Supplementary Information

Particle size dependent flexibility in DUT-8(Cu) pillared layer metal-organic framework

Mariia Maliuta,[a] Irena Senkovska,*[, a] Vitaliy Romaka,[a, ^] Volodymyr Bon,[a] Ronja Thümmler,[a, ‡] Sebastian Ehrling,[a, §] Sophi Becker,[a, ¶] Jack Evans,[a, #] and Stefan Kaskel*[, a]

[a] *Chair of Inorganic Chemistry, Technische Universität Dresden, Bergstraße 66, D-01069 Dresden, Germany*

Current affiliations:

^ *Leibniz Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany*

[‡] *Leibniz-Institute of Polymer Research Dresden, Hohe Str.6, 01069 Dresden, Germany*

[§] *3P INSTRUMENTS GmbH & Co. KG, Rudolf-Diesel-Str.12, 85235 Odelzhausen, Germany*

[¶] *Gymnasium Wilsdruff, An der Schule 9, 01723 Wilsdruff, Germany*

[#] *The University of Adelaide, Centre for Advanced Nanomaterials and Department of Chemistry, 5000 Adelaide, Australia*

S1 Experimental details

S1.1 Reagents and solvents

Copper nitrate trihydrate (≥ 99%, AppliChem), 2,6-naphthalene dicarboxylic acid (H_2(2,6-ndc), 99%, Sigma Aldrich), 1,4-diazabicyclo-[2,2,2]-octane (dabco, 99%, Sigma Aldrich), hydrochloric acid (37%, AnalaR NORMAPUR or Sigma Aldrich), *N,N*-dimethylformamide (DMF, 99.5%, Fischer Scientific or Sigma Aldrich), methanol (HPLC grade, HiPerSolv CHROMANORM or VWR Chemicals), ethanol (HPLC grade, HiPerSolv CHROMANORM or VWR Chemicals), DCM (Fischer Scientific, 99.5%), acetone (≥ 99.5%, Sigma Aldrich), 1-propanol (HPLC grade, HiPerSolv CHROMANORM), 1-butanol (HPLC grade, HiPerSolv CHROMANORM).

S1.2 Crystal size modulation and synthesis optimisation

In a typical synthesis, $Cu(NO_3)_2 \cdot 3H_2O$ (0.338 g, 1.4 mmol, 2 eq.), 2,6-naphthalene dicarboxylic acid (0.303 g, 1.4 mmol, 2 eq.), and dabco (0.078 g, 0.07 mmol, 1 eq) were dissolved separately in 5 ml, 15 ml, and 5 ml of DMF, respectively. To suppress fast nucleation, 8.8 ml of HCl solution (1 M in H_2O) was added to the reaction mixture. To study the role of alcohols, four different alcohols were used, namely methanol, ethanol, 1-propanol and 1- butanol. In addition, the ageing temperature was varied from 80 °C over 100 °C to 120 °C (Table S1.1). The DMF/methanol ratio was chosen randomly.

Table S1.1. Utilisation of different alcohols for the synthesis of DUT-8(Cu) at different ageing temperatures.

	methanol	**ethanol**	**1-propanol**	**1-butanol**
80 °C	60 µm	40 µm	40 µm	50 µm
100 °C	60 µm	30 µm	20 µm	20 µm
120 °C	X	20 µm	X	X

X - no product

The evaluation of the resulting materials concerning crystal size was performed by optical microscopy and SEM (Figure S1.2). The highest yield and the largest crystals could be obtained using a DMF/methanol mixture and an ageing temperature of 80 °C. In the next step, the ratio of the starting materials and the solvent was varied.

A variation of the DMF/methanol ratio (batches a-1 - a-3, Table S1.2) leads to the particles up to 100 µm in size, but also to the formation of an additional phase (Figure S 1.1). In the second series of experiments, the dabco content (batches b-1 - b-3, Table S1.2) was varied. The particle size could be further increased using an excess of dabco for the synthesis (Figure S1.2). In addition, the side phase obtained in batches a-1 - a-3 is not present in b-1 - b-3. If the H_2(2,6-ndc) concentration is varied (batches c-1 - c-4) also large particles (ca. 50 µm, Figure S1.2) can be obtained. However, only when an equimolar ratio is chosen, a phase pure product is obtained. In the final step, the ratio between dabco and H_2(2,6-ndc) was kept equal and copper was used as a limiting variable (batch d-1). Interestingly, within this experiment, the biggest crystals with a narrow size distribution could be obtained (Figure S 1.2).

Table S1.2. Synthetic parameters for the synthesis of **2** at 80 °C during 48 hours.

Batch	Cu^{2+} / mmol	H_2(2,6-ndc) / mmol	dabco / mmol	equiv.	DMF / mL	MeOH / mL
a-1	0.4	0.4	0.2	2:2:1	4.5	3.5
a-2	0.4	0.4	0.2	2:2:1	6	2
a-3	0.4	0.4	0.2	2:2:1	3	5
b-1	0.4	0.4	0.1	2:2:0.5	4.5	3.5
b-2	0.4	0.4	0.3	2:2:1.5	4.5	3.5
b-3	0.4	0.4	0.4	2:2:2	4.5	3.5
c-1	0.4	0.467	0.2	2:2.3:1	4.5	3.5
c-2	0.4	0.33	0.2	2:1.65:1	4.5	3.5
c-3	0.4	0.267	0.2	2:1.335:1	4.5	3.5
c-4	0.4	0.2	0.2	2:1:1	4.5	3.5
d-1	0.2	0.4	0.2	1:2:1	6.4	1.75

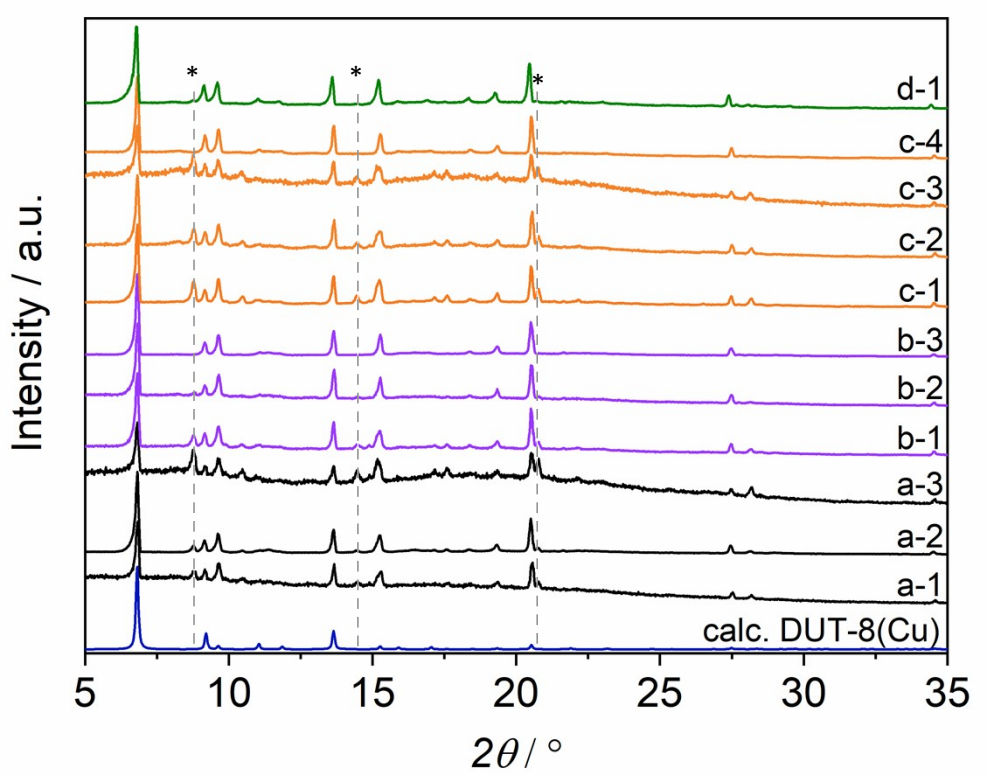

Figure S1.1. PXRD patterns of samples obtained in the synthesis optimisation studies. The peaks of the secondary phases are marked by *.

