Supporting Information for *Chemical Communications*

A highly porous flexible Metal-Organic Framework with corundum topology

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1. General Informations

$Zn(NO_3)_2 \cdot 4H_2O$ (Fluka) was used as received. *N,N*-diethylformamide (DEF) was distilled from phosphorous pentoxide and stored under argon.

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 (λ = 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 process, the reaction product was washed with DEF and placed in EtOH (abs.) to exchange the guest DEF molecules with a solvent miscible with liquid CO_2. The ethanol was replaced and the samples were placed in a Jumbo Critical Point Dryer 13200J AB (SPI Supplies). The occluded ethanol was exchanged with liquid carbon dioxide (purity: 99.995%) at ~ 15-20 °C for about 20 hours. Around 120 bar above the critical point, the supercritical CO_2 was released. 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 room temperature. N_2, CO_2 and H_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 105 bar was performed using approximately 0.3 g sample on a volumetric BELSORP-HP apparatus. High pressure CH_4 adsorption was studied using a magnetic suspension balance (Rubotherm Co.). Adsorption of *n*-butane was performed with a micro-balance (B111, Setaram) at ambient conditions. High purity gases were used (N_2: 99.999%, H_2: 99.999%, CH_4: 99.5%, n-C_4H_{10}: 99.95%).

Thermogravimetric analyses (TGA) were carried out under air atmosphere using a Netzsch STA 409 thermal analyzer. Infrared spectra (IR) were recorded in diffuse reflection geometry using a BIORAD Excalibur FTS3000 (Varian Inc.) infrared spectrometer. Elemental analysis (C, H, N) was performed with a CHNS 932 analyzer from LECO. The oxygen content was determined by coupling of the CHNS 932 analyzer with the pyrolysis furnace VTF-900. The respective metal content was determined with an ICP-OES Vista RL apparatus from Varian Inc.

2. Synthetic procedures for H_4BenzTB and DUT-13

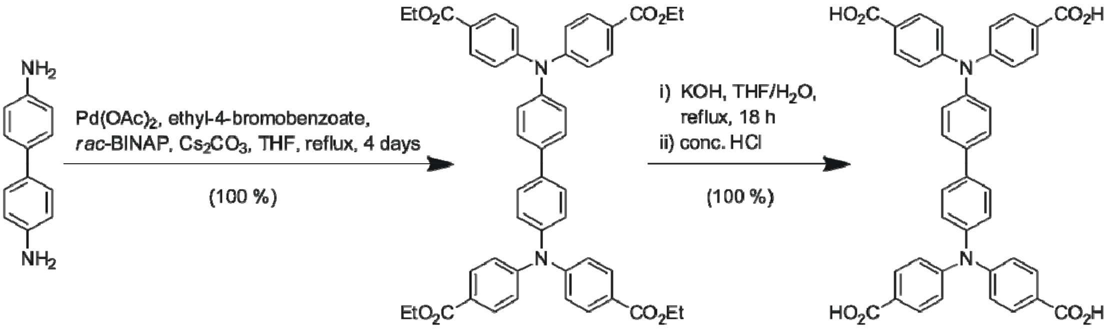

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Fig. S1 Two-step synthesis of H_4BenzTB (2) including fourfold Buchwald-Hartwig coupling and alkaline ester hydrolysis in an overall quantitative yield.

