Electronic Supplementary Material (ESI) for Chemical Communications.

## Supporting Information

# A new metal-organic framework with ultra-high surface area

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## Supplementary Index

## 1. General Information

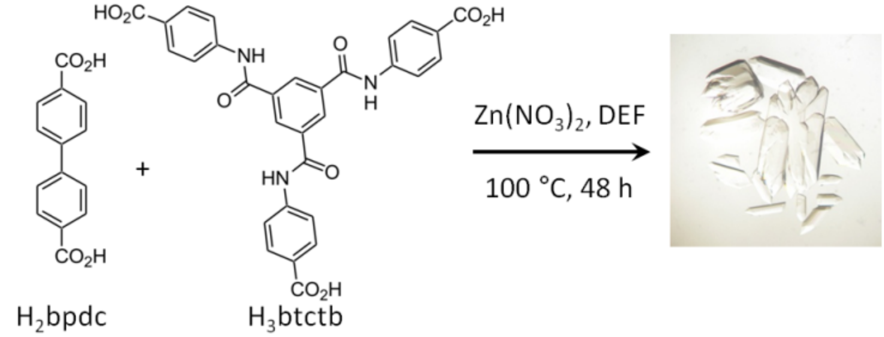
$K_2CO_3$ was dried in an oven at 80°C for 8 h. All other commercially available reagents and solvents were used as received without further purification. NMR-spectra were recorded on a Bruker DRX-500 P. Chemical shifts ($\delta$) are quoted in ppm downfield of tetramethylsilane. The elemental analysis for C, H, N was performed with a CHNS 932 analyzer (LECO). Thermogravimetric analyses were carried out using a Netzsch STA 409 PC Luxx thermal analyzer with a constant heating rate of 5 K/min in air from 303 K to 973 K. Powder X-ray diffraction data were collected in transmission geometry on a STADI P diffractometer with Cu-$K_{\alpha 1}$ radiation ($\lambda$ = 1.5405 Å) at room temperature. Low pressure nitrogen physisorption isotherms up to 1 bar were measured at 77 K using a volumetric BELSORP-HP apparatus. The 90-110 mg of MOF sample were used for physisorption experiments. Control measurements were performed on volumetric BELSORP-MAX apparatus using 10-30 mg of sample. High pressure methane physisorption at room temperature was studied using a magnetic suspension balance (Rubotherm). High pressure hydrogen adsorption measurements at 77 K were performed using volumetric BELSORP-HP apparatus. High purity gases were used: $N_2$: 99.999%, $H_2$: 99.999%, $CH_4$: 99.5%. Prior to all adsorption measurements, the supercritically dried samples were further activated for 2 h at 303 K in high vacuum to remove carbon dioxide and argon from the pores.

## 2. Syntheses

### *Synthesis of 4,4′,4′′-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid ($H_3$btctb)*

4-Aminobenzoic acid (16.53 g, 120.5 mmol, 3.2 eq.) and 18.22 g (131.8 mmol, 3.5 eq.) $K_2CO_3$ were dissolved in 300 mL of dry acetone and stirred under argon atmosphere using a mechanical stirrer. At room temperature a solution of 1,3,5-benzenetricarbonyltrichloride (10 g (37.7 mmol) in 50 mL of dry acetone) was added slowly *via* syringe and the mixture was stirred at 353 K for further 12 h. After cooling to room temperature the solid was separated by filtration, washed intensively with water (300 mL) and a small amount of acetone (50 mL). Drying of the solid under vacuum gave the product as a colorless solid. Yield: 35.12 g (61.891 mmol, 84 %). $^1$H-NMR (DMSO-$d_6$, 500 MHz): $\delta$ (in ppm): 7.97 (d, 6 H), 8.14 (d, 6 H), 8.91 (s, 3 H), 11.32 (s, 3 H), 12.84 (br, 3 H); $^{13}$C-NMR (DMSO-$d_6$, 125 MHz): δ (in ppm): 119.60 (CH), 125.77 ($C_q$), 130.24 (CH), 130.63 (CH), 134.80 ($C_q$), 143.32 ($C_q$), 164.76 ($C_q$), 166.98 ($C_q$).

***Synthesis of $Zn_4O(bpdc)(btctb)_{4/3}(DEF)_{39.7}(H_2O)_{11.3}$ (DUT-32)***



$Zn(NO_3)_2 \cdot 4H_2O$ (126 mg, 0.480 mmol), $H_3$btctb (55 mg, 0.096 mmol) and $H_2$bpdc (29 mg, 0.120 mmol) were dissolved in 8 cm$^3$ of *N,N*-diethylformamide (DEF). The mixture was sonicated for 5 min and heated to 373 K for 48 hours in a Pyrex® tube. The mother liquor was decanted and the crystals were washed five times with fresh *N,N*-dimethylformamide (DMF). Yield: 62 mg (51 % based on $H_3$btctb).

Elemental analysis for as made sample: calcd. (%) for $C_{54}H_{32}O_{17}N_4Zn_4 \times 39.7\ C_5H_{11}NO \times 11.3\ H_2O$ [$Zn_4O(bpdc)(btctb)_{4/3}(DEF)_{39.7}(H_2O)_{11.3}$]: C 55.25, H 9.02, N 11.15; found: C 55.28±0.4, H 9.06±0.1, N 11.1±0.3; Elemental analysis for supercritical dried sample: calcd. (%) for $C_{54}H_{38}O_{20}N_4Zn_4$ [$Zn_4O(bpdc)(btctb)_{4/3}(H_2O)_3$]: C 48.97, H 2.89, N 4.23; found: C 49.09±0.3, H 2.72±0.3, N 4.35±0.3.

## 3. Supercritical drying of DUT-32

Prior to the drying, the DMF containing crystals were soaked in ethanol (abs.), dry acetone or dry amyl acetate, respectively (3 days with renewing the solvent four times per day).

After exchange, the material was transferred into a Critical Point Dryer (SPI Supplies) tempered at 283 K and flushed with liquid $CO_2$, which was renewed three times a day. After the respective resting time in liquid $CO_2$ the temperature was raised to 310 K changing the $CO_2$ from a liquid to a supercritical state. Afterwards, the $CO_2$ was released over a period of 2-3 hours.

