallize in the cubic crystal system (space group  $Fm-3m$  No. 225). The 3D framework is built up by  $\text{Cu}_2(\text{COO})_4$  paddle-wheel SBUs, interconnected by 4 BBCDC linkers. Metal atoms from paddle-wheel SBUs are occupying  $4m.m$  symmetry sites in the unit cell. All carbon atoms from carbazole moieties that interconnect the mentioned SBUs and form SBB occupied  $m.$  symmetry sites. The distance and angle between carbazole carboxylates amount to 8.15 Å and  $92.2^\circ$ , the cubooctahedral SBB (Figure S2a) unit was formed by interconnection of 6 SBUs (copper paddle-wheels) and 12 BBCDC linkers. Interconnection of SBB units by biphenyl moieties and carbazole nitrogen results in 12-connected framework with **fcu** underlying topology. CCDC-889572, CCDC-890363 and CCDC-890364 contain the supplementary crystallographic data for DUT-49(Cu), DUT-49(Zn) and DUT-49(Co). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1** Single crystal data for DUT-49(Cu), DUT-49(Zn) and DUT-49(Co).

Empirical formula	$C_{66}H_{66.8}Cu_2N_{7.2}O_{15.2}$	$C_{66.5}H_{67.7}N_{7.3}O_{15.3}Zn_2$	$C_{63}H_{61.4}Co_2N_{6.6}O_{14.6}$
Formula weight	1331.15	1344.72	1261.84
Crystal system, space group	Cubic, <i>Fm-3m</i>	Cubic, <i>Fm-3m</i>	Cubic, <i>Fm-3m</i>
Unit cell dimensions, Å, deg.	$a = 46.588(5)$	$a = 46.806(5)$	$a = 46.730(10)$
Volume, Å <sup>3</sup>	101117(19)	102541(20)	102044(38)
Z, Calc. density, g/cm <sup>3</sup>	24, 0.525	24, 0.523	24, 0.493
$\mu$ , mm <sup>-1</sup>	0.504	0.553	0.397
<i>F</i> (000)	16627	16805	15756
Limiting indices	$2 \leq h \leq 58$ $0 \leq k \leq 32$ $-58 \leq l \leq 0$	$-63 \leq h \leq 60$ $-58 \leq k \leq 58$ $-61 \leq l \leq 59$	$0 \leq h \leq 32$ $2 \leq k \leq 59$ $0 \leq l \leq 59$
Reflections collected / unique	9285 / 5122 ( $R_{int} = 0.0515$ )	9434 / 5206 ( $R_{int} = 0.0266$ )	9373 / 5183 ( $R_{int} = 0.0343$ )
Data / parameters	5122 / 97	5206 / 97	5183 / 98
	Final residuals before SQUEEZE ( $w = 0.1$ )		
<i>Goof</i> on $F^2$	1.723	2.005	1.963
$R [I > 2\sigma(I)]^*$	0.1080	0.1047	0.1390
$wR$ (all data) <sup>*</sup>	0.3473	0.3419	0.4030
Largest diff. peak / hole, e/Å <sup>3</sup>	0.414 / -0.426	0.561 / -0.299	0.432 / -0.371
	Final residuals after SQUEEZE		
SQUEEZEd electrons count	6728	6866	5992
<i>Goof</i> on $F^2$	0.861	0.884	1.150
$R [I > 2\sigma(I)]^*$	0.0630	0.0548	0.0798
$wR$ (all data) <sup>*</sup>	0.1857	0.1968	0.2487
Largest diff. peak / hole, e/Å <sup>3</sup>	0.364 / -0.375	0.263 / -0.287	0.466 / -0.304