***N,N,N′,N′*-tetrakis-(4-carboethoxyphenyl)-biphenyl-4,4'-diamine (1)**

A mixture of ethyl-4-bromobenzoate (8.86 mL, 12.43 g, 54.277 mmol), $Pd(OAc)_2$ (97.5 mg, 0.434 mmol), Cs_2CO_3 (21.221 g, 65.130 mol) and *rac*-2,2′–bis(diphenylphosphino)–1,1′–binaphthyl (*rac*-BINAP) (540.7 mg, 0.868 mmol) were solved in 1,4-dioxane (30 mL) and stirred 20 min at 100 °C. Subsequently a solution of benzidine (2.00 g, 10.855 mmol) in 1,4-dioxane (75 mL) was added. After 90 h at 100 °C the orange suspension was cooled to room temperature and the inorganic salts were removed by filtration through a pad of Celite®. After removal of the solvent in vacuum, the crude product was either purified by column chromatography (diethylether/pentane (1:1)) or recrystallized from a mixture of diethylether and dichloromethane (4:1) to give the product **1** (8.420 g, 100%) as a light yellow solid (Found: C, 73.43; H, 5.53; N, 3.52, requires for $C_{48}H_{44}N_2O_8$ (776.31): C, 74.21; H, 5.71; N, 3.61%); δ_H(500 MHz, *CDCl₃*) 1.38 (12 H, t, $J_{11,10}$ 7.3 Hz, 11-H_3), 4.35 (8 H, q, $J_{10,11}$ 7.3 Hz, 10-H_2), 7.13 (8 H, d, $J_{6,7}$ 8.8 Hz, 6-H), 7.19 (4 H, d, $J_{3,2}$ 8.5 Hz, 3-H), 7.54 (4 H, d, $J_{2,3}$ 8.5 Hz, 2-H) and 7.93 (8 H, d, $J_{7,6}$ 8.8 Hz, 7-H); δ_C(125 MHz, *$CDCl_3$*) 14.38 (CH_3, C-11), 60.79 (CH_2, C-10), 122.66 (CH, C-6), 124.72 (C_q, C-8), 126.38 (CH, C-3), 128.06 (CH, C-2), 130.99 (CH, C-7), 136.81 (C_q, C-1), 145.38 (C_q, C-4), 150.76 (C_q, C-5) and 166.12 (C_q, C-9); υ_{max}/cm^{-1} 3068, 3037, 2985, 2904, 1720, 1605, 1500, 1367, 1325, 1182, 1111, 1028, 845, 768; *m/z* (EI) calc. 776.3098, requires 776.3093;

***N,N,N′,N′*-benzidinetetrabenzoic acid (H_4BenzTB) (2)**

In a round bottom flask *N,N,N′,N′*-tetrakis-(4-carboethoxyphenyl)-biphenyl-4,4'-diamine (**1**) (8.074 g, 10.393 mmol) was dissolved in tetrahydrofuran (THF) (150 mL) and a solution of KOH (11.660 g, 207.86 mmol) in H_2O (50 mL) was added. This mixture was refluxed for 24 h. After cooling down to room temperature the THF was evaporated and the resulting water phase was acidified with conc. HCl until no further precipitate was detected. The slightly yellow solid **2** was collected by filtration, washed with water, a small amount of acetone and diethylether and dried in vacuum (90 g, 100%). δ_H(500 MHz, *d_6-DMSO*) 7.11 (8 H, d, $J_{6,7}$ 8.8 Hz, 6-H), 7.20 (4 H, d, $J_{3,2}$ 8.8 Hz, 3-H), 7.71 (4 H, d,

$J_{2,3}$ 8.8 Hz, 2-H), 7.88 (8 H, d, $J_{7,6}$ 8.8 Hz, 7-H) and 12.76 (4 H, br, CO_2H); δ_C(125 MHz, *d_6-DMSO*) 122.49 (CH, C-6), 124.90 (C_q, C-8), 126.40 (CH, C-3), 128.07 (CH, C-2), 131.09 (CH, C-7), 136.00 (C_q, C-1), 144.97 (C_q, C-4), 150.24 (C_q, C-5) and 166.82 (C_q, C-9); υ_{max}/cm^{-1} 3070, 3035, 2958, 2873, 2663, 2559, 1699, 1603, 1510, 1435, 1331, 1304, 1184, 852, 775; *m/z* (EI) $[M]^+$ requires 664.1846, found 664.1827, $[M\text{-}CO_2]^+$ requires 620.6494, found 620.1959, $[M\text{-}2CO_2]^+$ requires 576.6399, found 576.2033, $[M\text{-}3CO_2]^+$ requires 532.6304, found 532.2159.

