Supporting Information:

Post-synthetic paddle-wheel crosslinking and functionalization of 1,3-phenylenebis(azanetriyl)tetrabenzoate based MOFs.

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1. General information

Sample treatment for supercritical CO_2 drying

A fresh prepared MOF sample was at first washed with mixture of DMF and ethanol (1:1), three times per day during 2 days. Afterward the solvent was exchanged by ethanol or acetone in the following way:

The sample was soaked in the corresponding solvent, and the solvent was exchanged 3-4 times over 4-5 days. The samples were transferred into a Jumbo Critical Point Dryer 13200J AB (SPI Supplies). The solvent was exchanged with liquid carbon dioxide (purity: 99.995%) at ~ 15°C for about 48 h. 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 5 h. Finally, the Critical Point Dryer was purged with Ar and the samples were transferred to a glove box.

Characterization:

N_2 physisorption isotherms were measured at -196°C and ethanol pysisorption isotherms were measured at 25°C using a BELSORP-max apparatus (BEL JAPAN INC).

All powder X-ray diffraction patterns were measured in a range of 2° - 50° 2 Theta, with a scan step of 0.1°C at 40kV and 30 mA, at STOE STADI P (STOE, Darmstadt, Germany), with a Cu-$K\alpha_1$ radiation (λ = 0.15405 nm).

Thermogravimetric analyses were performed from 25 up to 800°C using a STA 409 or STA 409 PCLuxx (Netzsch, Selb, Germany).

UV/Vis experiments were carried at 25°C using a Cary 4000 (Varian) equipped with a praying mantis and a high temperature reaction chamber (Harrick Sci) in diffuse reflection.

UV/Vis experiments

Table S1. shows the correlation between concentration of ethanol in nitrogen stream and p/p_o for ethanol at 25°C. Saturated vapour pressure of ethanol p_o = 7.874 kPa.

Table S1: Correlation between ethanol concentration in nitrogen flow and p/p_o.

ethanol concentration in nitrogen in ppm	**ethanol flow, ml/min**	**nitrogen flow, ml/min**	**p/p_o**
100	0.175	99.824	0.00128
250	0.437	99.563	0.00321
400	0.700	99.300	0.00541
550	0.962	99.038	0.00707
700	1.225	98.775	0.00901
850	1.488	98.512	0.01093
1000	1.750	98.250	0.01286

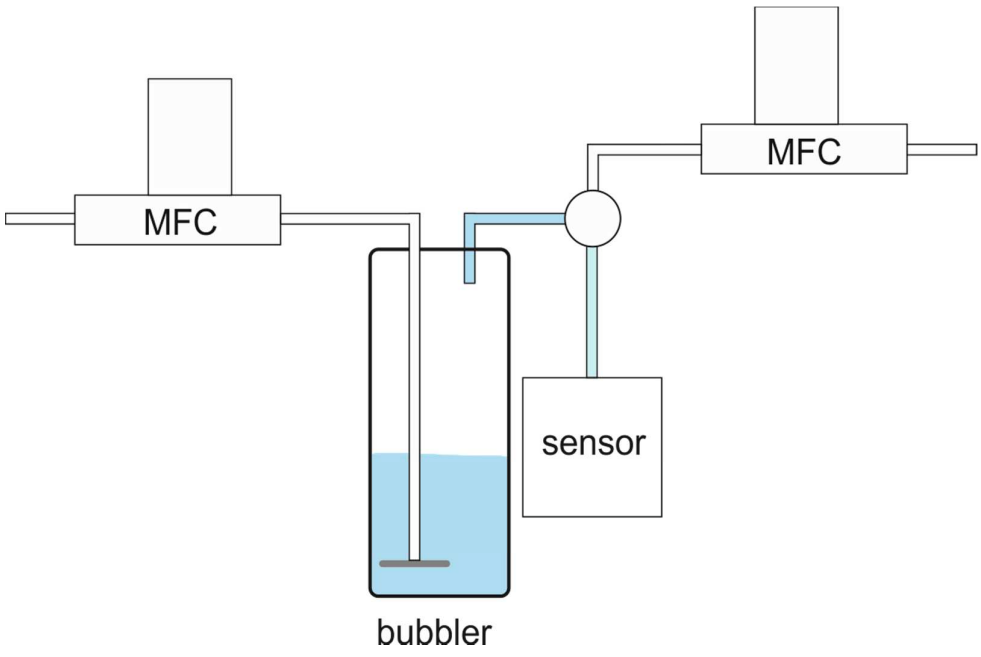
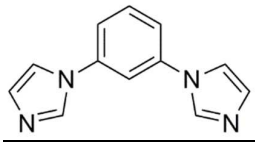