## 4. Single crystal X-ray structure analysis and crystallographic data

Single crystals of DUT-32 and DUT-59 were sealed in glass capillaries with small amount of solvent. The datasets were collected at beamline BL14.2, Joint Berlin-MX Laboratory of Helmholtz Zentrum Berlin, equipped with a MX-225 CCD detector (Rayonics, Illinois) and 1-axes goniometer.[1] The data collection was performed using monochromatic radiation with $\lambda = 0.88561$ Å.

All non hydrogen atoms were refined in anisotropic approximation. The hydrogen atoms were positioned geometrically and refined using a riding model. The lattice solvent molecules could not be located from difference Fourier map due to disorder in the highly symmetrical space group. Thus, the SQUEEZE procedure in PLATON was performed to correct the intensities, corresponding to disordered part of the structure.[2] It results in 15069 electrons that were cut out from the void of 121980 Å$^3$ in the case of DUT-32 and in 7884 electrons squeezed from 53647 Å$^3$ in the case of DUT-59.

### ***DUT-32***

In spite of sufficient size of single crystals and highly intensive synchrotron radiation, the diffraction images of DUT-32 show reflexes with significant intensities only up to 30° 2θ. This could be explained by ultra-high porosity of the sample that leads to a very low fraction of the ordered framework in the crystal. A plethora of single crystals of various sizes (up to 0.5 mm in all dimensions) from different batches were screened by singe crystal diffraction. The experiments were performed at 295 K and at 100 K. Nevertheless, the data set of high quality could not be obtained. The best collected dataset was used for the data processing. The indexing of the image frames suggests a hexagonal crystal system. The image frames were integrated and scaled using Mosflm 1.0.5 and Scala programs, respectively.[3] The obtained set of intensities was carefully analyzed against systematic extinctions. As a result, a systematic absence of every 3rd reflection was found along *c* direction. This suggests the presence of $6_3$ symmetry in the crystal structure. Because the $R_{sym}$ value for the 6/m point group was significantly lower than for 6/mmm, the $P6_3/m$ space group was chosen for the structure solution. The structure was solved by direct methods and refined by full-matrix least square on F$^2$ using SHELXS and SHELXL[4] programs, respectively. $Zn_4O^{6+}$ cluster in the structure of DUT-32 is disordered between two positions. The atom site occupancies were refined as free variables, resulting in values 0.85

and 0.15. Considering this point, only organic ligand molecules with higher occupancy could be found from electron density map. Reduced occupancy of the main position (0.85) in combination with poor scattered single crystal results in a structural model that is not very sensitive to the changes in the geometry of organic part.

This prompted us to use 159 restraints to fix the geometry of highly flexible organic $H_3$btctb ligand. Namely, DFIX, FLAT and SADI instructions were used. The first $Zn_4O$ cluster (Zn1, Zn2, Zn3, Zn4 and O1) is located in the general position. The atoms Zn5, Zn7 and O2 from the second metal cluster are located on the mirror plane. The bpdc linker, involving C1-C7, O3, and O4 atoms, which connects two $Zn_4O$ clusters (Zn1-Zn4, O1) contains an inversion center. Two btctb$^{3-}$ linkers (involving O15, O16, O26, C62-C71, N5 and O13, O14, O25, C52-C61, N4) are located on 3-fold rotation axis. Further btctb$^{3-}$ anion (C72-C87, O19, O20, O21, O27, O28, N6, N7) is mirror-symmetric.

### *DUT-59*

The asymmetric unit of DUT-59 contains two disordered $Zn_4O$ clusters and two and one third btctb$^{3-}$ linkers. One of the clusters is located in general position. The Zn11, Zn12 and O2 atoms of the second cluster are located on the 3-fold axes. Both independent $Zn_4O^{6+}$ clusters are disordered over two equally occupied positions that lead to disorder of carboxylate oxygen atoms, as well as whole molecule of the highly flexible btctb$^{3-}$ linker. Therefore, 179 restraints (DFIX, SADI, FLAT etc.) were used during the structure refinement.

***Crystal data for DUT-32:*** $C_{252.5}H_{491.3}N_{68}O_{43.7}Zn_4$, $M$ = 5441.09 g mol$^{-1}$, hexagonal, $P6_3/m$ (Nr. 176), $a$ = 50.710(7) Å, $c$ = 62.920(13) Å, $V$ = 140122(40) Å$^3$, $Z$ = 18, $\rho_{calc}$= 1.161 g cm$^{-3}$, $\lambda$ = 0.88561 Å, $T$ = 293 K, $\theta_{max}$ = 28.2°, reflections collected/unique 118656/60048, $R_{int}$ = 0.0497, $R_1$ = 0.0688, $wR_2$ = 0.1815, S = 1.010, largest diff. peak 0.229 e Å$^{-3}$ and hole -0.196 e Å$^{-3}$.

***Crystal data for DUT-59:*** $C_{148}H_{229.6}N_{23.6}O_{36.6}Zn_4$, $M$ = 3186.62 g mol$^{-1}$, trigonal, $P31c$ (Nr. 159), $a$ = 44.670(6) Å, $c$ = 36.140(7) Å, $V$ = 62453(22) Å$^3$, $Z$ = 8, $\rho_{calc}$= 0.678 g cm$^{-3}$, $\lambda$ = 0.88561 Å, $T$ = 293 K, $\theta_{max}$ = 30.02°, reflections collected/unique 62028/ 32777, $R_{int}$ = 0.0412, $R_1$ = 0.0611, *wR*$_2$ = 0.1542, S = 1.018, largest diff. peak 0.171 e Å$^{-3}$ and hole -0.161 e Å$^{-3}$, Flack parameter x = 0.107(6).