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

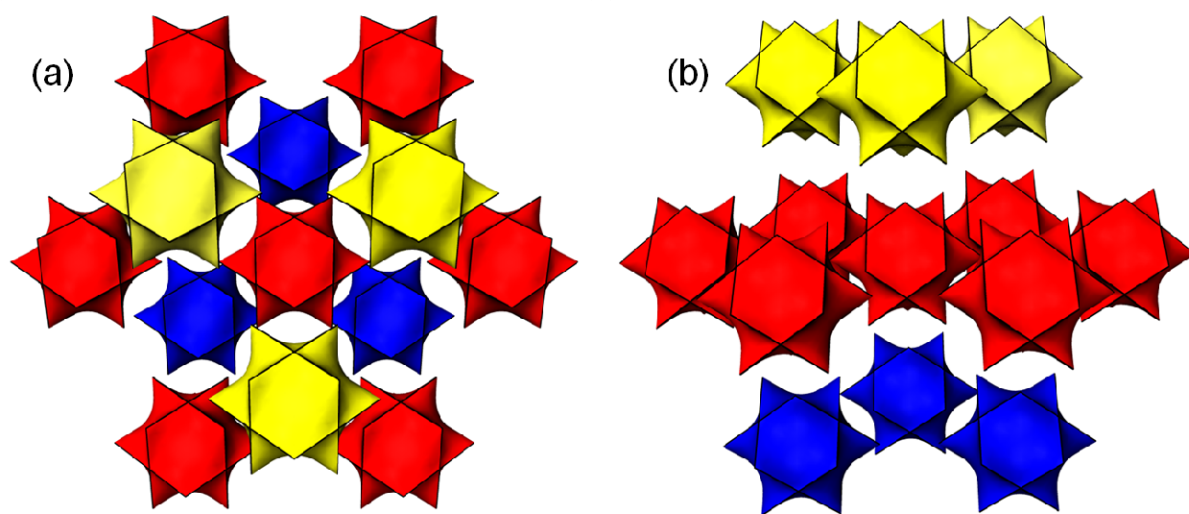


Figure S1. View of the characteristic ABC-stacking in the extended cubic close packing of the cuboctahedral SBB in DUT-49: (a) view along  $[111]$ ; (b) view of the A (yellow), B (red) and C (blue) layers.

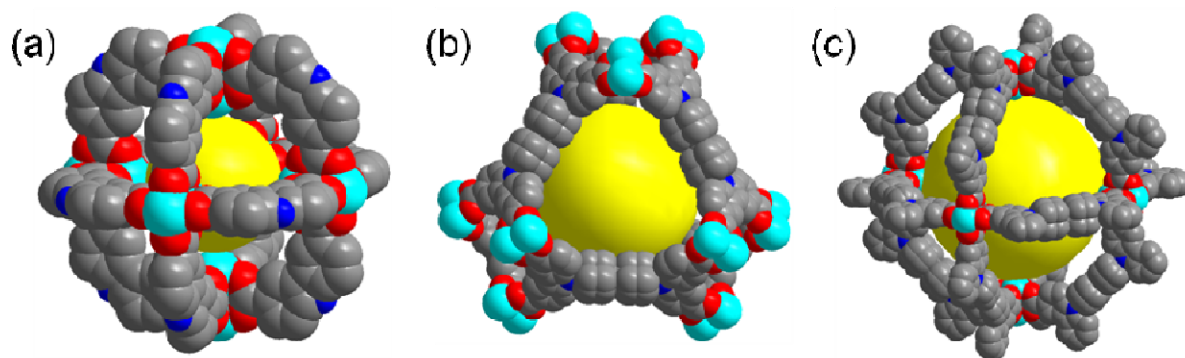


Figure S2. Inner spheres of the (a) cuboctahedral pore (b) tetrahedral pore (c) octahedral pore.