Synthesis of $Zn_4O(BenzTB)_{3/2}$ (DUT-13)

$Zn(NO_3)_2 \cdot 4H_2O$ (156 mg, 0.597 mmol) and H_4BenzTB (40 mg, 0.06 mmol) were dissolved in DEF (8 mL) by sonication for 2 min. The mixture was spiked with 2 drops of glacial acetic acid and heated to 80 °C in a Pyrex tube. After 48 h the hot mother liquor was taken off *via* syringe and the light yellow crystals were washed with fresh DEF (8 mL). For drying the solvent was exchanged with absolute EtOH four times over a period of one day. Drying of the crystals was performed by use of supercritical CO_2. Yield: (30 mg, 59%). Elemental analysis for $Zn_4O(BenzTB)_{3/2} \cdot 19.7\ DEF \cdot 4.5\ H_2O$ Found: C, 57.0; H, 7.5; N, 9.9; O, 18.2; Zn, 8.4. Calc. C, 56.96; H, 7.89; N, 9.51; O, 17.81; Zn, 7.83%. Elemental analysis for $Zn_4O(BenzTB)_{3/2} \cdot EtOH \cdot H_2O$ (1332.59 g mol^{-1}) Found: C, 56.2; H, 3.32; N, 3.38; O, 18.1; Zn, 19.6. Calc. for $Zn_4C_{62}H_{44}N_3O_{15}$ C, 55.88; H, 3.33; N, 3.15; O, 18.01; Zn, 19.63%. The phase purity of the product was further confirmed by PXRD and thermogravimetic analysis.

3. Crystal structure

Suitable crystals were selected under polarized light, washed with solvent and prepared in a sealed glass capillary in a solvent atmosphere. The single crystal was mounted and aligned on a one circle goniometer on BESSY-II synchrotron beamline MX-14.2 in Berlin. 200 Frames of diffracted data (1° rotating increment) were collected on a MAR-CCD-225 detector with a wavelength of $\lambda = 0.88561$ Å in a resolution range of $1.22° < \theta < 35.92°$. Cell determination and data reduction was performed with the XDS package.[1] The trigonal cell (a = 25.682(4), c = 114.90(2) Å, V = 65630(18) Å^3) was indexed with approximately 2000 reflections. Integration of the diffracted data resulted in 167128 reflections. Analysis of systematic absences resulted in choice of space group *R-3c*. We chose to set up the cell in hexagonal setting (Z = 12) because rhombohedral setting exhibits a strange $\alpha = 36°$. In this setting 16481 reflections are independent ($R_{merg} = 0.048$). The structure was solved with the Patterson method which yielded the positions of the heavy atoms. With those starting phases the remaining lightweight atom positions could be localized *via* difference fourier map. The structure was further full matrix least square refined (SHELXL-97)[2] against F². Non hydrogen atoms were refined anisotropically, H-positions were constrained to their ideal positions. Due to the high porosity of the structure (PLATON-void-volume: 82%) the F_{obs} were corrected with the PLATON[3] SQUEEZE routine, because the disordered solvent molecules in the pores could not be located by fourier map. Structure refinement against the corrected data finally converged to R_1 (obs) = 0.0542, wR_2 (all) = 0.1644 and a max./min. residual electron density of 0.458 /- 0.522 e/Å^3.