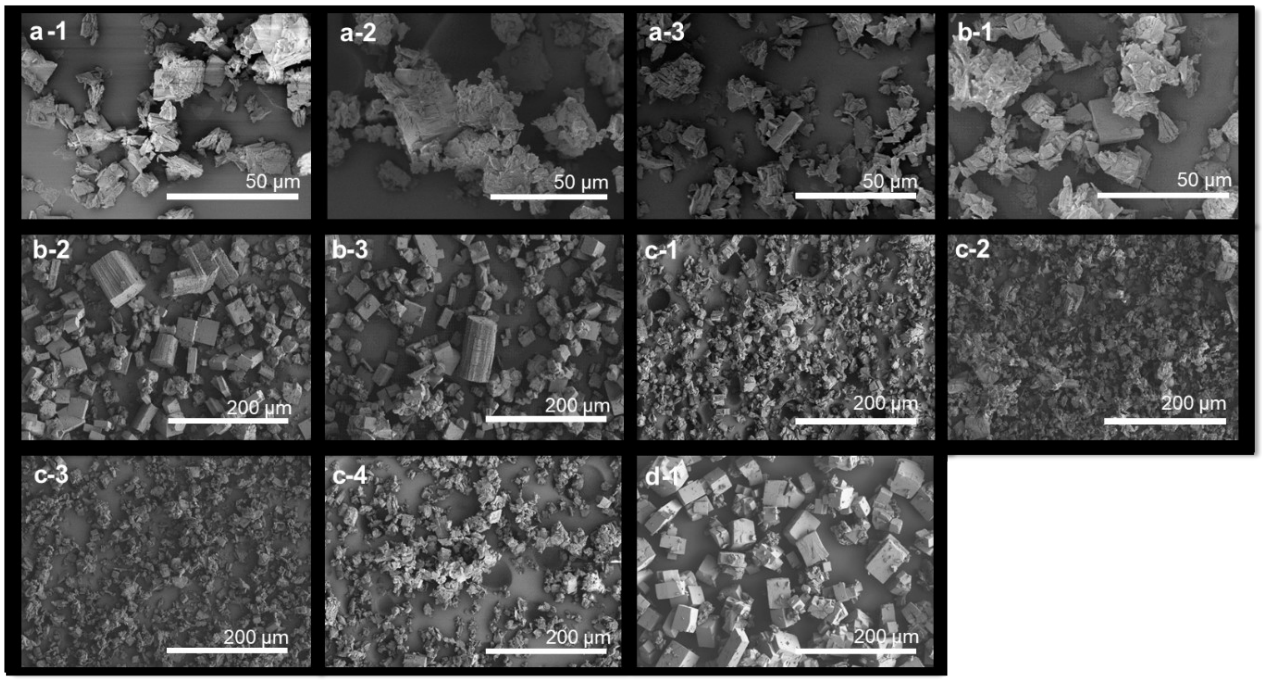

Figure S1.2. SEM images of the crystals obtained in the synthesis optimisation studies.

S2 Synthesis of DUT-8(Cu) in DEF according to Klein *et al.*[1]

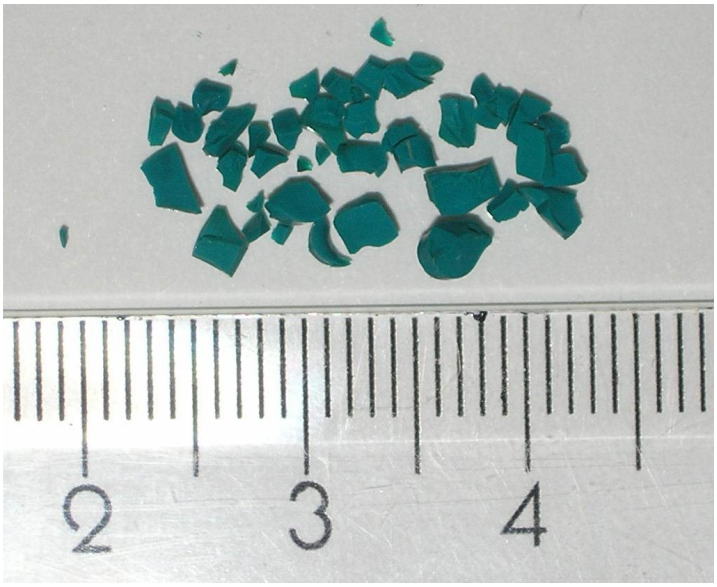

Fig. S2.1. Microscopy image of the DUT-8(Cu) monolith-like solid obtained after drying of the product at 120 °C for 36 h in 2012.[2]

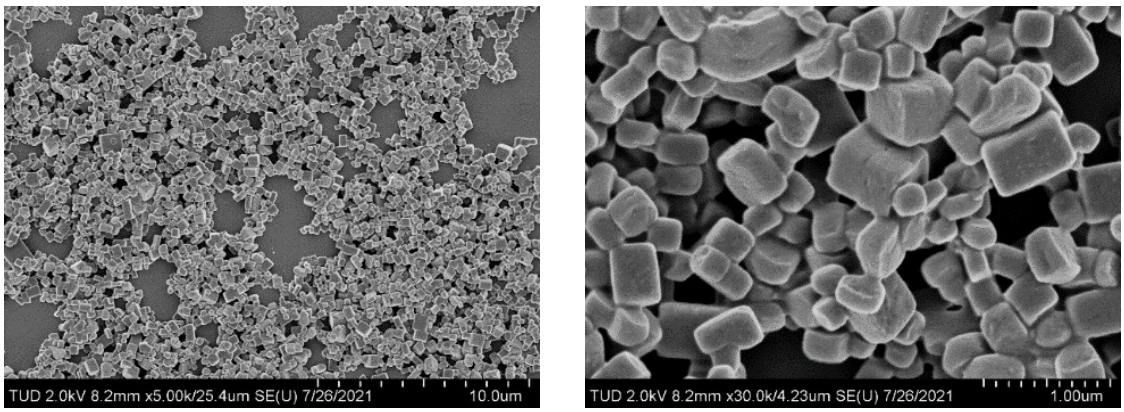

Fig. S2.2. SEM images of the DUT-8(Cu) crystals obtained upon the synthesis in DEF (**1a**), following a synthetic procedure published in 2012.[1]