## 2. Powder X-ray diffraction

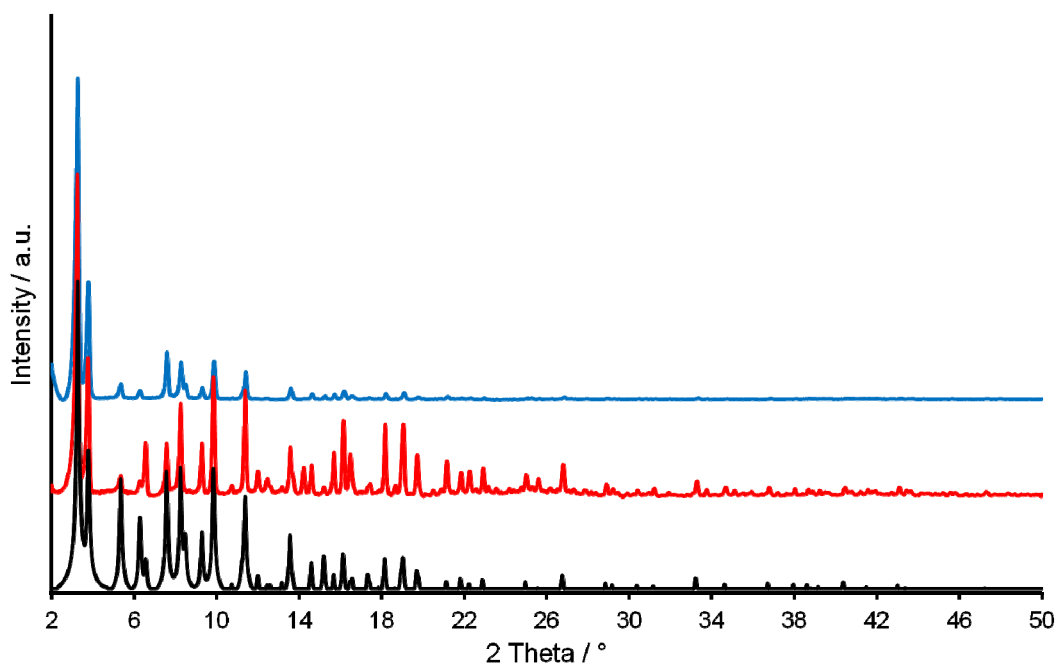


Figure S3. Powder X-ray diffraction patterns of DUT-49 (Cu): theoretical pattern (black), as-made material (red), fully activated material (blue).

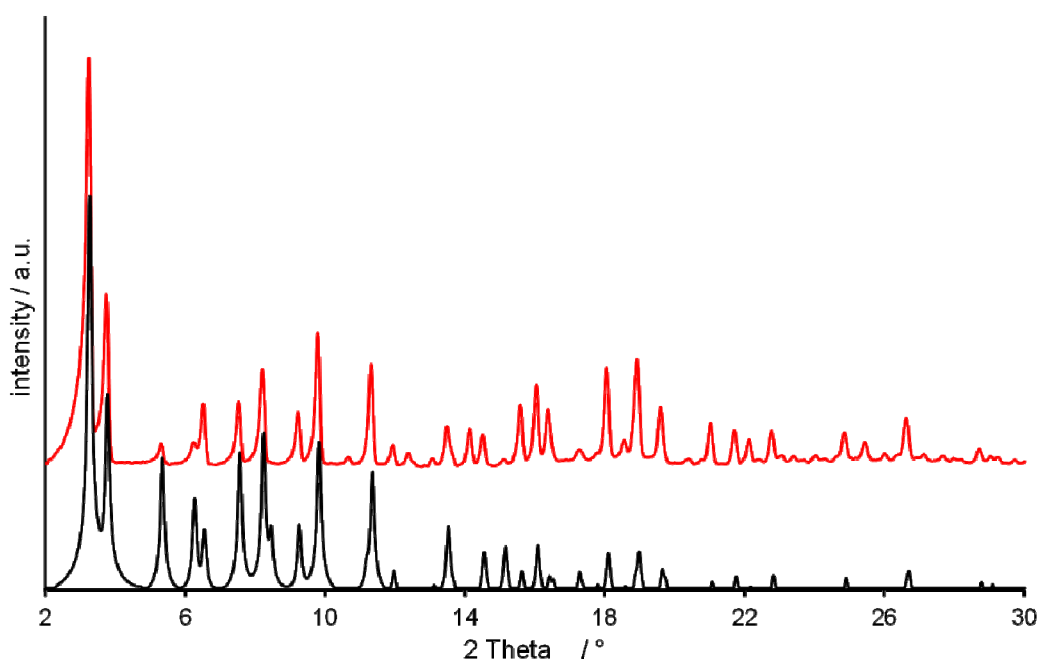


Figure S4. Powder X-ray diffraction patterns of DUT-49(Co): theoretical pattern (black), as-made material (red).