CCDC-968887 and CCDC-968888 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

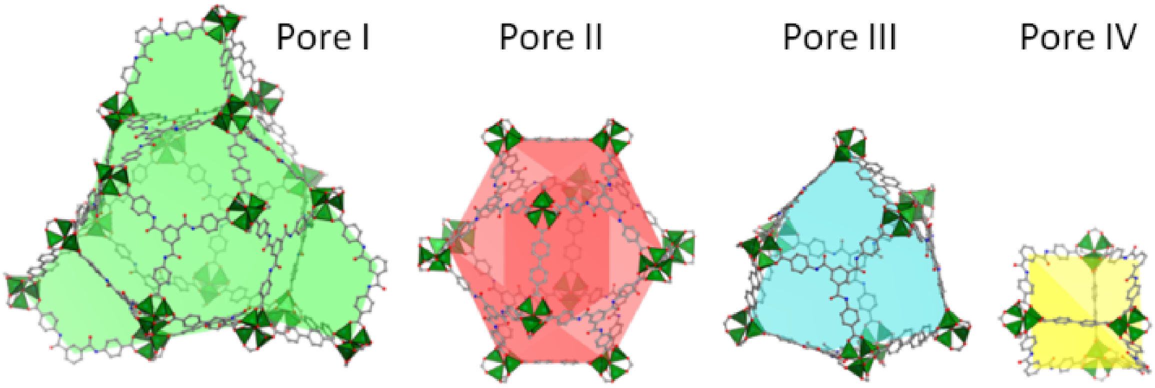


**Figure S1** Four different pores within the structure of DUT-32.

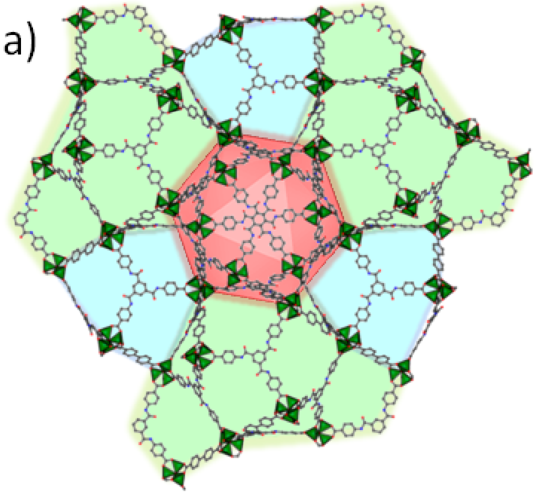


**Figure S2** Crystal structure of DUT-32 (the micropore named “pore IV” in figure 1 is not colored for clarity).

## 5. Overview of linker length ratios for the combination of ditopic and tritopic linkers.

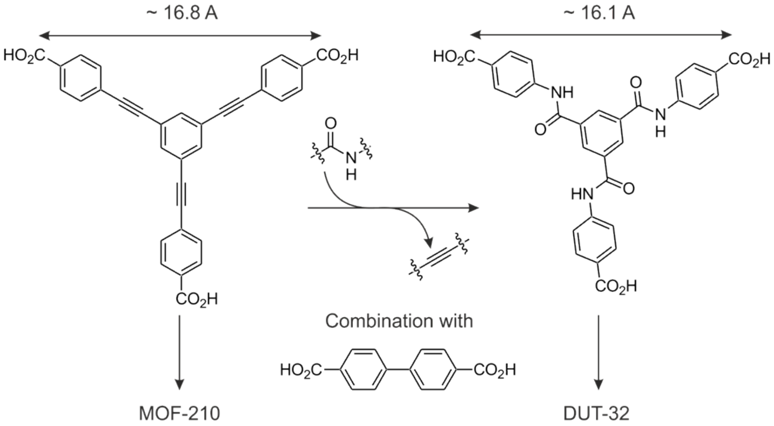
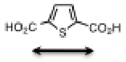
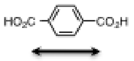
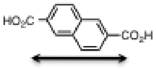
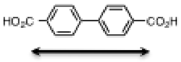
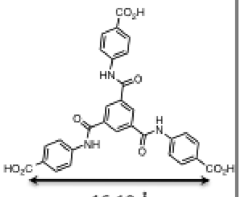
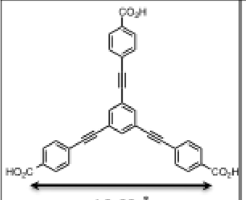
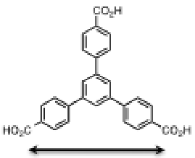
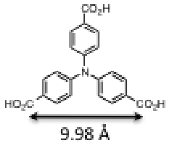


**Figure S3** Similarities in linker length between 4,4',4''-[benzene-1,3,5-triyltris(ethyne-2,1-diyl)]tribenzoic acid ($H_3$bte) used for the construction of MOF-210 (left) and 4,4´,4´´-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid ($H_3$btctb) used for DUT-32.

**Table S1 |** Linker length ratios for the combination of ditopic and tritopic linkers in MOFs published up to now.

| | <br>5.34 Å | <br>5.76 Å | <br>7.39 Å | <br>8.00 Å | <br>10.21 Å |
|---|---|---|---|---|---|
| <br>16.10 Å | --<br>$L_d/L_t = 0.332$ | --<br>$L_d/L_t = 0.358$ | --<br>$L_d/L_t = 0.459$ | --<br>$L_d/L_t = 0.497$ | DUT-32<br>$L_d/L_t = 0.634$ |
| <br>16.68 Å | --<br>$L_d/L_t = 0.320$ | --<br>$L_d/L_t = 0.346$ | --<br>$L_d/L_t = 0.443$ | --<br>$L_d/L_t = 0.480$ | MOF-210<br>$L_d/L_t = 0.612$ |
| <br>12.18 Å | UMCM-3<br>$L_d/L_t = 0.439$ | UMCM-1<br>$L_d/L_t = 0.473$ | UMCM-2<br>$L_d/L_t = 0.607$ | DUT-6<br>$L_d/L_t = 0.657$ | --<br>$L_d/L_t = 0.838$ |
| <br>9.98 Å | --<br>$L_d/L_t = 0.535$ | UMCM-4<br>$L_d/L_t = 0.577$ | --<br>$L_d/L_t = 0.740$ | --<br>$L_d/L_t = 0.802$ | --<br>$L_d/L_t = 1.022$ |

## 6. DUT-59

The excess of $H_3$btctb in the reaction mixture during the synthesis of DUT-32 leads to the formation of byproduct $Zn_4O(btctb)_2$ (DUT-59), which is a isoreticular to MOF-177 (for crystallographic data see section 4 ESI).[5]

DUT-59 can be synthesized as pure phase using following synthetic procedure: $H_3$btctb (0.032 g) end $Zn(NO_3)_2 \cdot 4H_2O$ (0.037 g) were solved in DEF (7 ml) and heated to 373 K for 24 hours in a Pyrex® tube. Yield: 34 mg (0.024 mmol, 43 %).