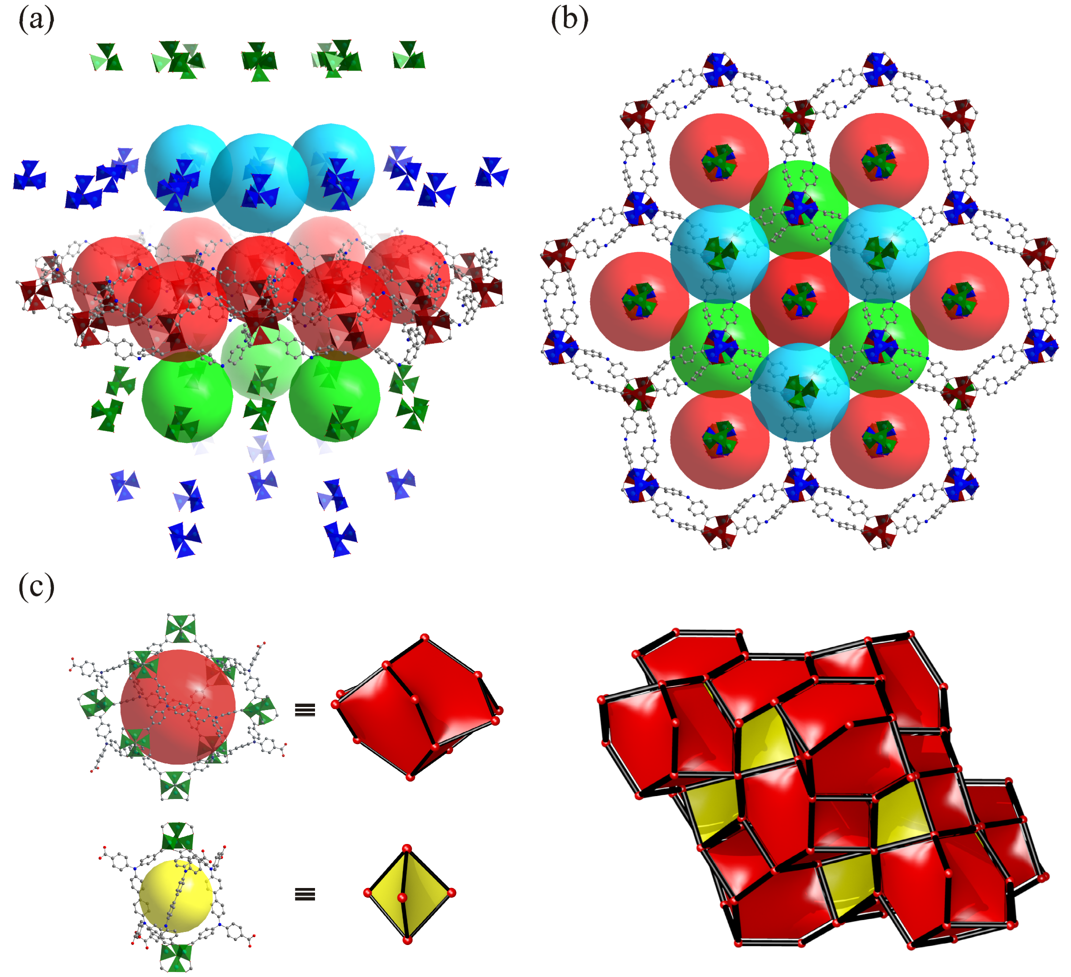

Fig. S2 Illustration of the rhombohedral distorted cubic close packing (*ccp*) of large pores. Green, red and light blue balls represent the typical A,B,C-layer stacking in *ccp* viewed along (a) and perpendicular (b) to the layers. (c) Simplified tiling representation: large pores forming a rhombohedral distorted *ccp* with the small pores occupying the pseudo-octahedral holes ending up in a corundum net.

[1] W. Kabsch, *Journal of Applied Crystallography* **1993**, *26*, 795.
[2] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64,* 112-122.
[3] Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **A46**, 194.

4. N_2 physisorption measurements

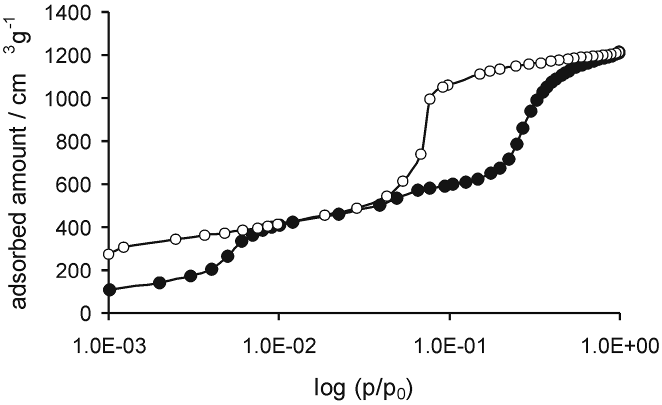

Fig. S3 Logarithmic plot of N_2 physisorption isotherm with two hysteresis loops at $p/p_0 < 0.01$ and $p/p_0 > 0.02$.