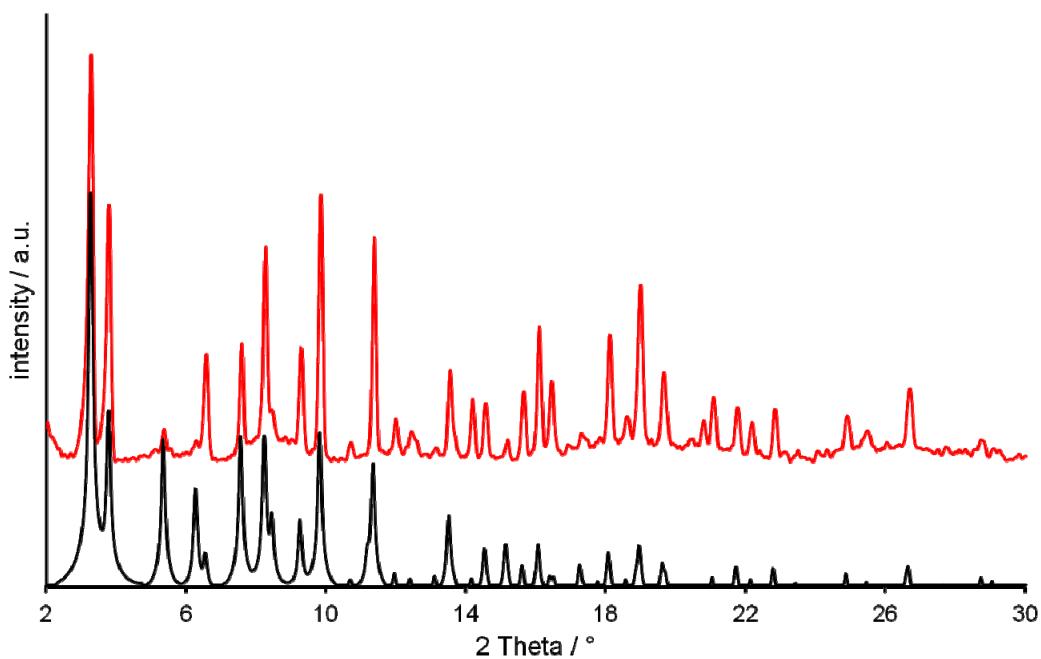


Figure S5. Powder X-ray diffraction patterns of DUT-49(Zn): theoretical pattern (black), as-made material (red).