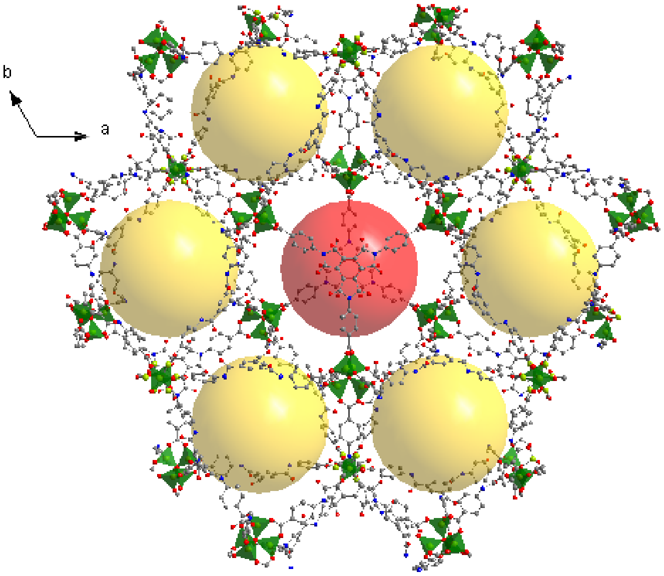


**Figure S4** Crystal structure of DUT-59.

## 7. Topology of DUT-32

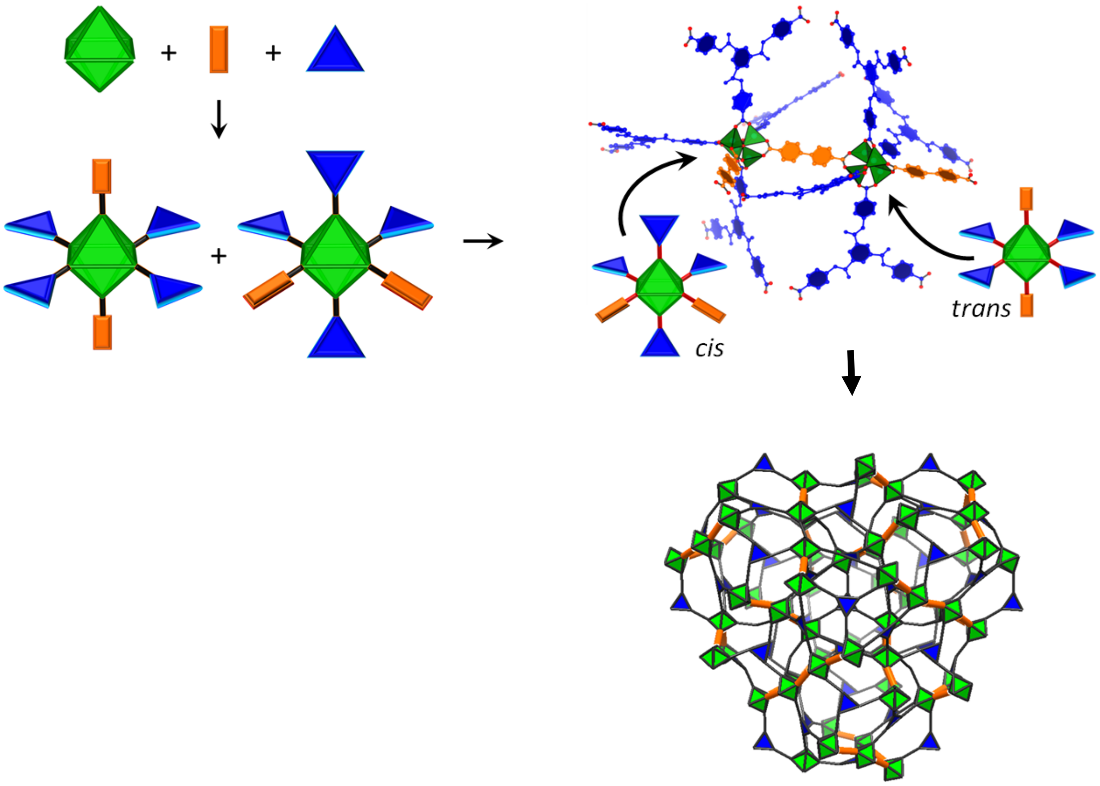


**Figure S5** *Cis* and *trans* position of linear linkers in the clusters (left) leading to the rare **umt** topology observed in DUT-32 (right).