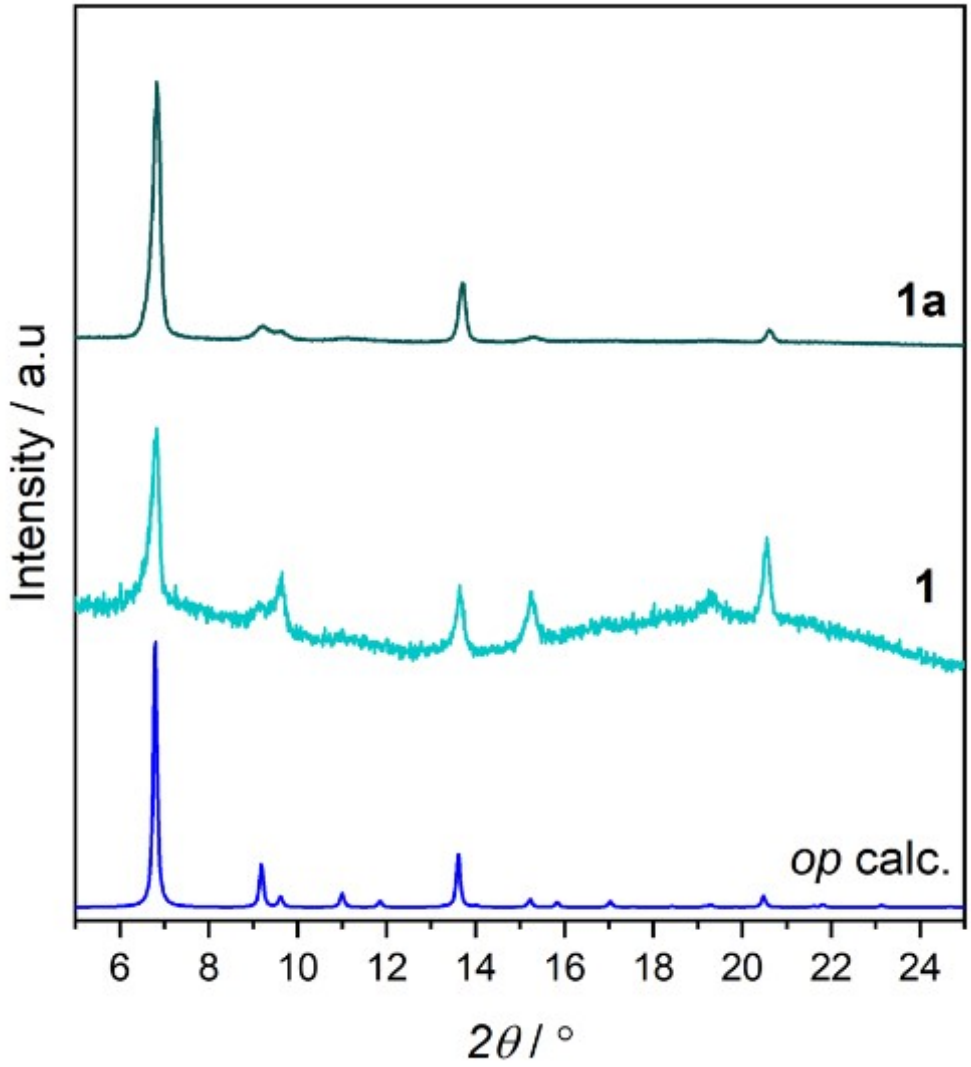

Fig. S2.3. PXRD patterns of **1** and **1a**.

S3 Desolvation

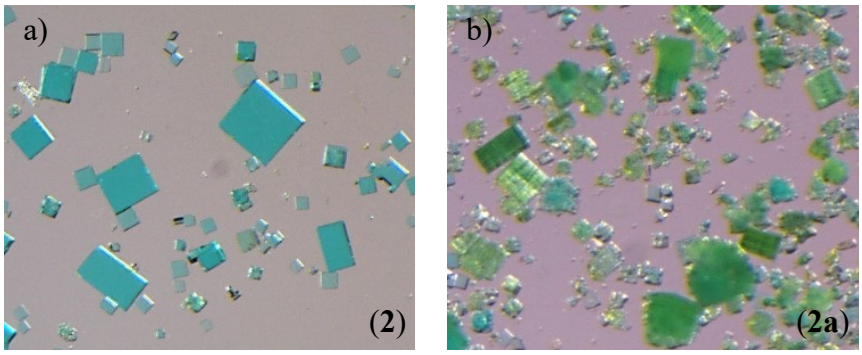

Fig. S3.1. Colour changes of sample **2** upon evacuation: a) before, b) after.

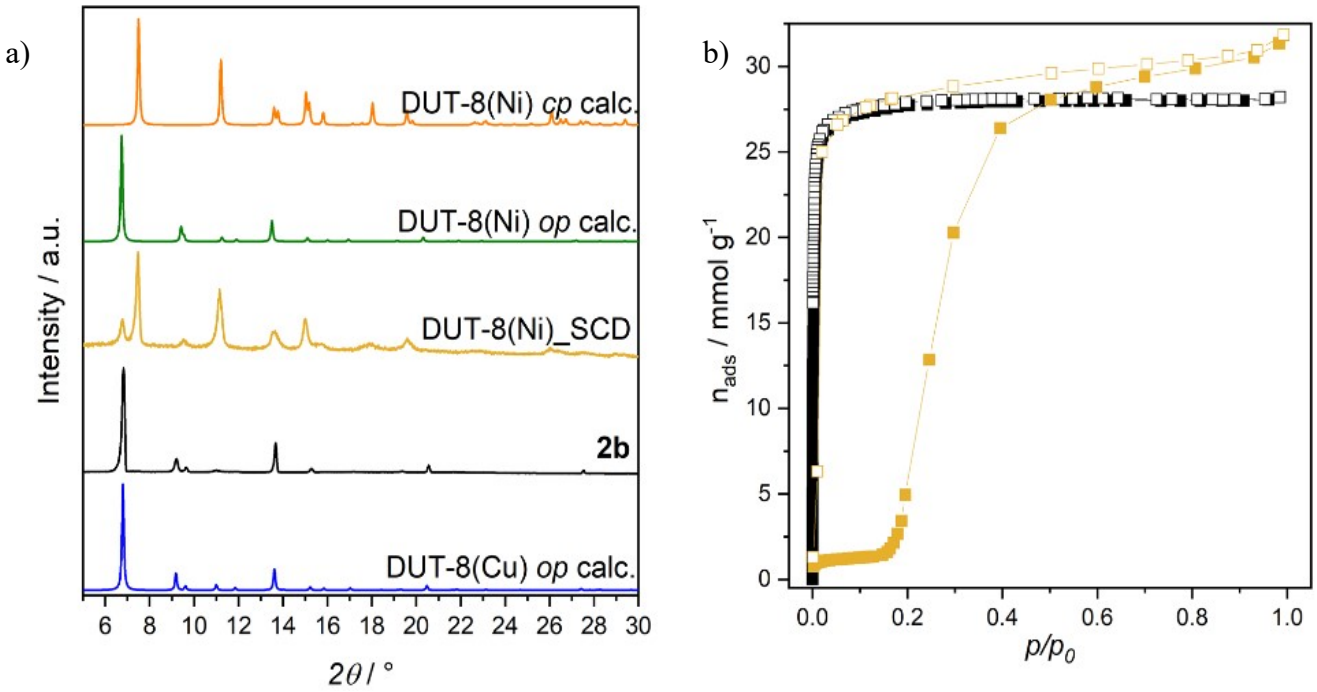

Fig. S3.2. a) PXRD patterns of the macro-sized particles, supercritically dried from acetone: DUT-8(Ni) (yellow) and **2b** (black) in comparison with PXRD calculated for DUT-8(Cu)_op (blue), DUT-8(Ni)_op (green) and DUT-8(Ni)_cp (orange); b) N_2 physisorption at 77 K on macro-sized DUT-8(Ni) particles supercritically dried from acetone (yellow) and **2b** (black). Solid symbols – adsorption, empty symbols – desorption.

As it can be seen from Figure 3.2, the same desolvation procedure applied to the macro-sized DUT-8(*M*) particles containing Cu or Ni results in different phases: mainly cp phase of DUT-8(Ni) and pure op phase of DUT-8(Cu).