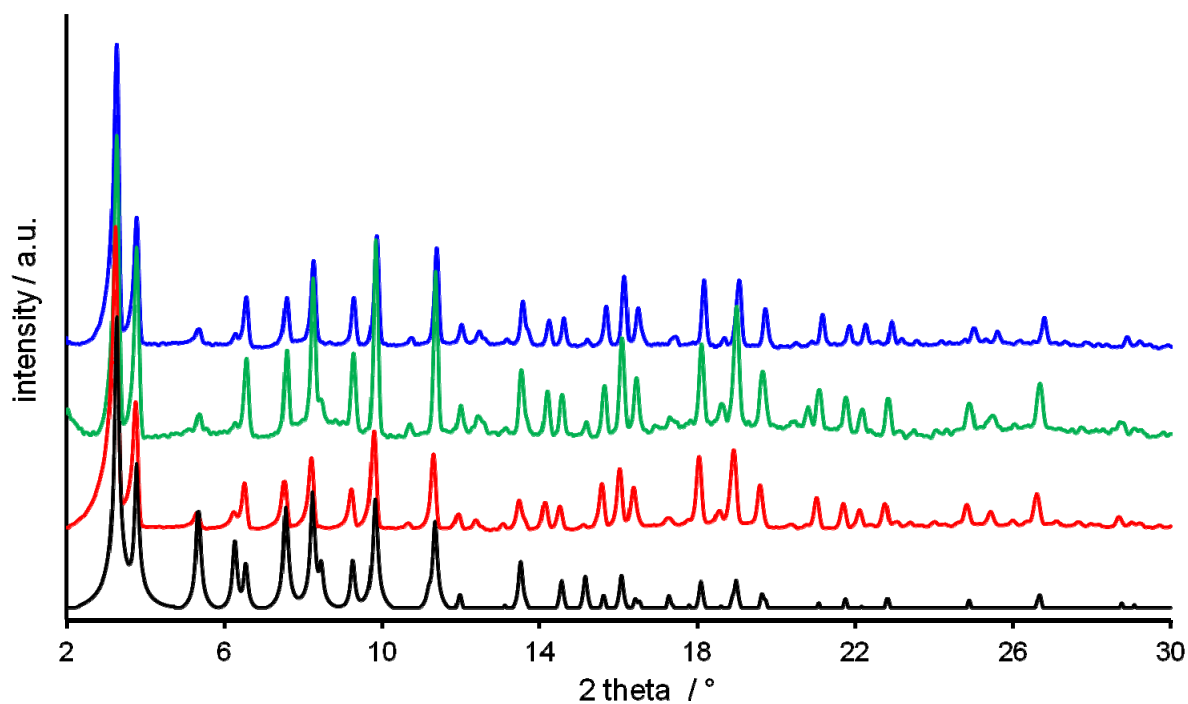


Figure S6. Powder X-ray diffraction patterns of DUT-49(M): theoretical pattern of DUT49(Co) (black), as-made material DUT-49(Co) (red), as-made material DUT-49(Zn) (green), as-made material DUT-49(Cu) (blue).

### 3. Thermogravimetric analysis

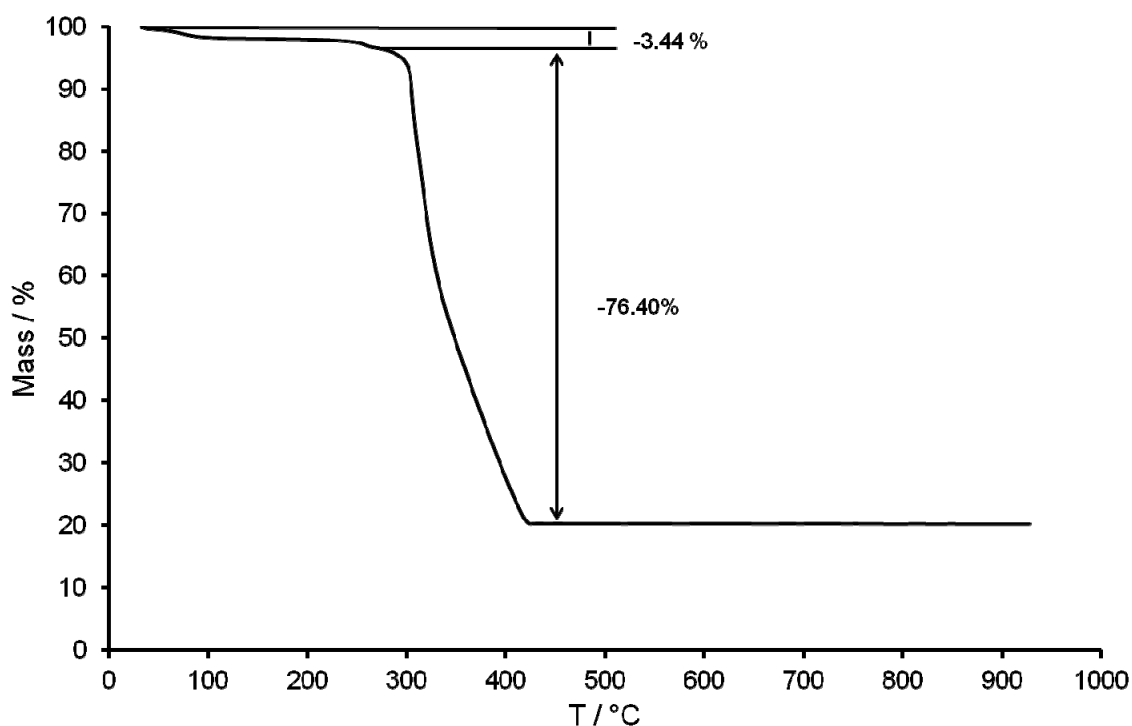


Figure S7. Thermogravimetric analysis of activated DUT-49.