## 8. PXRD patterns

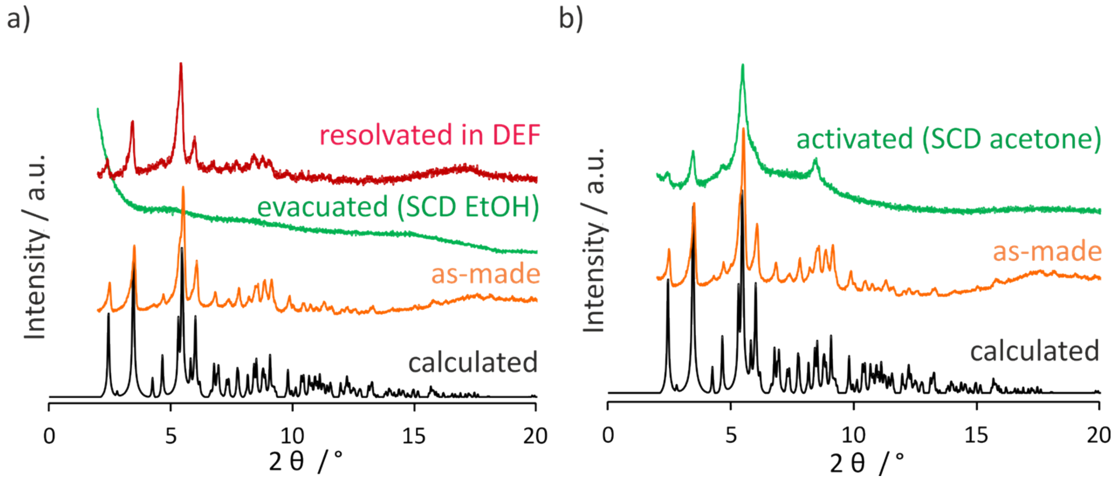


**Figure S6** Powder X-ray diffraction pattern of DUT-32 (a) dried from ethanol, (b) acetone; calculated from the crystal structure (black), synthesized sample (orange), supercritically dried sample (green) and resolvated sample (red).