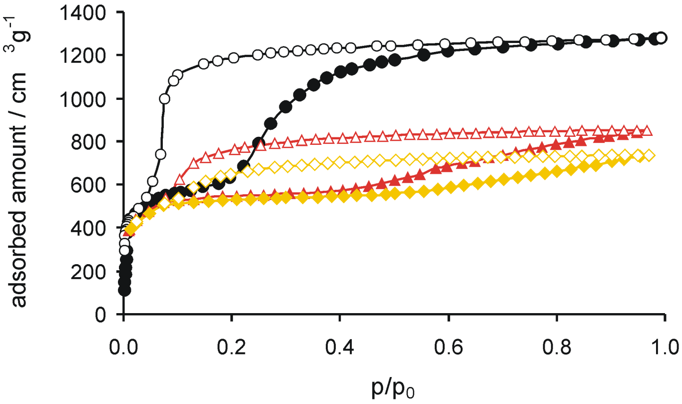

Fig. S4 N_2 physisorption isotherms of DUT-13 at -196°C: 1st run (adsorption/desorption ●/○), 2nd run (adsorption/desorption ▲/△) and 3rd run (adsorption/desorption ◆/◇). The huge hysteresis loop decreases with run to run and the isotherm approximates type I.

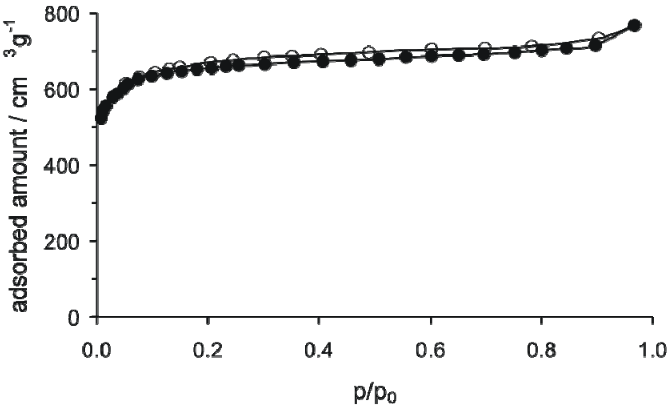

Fig. S5 N_2 physisorption of DUT-13 measured after CO_2 adsorption.

5. *n*-Butane physisorption measurements

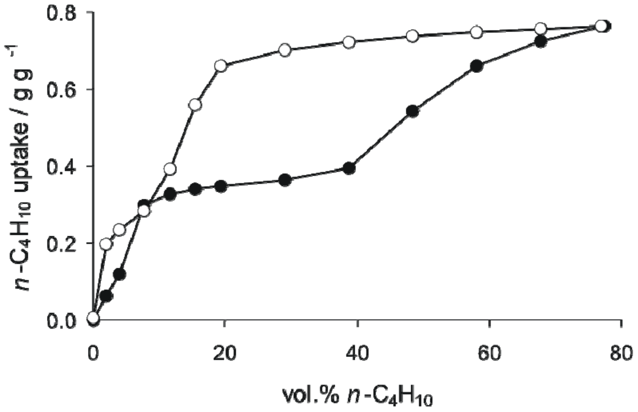

Fig. S6 *n*-Butane adsorption/desorption (●/○) isotherms of DUT-13 measured at 20 °C.