S4 Crystal structure

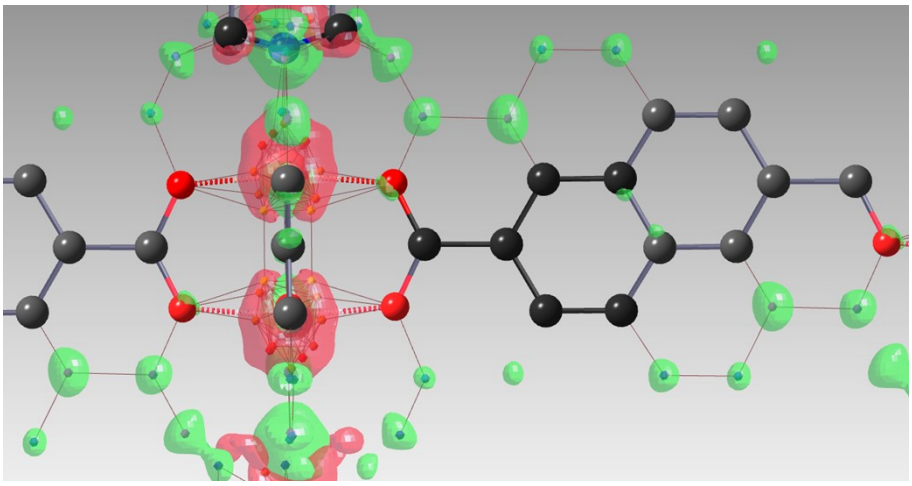

Figure S4.1 Difference Fourier map of the DUT-8(Cu) single crystal indicates localised maxima of the electron density (green) in addition to the main structural motif of the linker and cluster (in black). When connected (thin lines), they resemble a different linker orientation and a disorder along the *c*-axis.

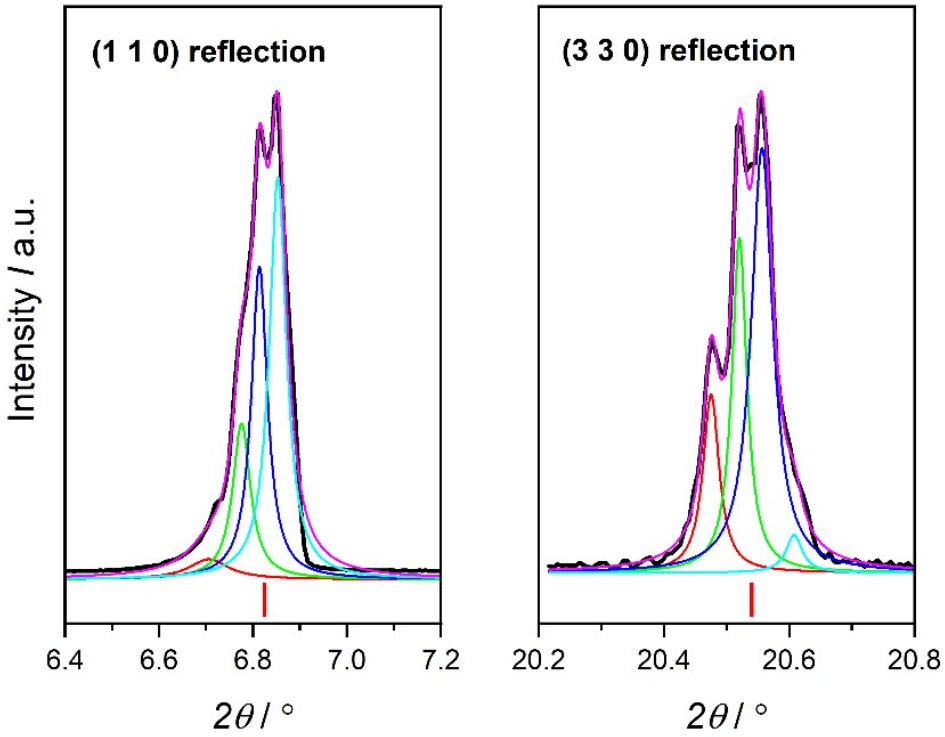

Figure S4.2. Diffraction peaks splitting in **2b**.

S5 Adsorption behaviour

Table S5.1. Adsorption characteristics of the investigated samples.*

Sample name	$n_{ads}(N_2, 77K)$, mmol g^{-1}	α_{max}**	$n_{ads}(CO_2, 195K)$, mmol g^{-1}	α_{max}
1a	29.3	1	23.47	0.93
2a	9.82	0.33	9.27	0.37
2b	28.2	0.96	22.11	0.88

** $\alpha_{max} = n_{ads}$(experimental) / n_{ads} (theoretical), n – amount of substance adsorbed.

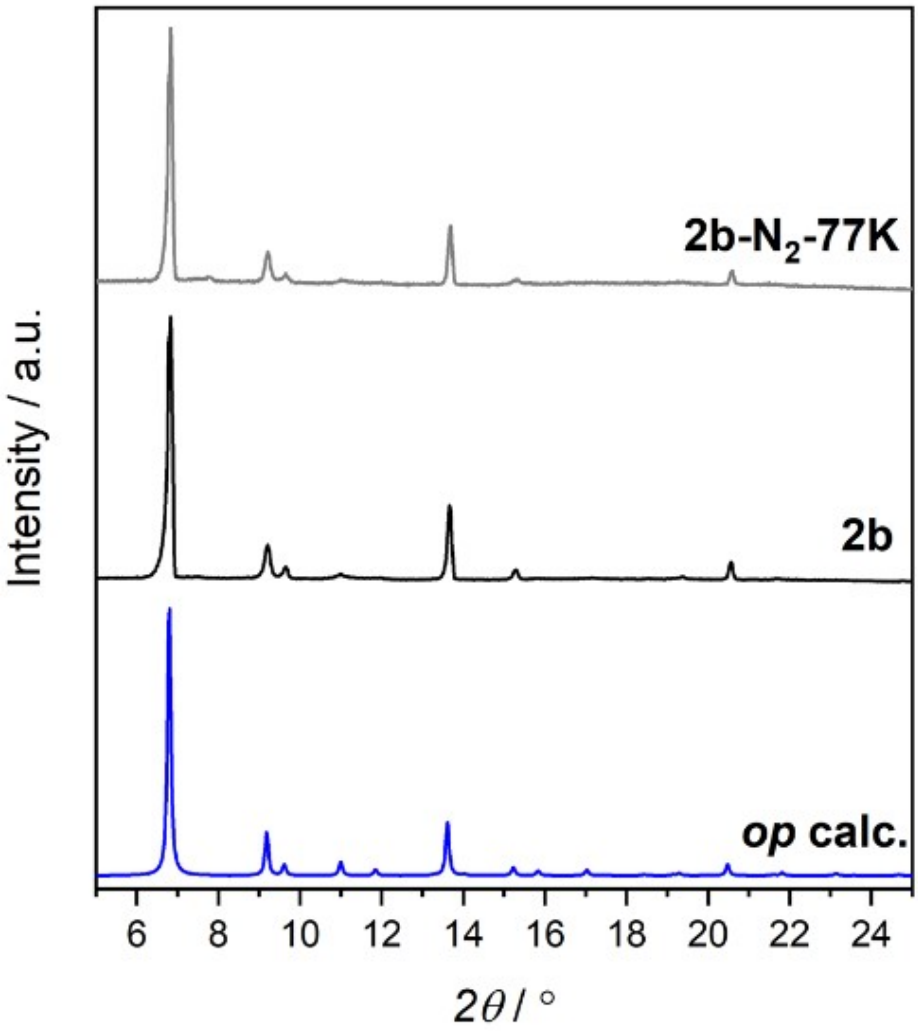

Fig. S5.1. PXRD patterns of **2b** before (black) and after N_2 physisorption at 77 K (gray).