## 9. Thermogravimetric analysis

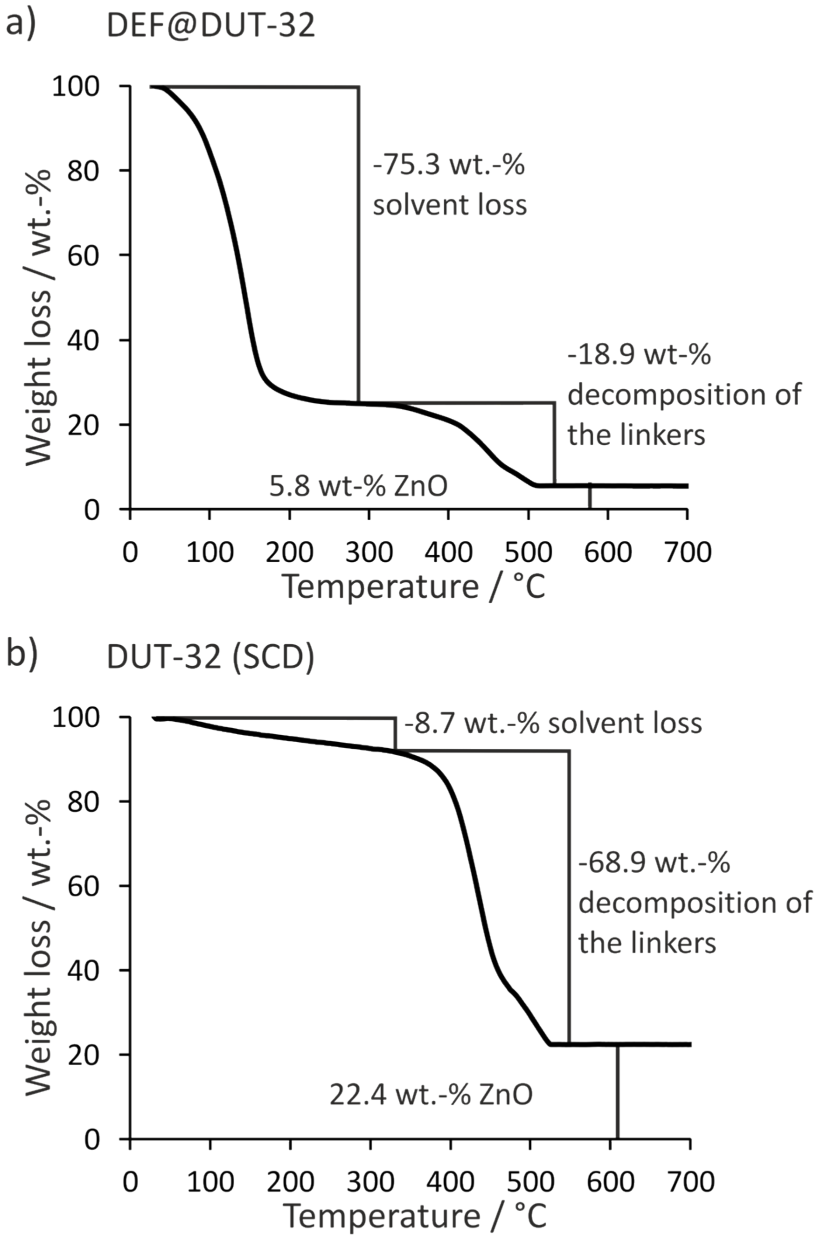


**Figure S7** Thermogravimetric analyses of (a) solvated and (b) dried DUT-32.

## 10. NMR-data

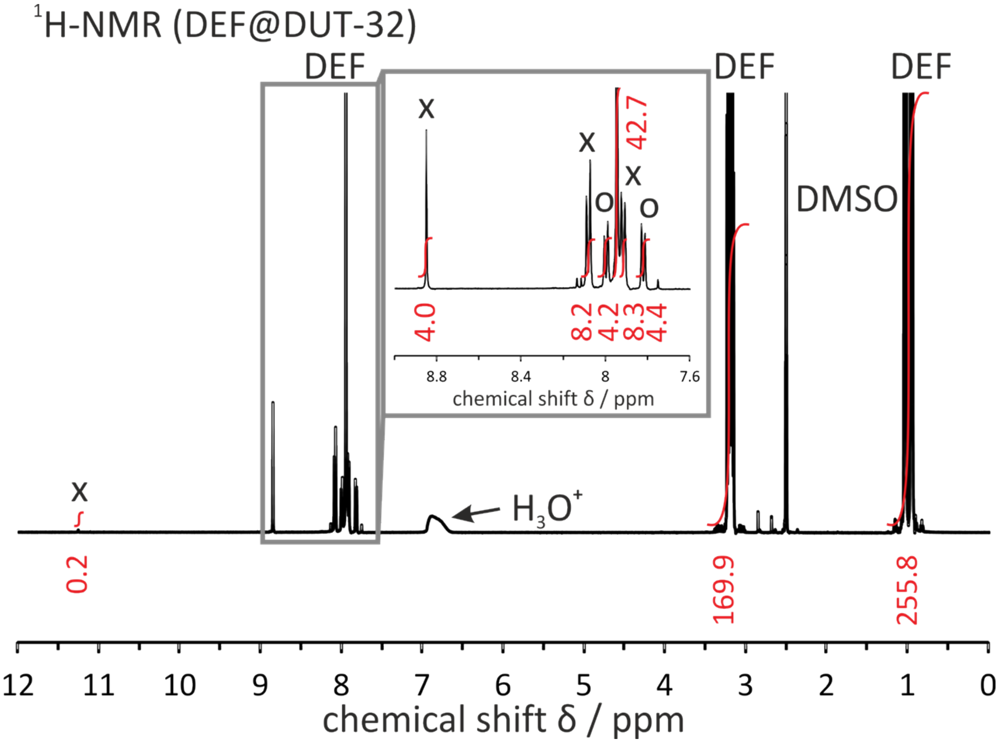
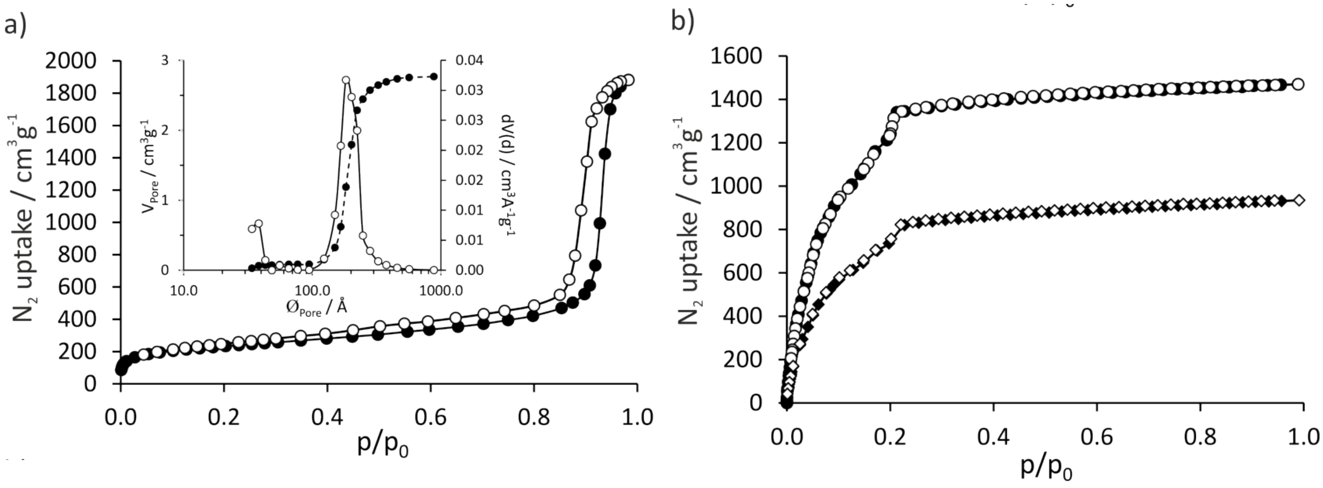


**Figure S8** $^1$H-NMR spectra of as-made DUT-32, digested after the synthesis. Solvent peaks are assigned, peaks marked with a "X" correspond to btctb-, peaks marked with a "O" correspond to bpdc-linker.

## 11. Physisorption



**Fiure S9** a) $N_2$ physisorption isotherm at 77 K of DUT-32 after supercritical drying from ethanol as solvent; inset: corresponding pore size distribution; b) $N_2$ physisorption isotherms at 77 K of DUT-32 after supercritical drying from acetone as solvent with different MOF/liquid_$CO_2$ ratio used for the drying process (diamonds: 100 mg of sample were used for drying; circles: 30 mg sample were used for drying). The same results can be observed by use of amyl acetate as solvent.