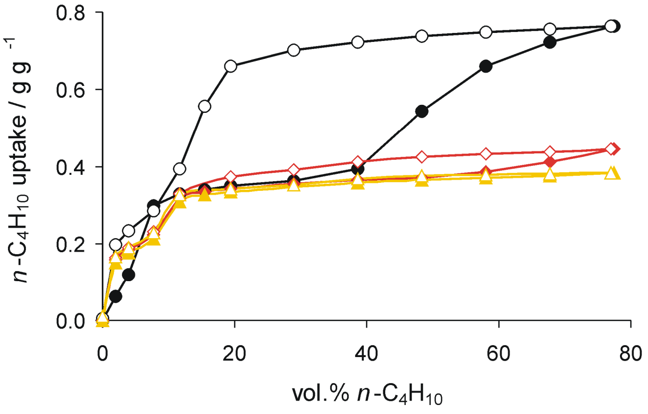

Fig. S7 *n*-Butane physisorption isotherms of DUT-13: 1st run (adsorption/desorption ●/○), 2nd run (adsorption/desorption ◆/◇), and 3rd run (adsorption/desorption ▲/△).

6. Methane physisorption measurement

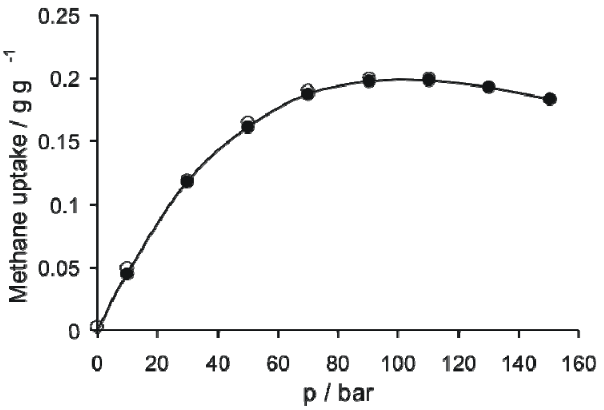

Fig. S8 High-pressure excess methane adsorption/desorption (●/○) isotherms at 25 °C.

7. Carbon dioxide physisorption measurement

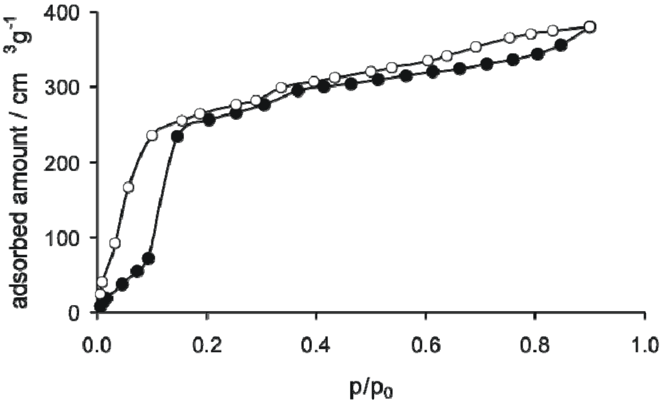

Fig. S9 CO_2 adsorption/desorption (●/○) isotherms measured at -78 °C.