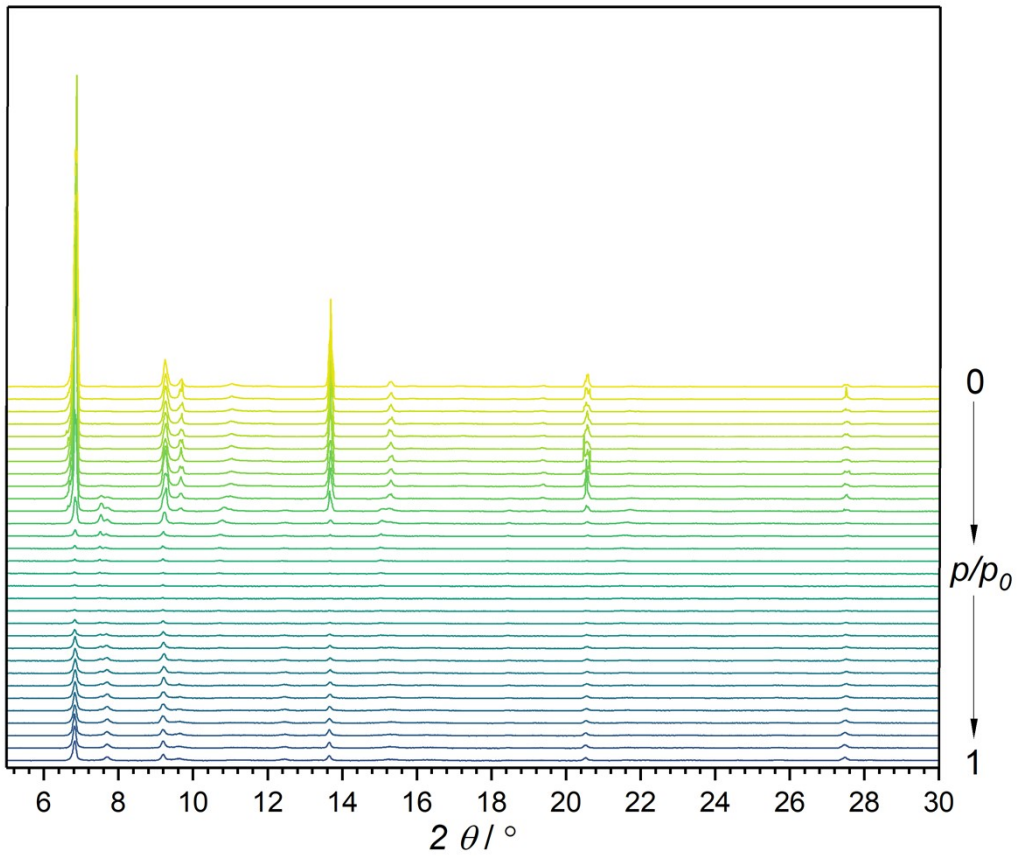

Fig. S5.2. PXRD patterns collected i*n situ* upon CO_2 adsorption at 195 K on **2b**.

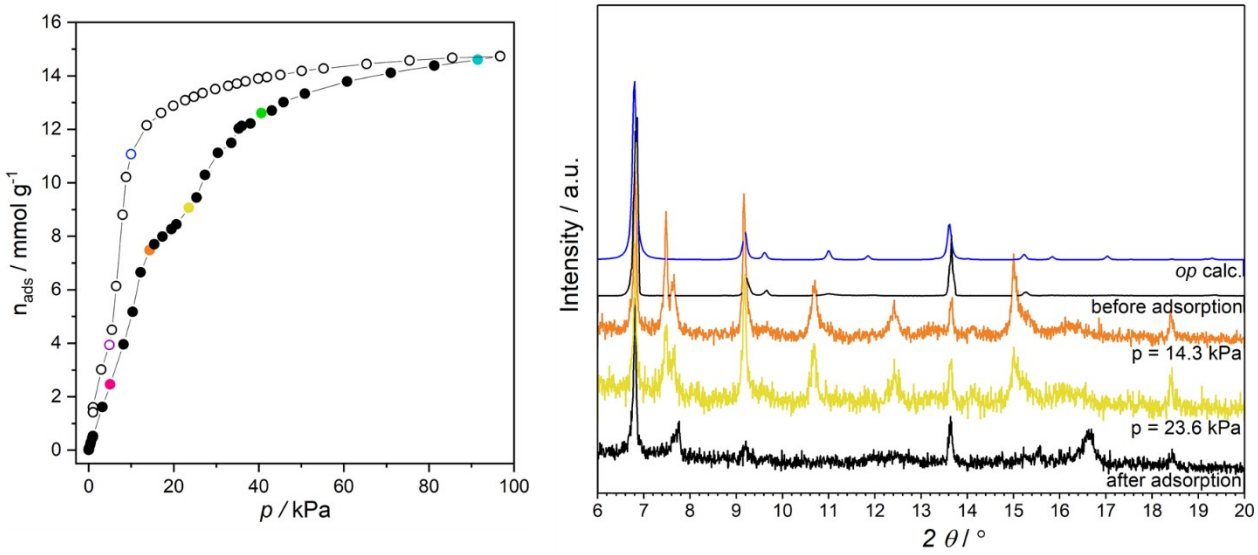

Fig. S5.3. *In situ* CO_2 physisorption isotherm at 195 K and some selected PXRD patterns for **2b**.