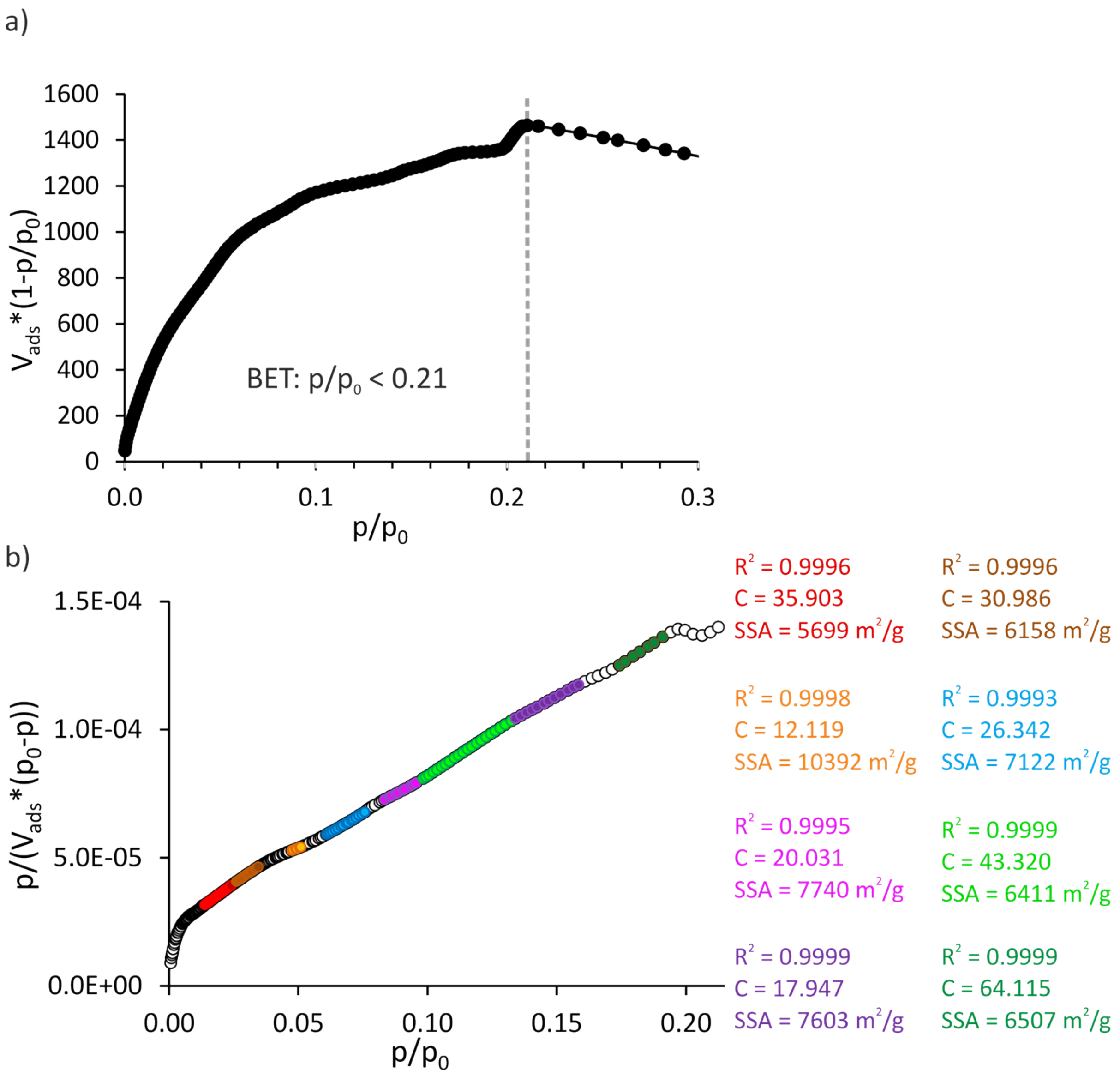


**Figure S10** a) $V(1-p/p_0)$ *vs.* $p/p_0$ for DUT-32 supercritically dried from amyl acetate for seven days. Only the range below $p/p_0 = 0.14$ satisfies the first consistency criterion for applying the BET theory. BET plot of the $N_2$ isotherm shown in a); colored points within the plot illustrated different possible linear regions for the estimation of the BET specific surface area.

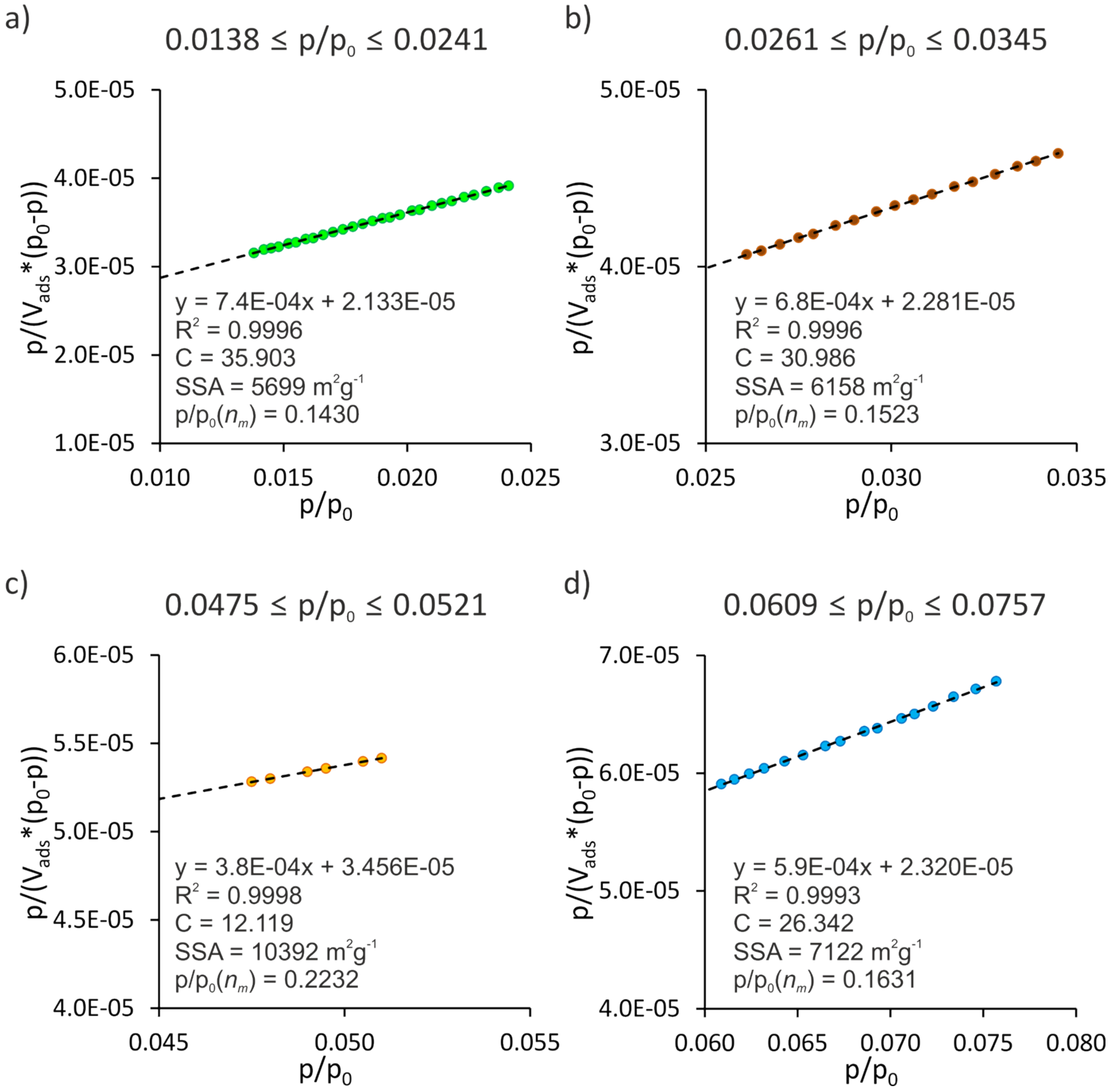


**Figure S11** Magnified illustrations of the first four linear regions of the BET plot shown in Fig. S6b with the corresponding relative pressure ranges, linear regressions, BET *C* constants, estimated specific surface areas and calculated relative pressures attributed to the monolayer capacity.