The first step is attributed to the moisture, which was adsorbed during the preparation of the sample under ambient conditions.

### 4. Physisorption data

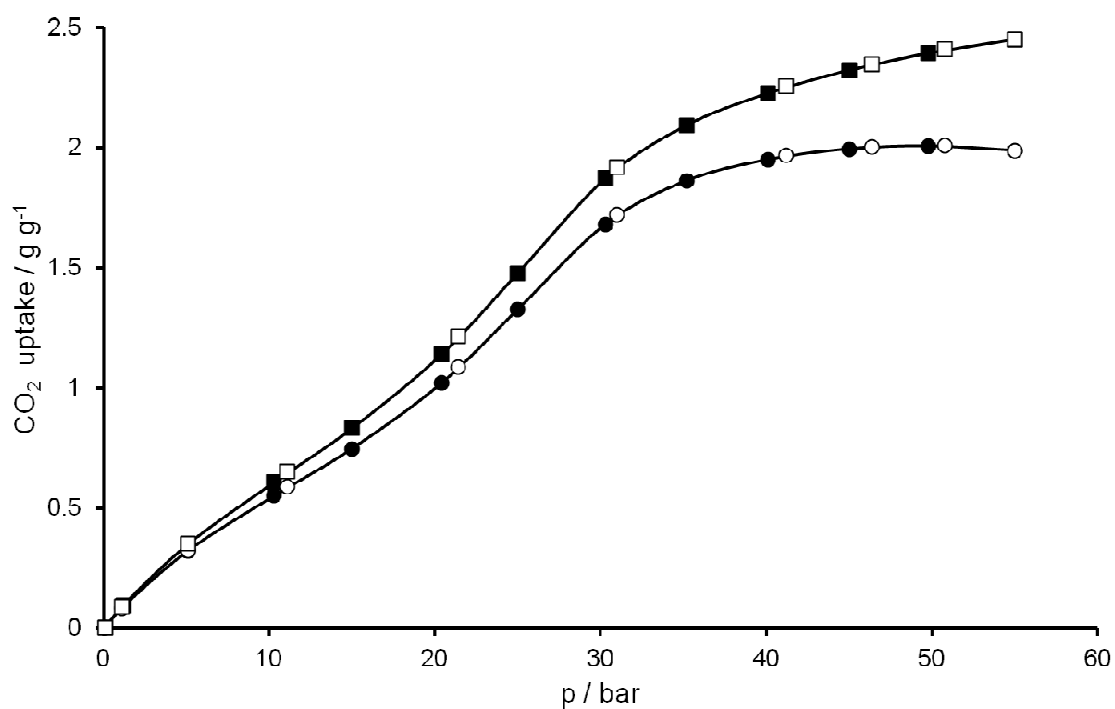


Figure S8. High pressure excess (circles) and total (squares) carbon dioxide physisorption isotherms of DUT-49 at 298 K. Adsorption- closed symbols, desorption - open symbols.