8. Powder X-ray diffraction measurements

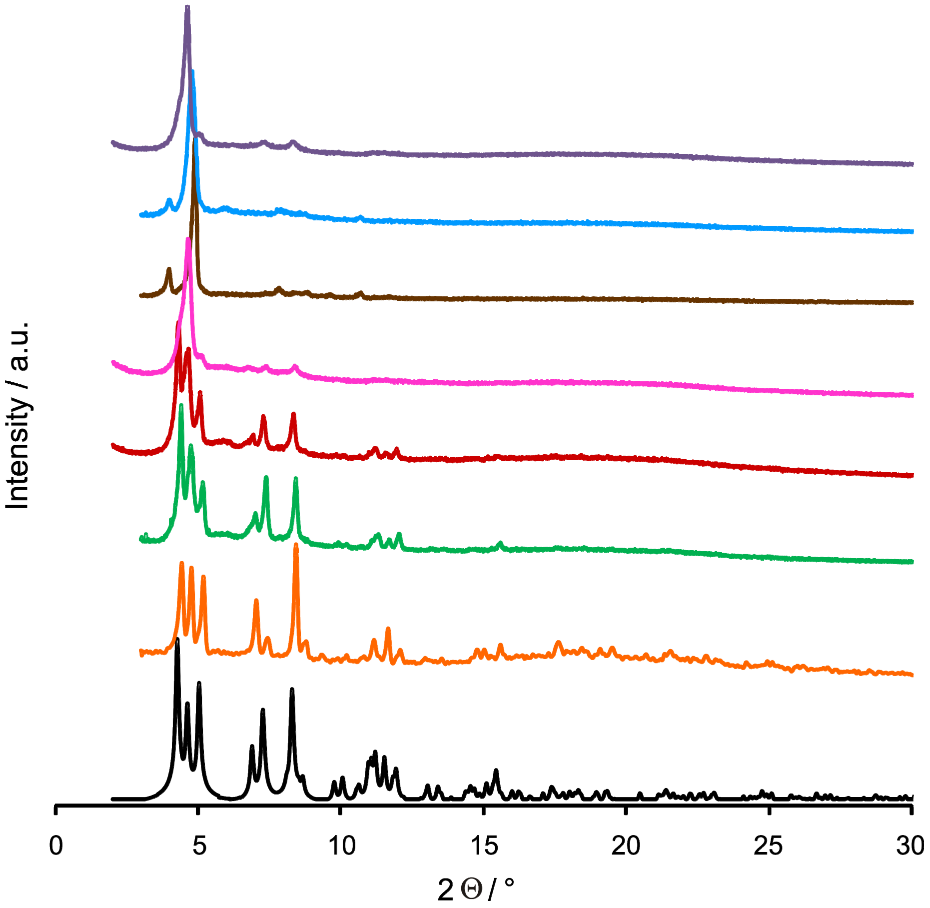

Fig. S10 X-ray powder diffraction patterns: calculated from single crystal data (black); as synthesized DUT-13 (orange); after supercritical drying using CO_2 (green); after high-pressure H_2 and CH_4 physisorption (red); after once N_2 physisorption (magenta); after thrice N_2 physisorption (brown); after CO_2 physisorption (blue); after twice *n*-butane physisorption (purple).

9. Thermogravimetric measurements

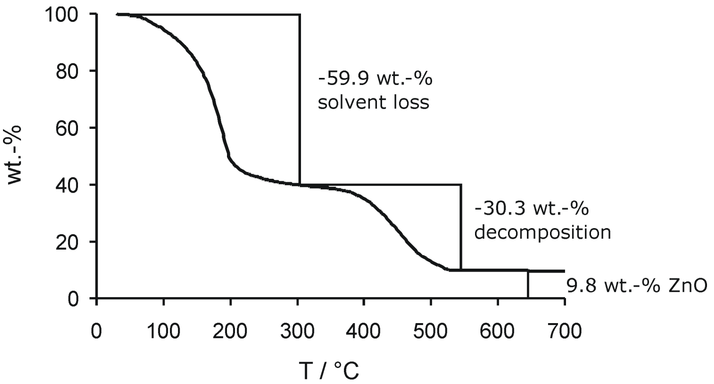

Fig. S11 TGA curve of as synthesized DUT-13 in air.

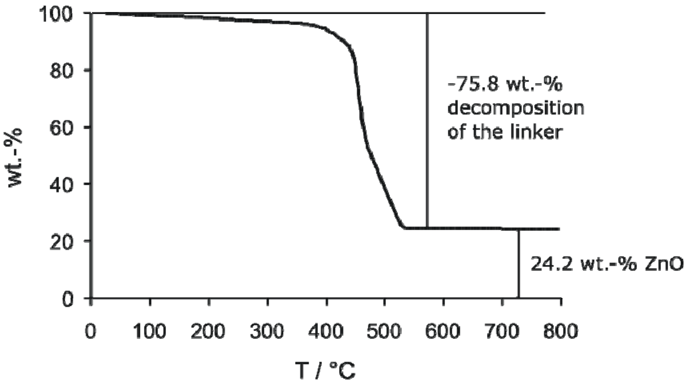

Fig. S12 TGA curve of desolvated DUT-13 in air. DUT-13 shows high thermal stability up to 375 °C.