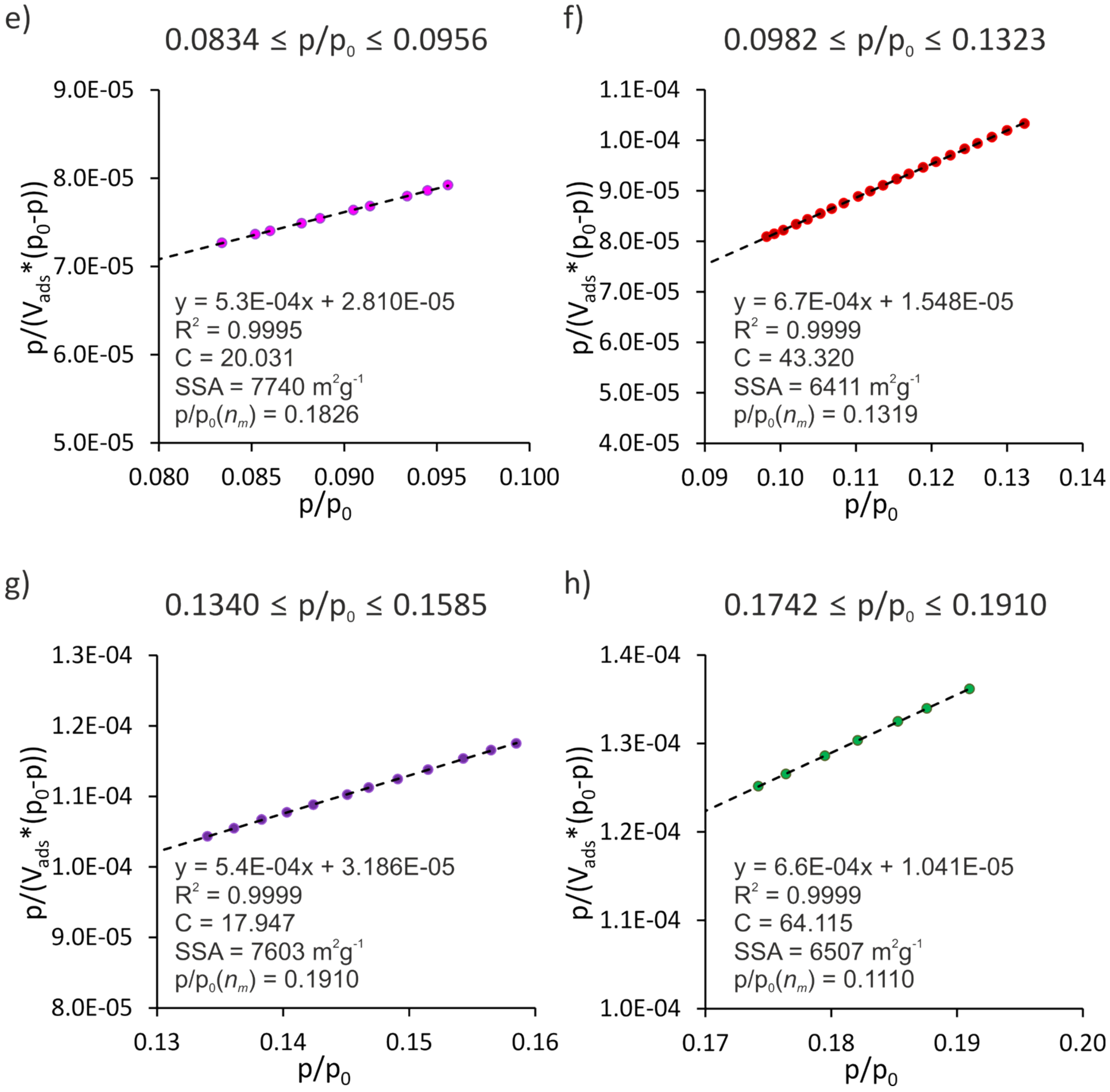


**Figure S12** Magnified illustrations of the last four linear regions of the BET plot shown in Fig. S6b with the corresponding relative pressure ranges, linear regressions, BET *C* constants, estimated specific surface areas and calculated relative pressures attributed to the monolayer capacity.

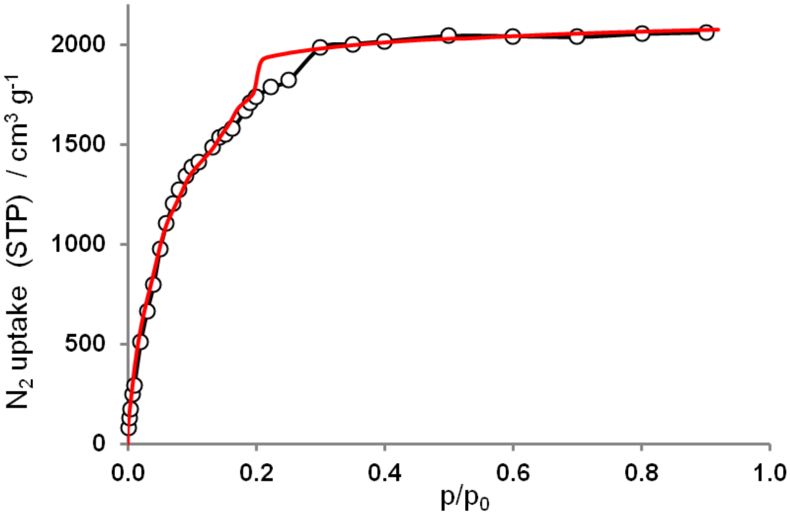


**Figure 13** Simulated (black) and measured (red) $N_2$ physisorption isotherm at 77 K of DUT-32_10d.

## 12. 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, Facilities for macromolecular crystallography at the Helmholtz-Zentrum Berlin*, J. Synchrotron Rad.* **2012**, *19*, 442.
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