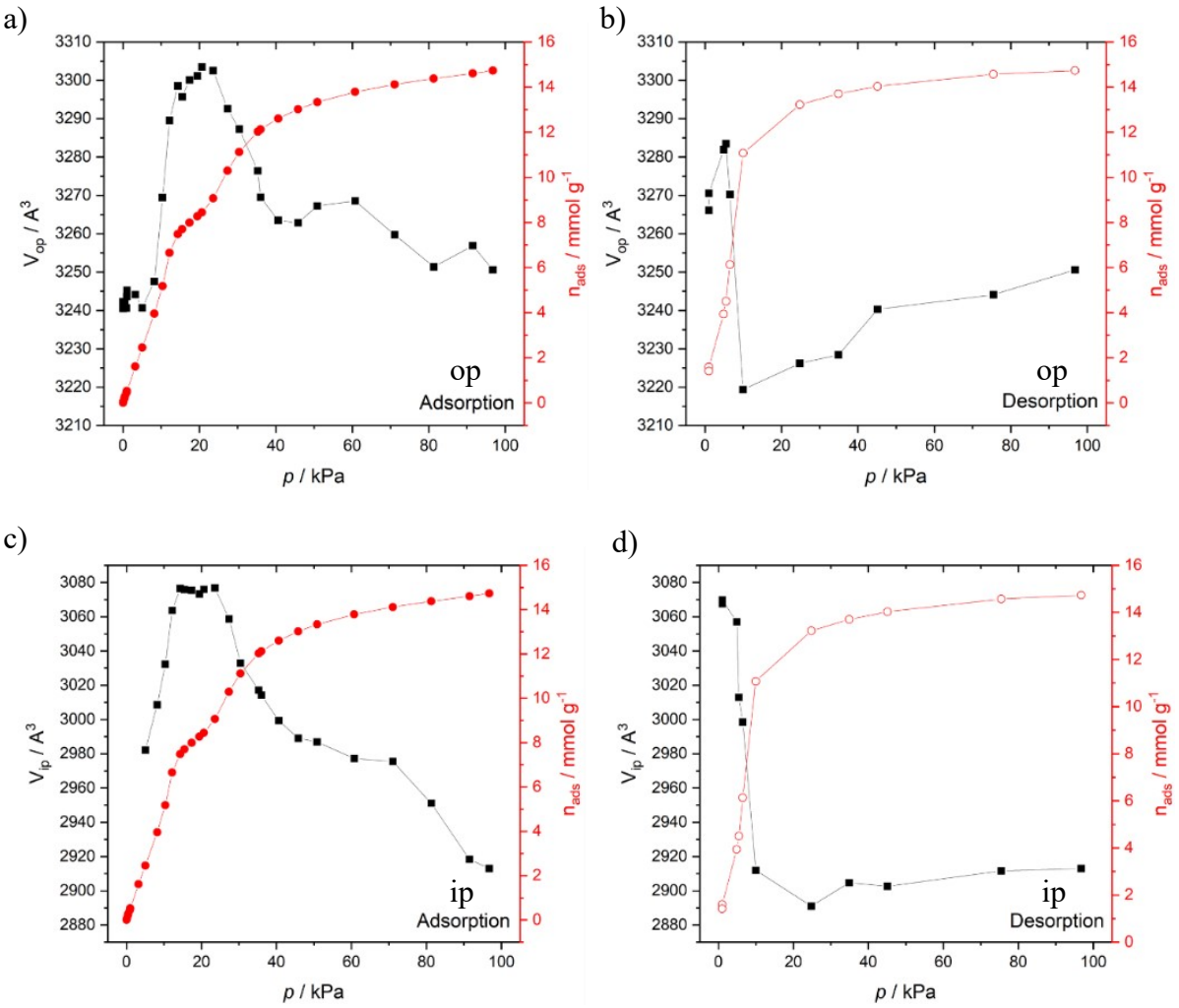

Fig. S5.4. Unit cell volume change of the open pore (op) and intermediate pore (ip) phases upon adsorption (a, c) and desorption (b, d) of CO_2 at 195 K, performed on **2b**.

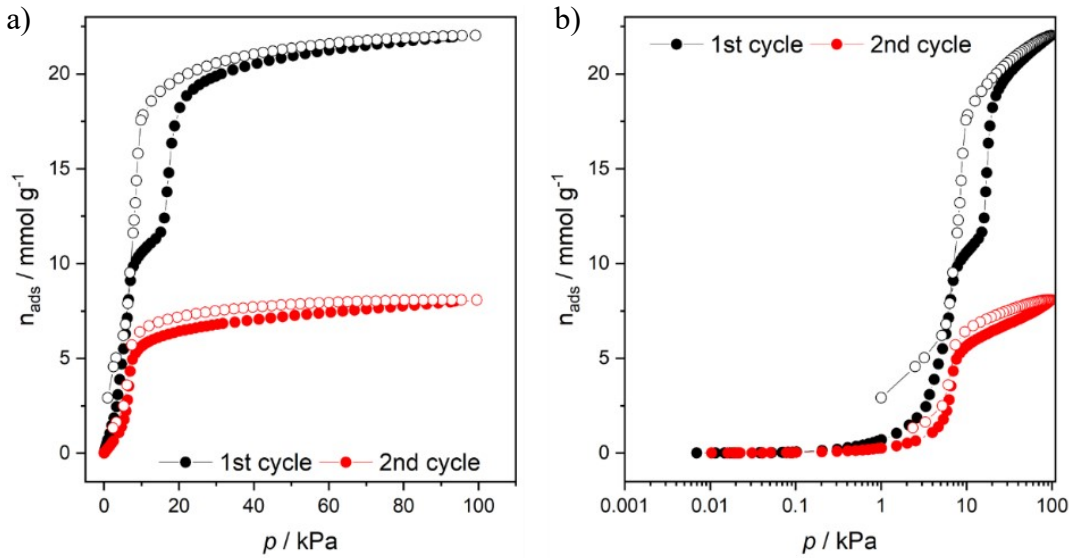

Fig. S5.5. Cyclic adsorption/desorption of CO_2 at 195K for **2b**: (a) linear scale; (b) logarithmic scale. Black – 1st adsorption/desorption cycle, red – 2nd adsorption/desorption cycle. Solid symbols – adsorption, empty symbols – desorption.

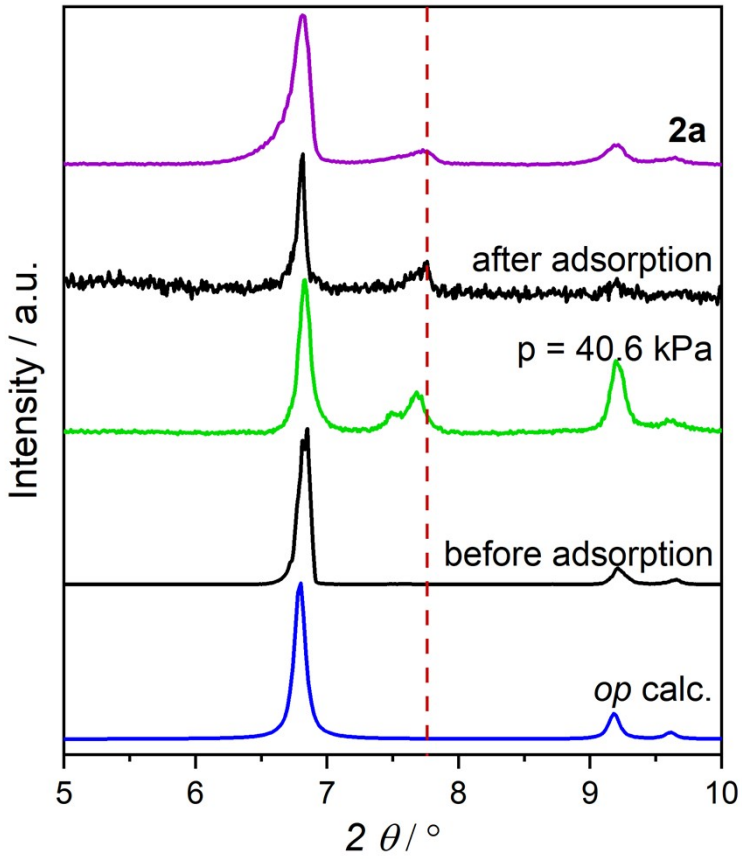

Fig. S5.6. PXRD patterns of: **2b** at 298 K before *in situ* adsorption were measured (lack) **2b** loaded with CO_2 at 195 K at *p* = 40.6 kPa (green), **2b** evacuated at 298 K after CO_2 adsorption/desorption (black), of **2a** (violet). Red line marks the position of the peak of the new phase.

S6 Cluster optimisation

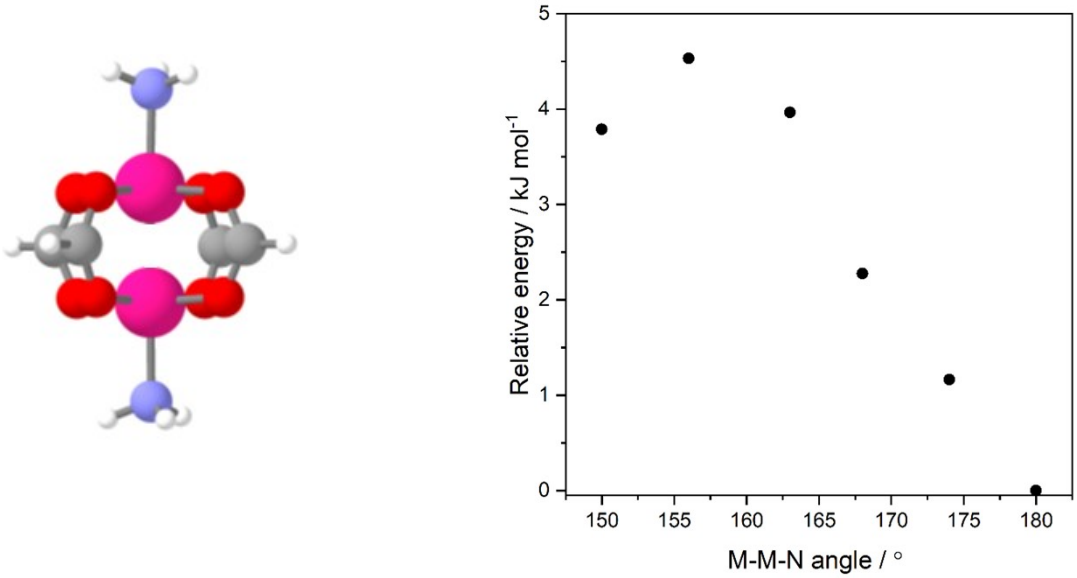

Fig. S6.1 Structure of the Cu paddle wheel cluster molecular analogue (left). The constrained geometry scans of the Cu-Cu-N angles in the paddle wheel cluster (right).