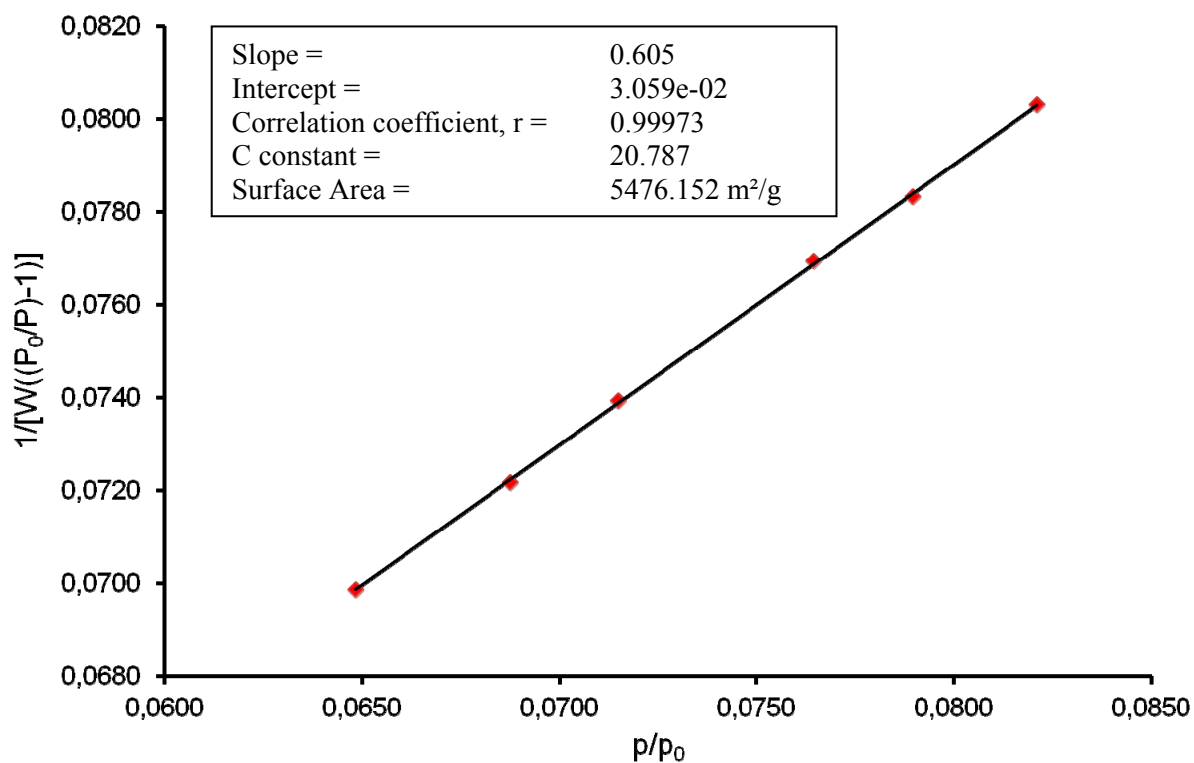


Figure S9. Linear region of the BET plot and corresponding specific surface area of DUT-49.