S7 Thermal analysis

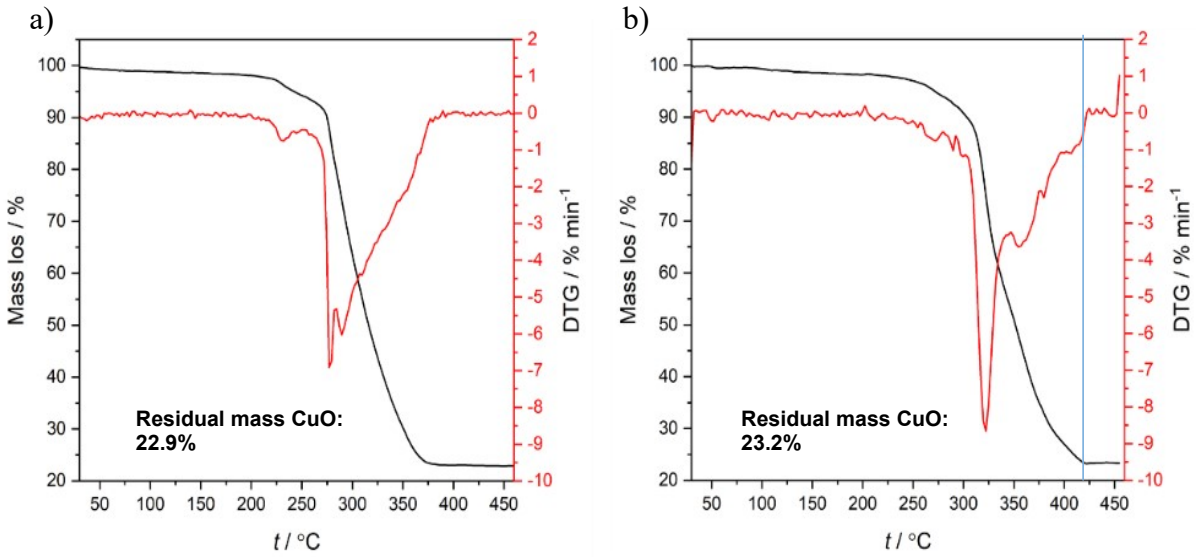

Fig. S7.1 Thermogravimetric analysis (black) / differential thermogravimetric analysis (red) curves of the **1a** (a) and **2b** (b).

***In situ* thermo-PXRD**

Thermo-PXRD measurements were performed on an Empyrean diffractometer (PANALYTICAL GmbH) equipped with a high-temperature chamber in the temperature range of 298 - 723 K with a heating rate of 5 K min^{-1} under nitrogen flow. The temperature steps are 25 K and the equilibration time at a given temperature is 30 min. The powder patterns were taken in reflection mode using copper $K\alpha_1$ radiation and a wavelength of 1.5406 Å.

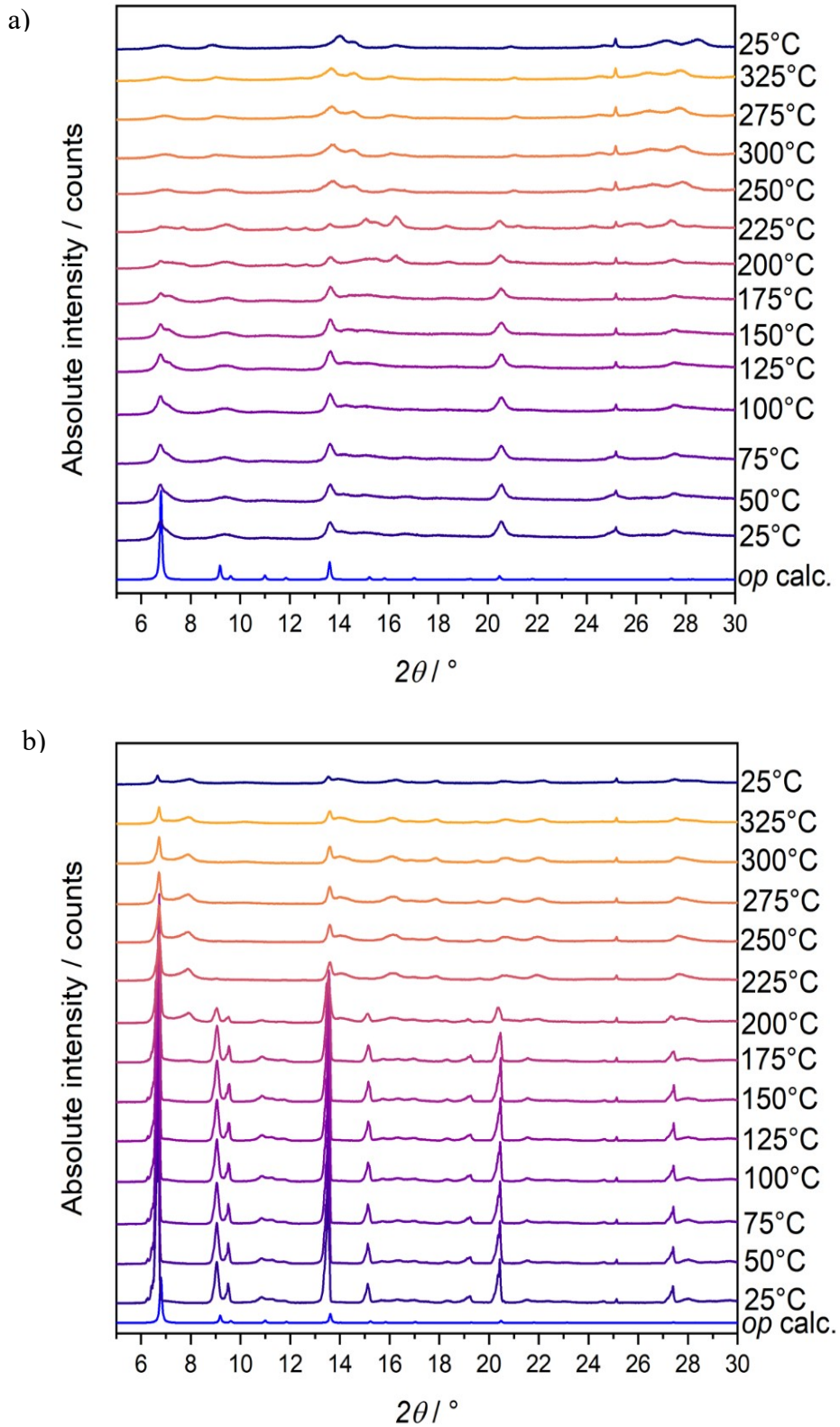

Figure S7.2. Thermo-PXRD patterns of **1a** (a) and **2a** (b) collected upon heating in an inert gas atmosphere (N_2 flow).

Table S7.1 Ratio of 2,6-ndc to dabco in **1a** and **2b** found after thermal treatment in the inert gas atmosphere at elevated temperatures. The ratios were calculated from ^{1}H NMR spectra obtained from the digested samples.

2,6-ndc: dabco	**Initial**	**200 °C**	**240 °C**	**300 °C**	**340 °C**	**Vacuum 160 °C**
1a	1:0.95	1:0.723	1:0.597	1:0.306	1:0.291	
2b	1:0.99	1:0.849	1:0.417	1:0.427	1:0.243	1:0.96

S8 ^{1}H NMR spectroscopy

Before measurements, the samples **1a**, **2a** and **2b** were digested in the mixture of DMSO-d_6 (0.6 ml) and deuterium chloride solution (2 drops) under ultrasonication. The spectra were measured using the Bruker spectrometer at 300 MHz.