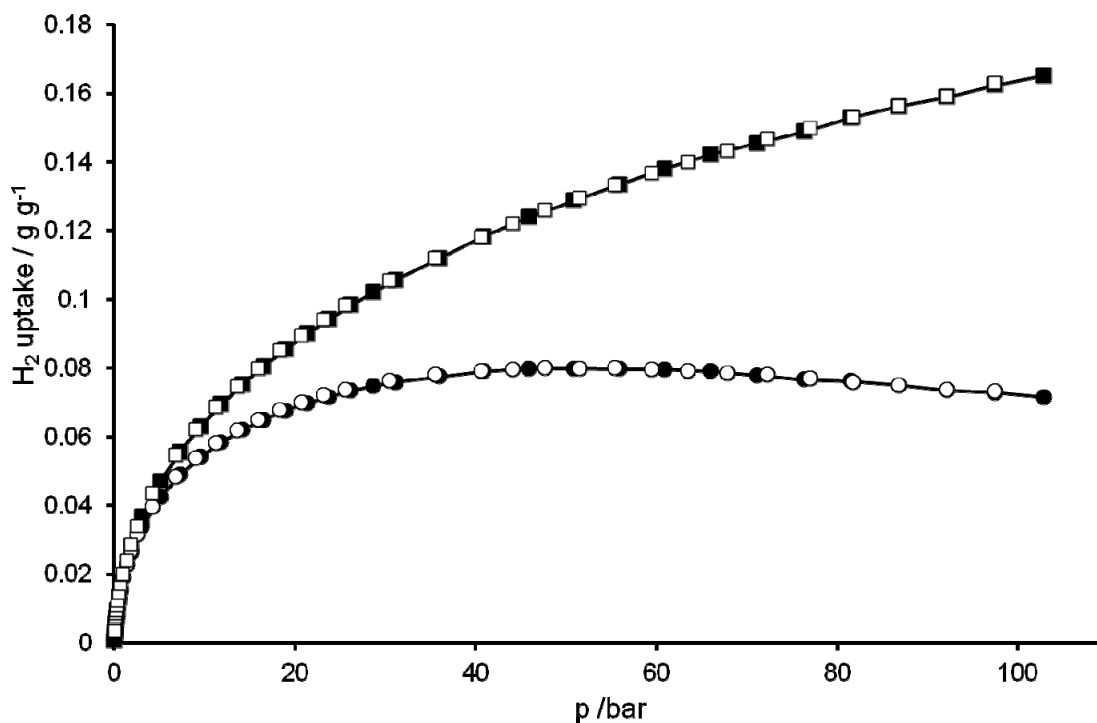


Figure S10. Hydrogen high pressure excess (circles) and total (squares) sorption isotherm of DUT-49; adsorption - open symbols, desorption - closed symbols.

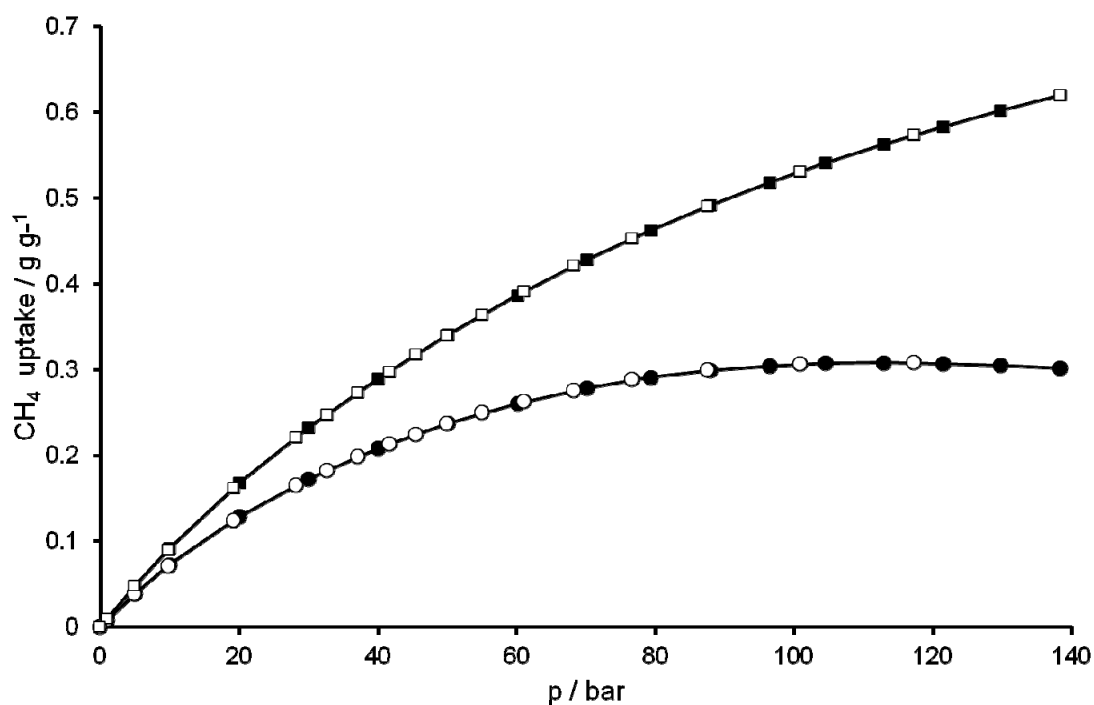


Figure S11. Methane high pressure excess (circles) and total (squares) physisorption isotherms of DUT-49; adsorption - open symbols, desorption - closed symbols.

## References

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