Based on the chemical formula of the DUT-8(Cu) ($[Cu_2(2,6\text{-ndc})_2dabco]_n$), the theoretical ratio of the peaks at 8.65 ppm (2H, 2,6-naphthalene dicarboxylate) and 3.55 ppm (12H, dabco) of the linker to pillar should be 1:3.

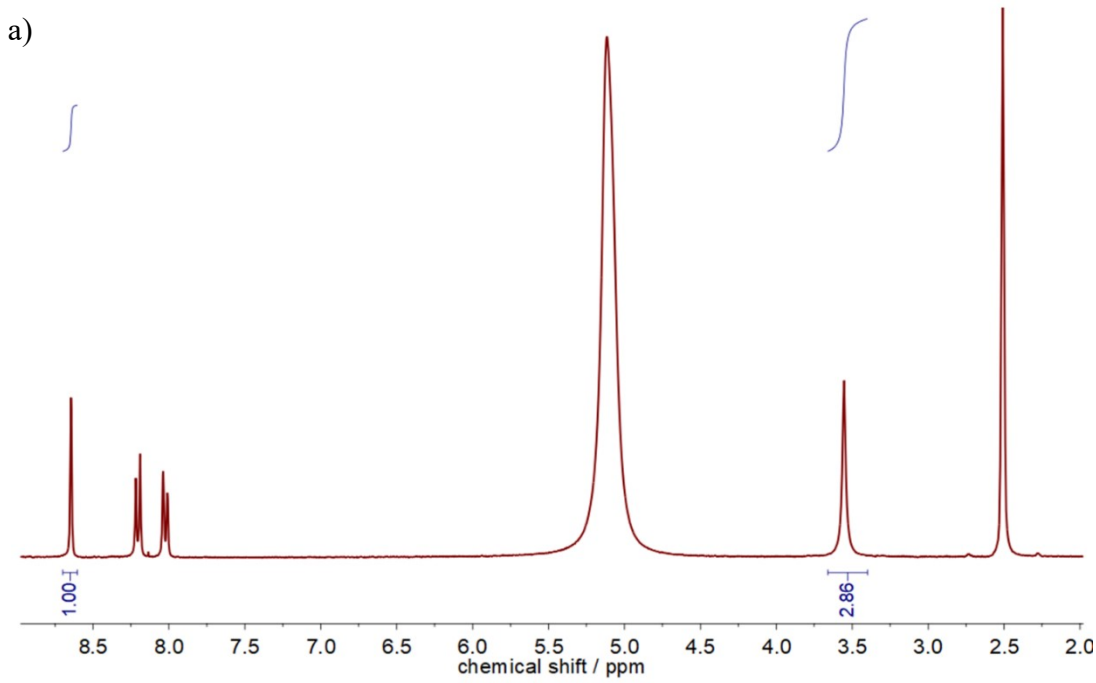

Fig. S8.1 a) ^{1}H NMR spectra of **1a**.

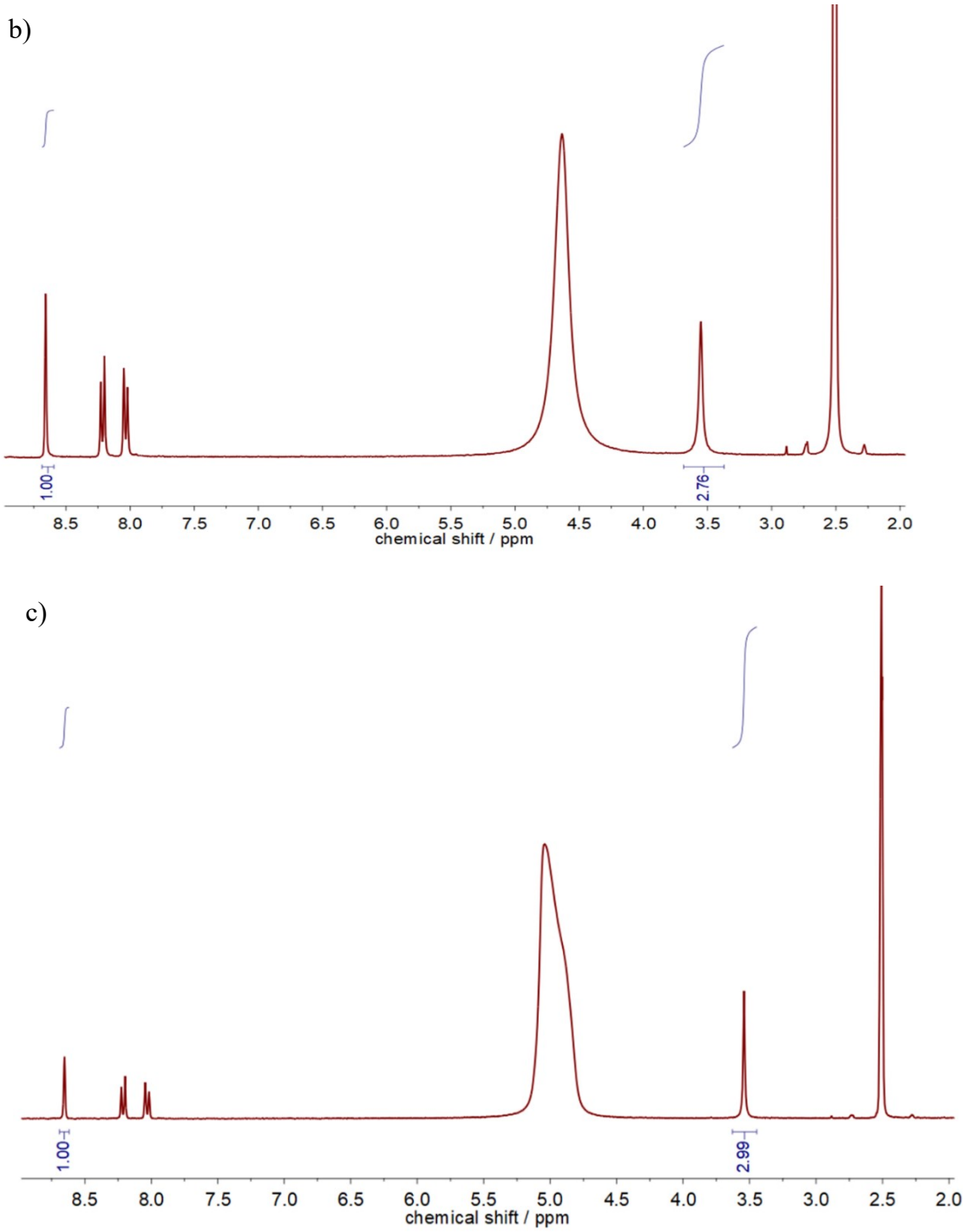

Fig. S8.1 a-b) ^{1}H NMR spectra of **2a** (b) and **2b** (c).

Table S8.1 Ratio of 2,6-ndc to dabco in **1a**, **2a,** and **2b** found after desolvation. The ratios were calculated from ^{1}H NMR spectra shown in Fig. S8.1 and obtained from the digested samples.

Ratio	**1a**	**2a**	**2b**
2,6-ndc : dabco	1:0.95	1:0.92	1:0.99

References

1. N. Klein, H. C. Hoffmann, A. Cadiau, J. Getzschmann, M. R. Lohe, S. Paasch, T. Heydenreich, K. Adil, I. Senkovska, E. Brunner and S. Kaskel *J. Mater. Chem.*, 2012, **22**, 10303.
2. N. Klein 2012, *PhD thesis*, Department of Inoranic Chemistry, Technische Universität Dresden.