Figure S1: Schematic representation of equipment for dynamic vapor dosing.

2. Synthetic procedures

All chemicals were used without further purification. BINAP(*rac*) and cyanopyridine were purchased from ABCR, copper(II)chloride dihydrate, cesium carbonate, DABCO, 1,2-dibromobenzene, 1,4-dibromobenzene, and *N,N*-dimethylglycine from Alfa Aesar, ethanol (abs.) form Fischer Chemical, imidazole from Merck, potassium carbonate from Grüssing, copper(I)iodide from Riedel-de Haën, *N, N*-dimethylformamide, dioxane, and sodium nitrite from Sigma Aldrich, ethyl-4-bromobenzate and palladium acetate from TCI, and dimethylsulfoxide form VWR Chemicals.

1,3-bi(1*H*-imidazol-1-yl)benzene (1,3-bib)



A two necked round bottom flask was charged with 12.24 g (180 mmol, 2.5 eq) imidazole, 2.74 g (14.3 mmol, 0.2 eq) copper(I)iodide, 39.8 g (288 mmol, 4 eq) potassium carbonate and 2.97 g (28.8 mmol, 0.4 eq) *N,N*-dimethylglycine and flushed with argon. A solution of 16.92 g (72 mmol, 8.67 ml) 1,3-dibromobenzene in 350 ml DMSO was added and the mixture was heated to 120°C. After 48 h the mixture was allowed to cool down to room temperature, filtered through a plug of celite®, and the filter cake was washed with ethylacetate. During the washing, the precipitation in the filtrate takes place. To this suspension, an aqueous ammonia solution (25wt.%) was added and the mixture was stirred until complete dissolution of the solid. The aqueous phase was extracted with ethylacetate for three times. The solvent was evaporated and the resulting solid was solved again in pentane/diehtylether mixture. After 30 min the precipitation starts. The product was collected by filtration, washed with small amounts of diethylether and dried over night in vacuum (Yield: 9.78 g, 64.6 %).

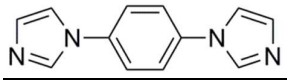
^{1}H-NMR (*$CDCl_3$*, 500 MHz):

δ (in ppm): 7.24 (m, 2 H), 7.32 (m, 2 H), 7.39 (d, 1 H), 7.42 (m, 2 H), 7.60 (t, 1 H), 7.90 (s, 2 H).

^{13}C-NMR (*$CDCl_3$*, 125 MHz):

δ (in ppm): 114.58 (CH), 118.09 (CH), 120.22 (CH), 131.07 (CH), 131.55 (CH), 135.53 (CH), 138.76 (C_q).

1,4-bi(1*H*-imidazol-1-yl)benzene (1,4-bib)



A two necked round bottom flask was charged with 6.29 g (26.66 mmol) 1,4-dibromobenzene, 4.54 g (66.66 mmol, 2.5 eq) imidazole, 1.015 g (5.33 mmol, 0.2 eq) copper(I)iodide, 14.7 g (106.67 mmol, 4 eq) potassiumcarbonate and 1.1 g (10.67 mmol, 0.4 eq) *N,N*-dimethylglycine and flushed with argon. 67 ml DMSO were added and mixture was heated at 110°C for 48 h. After cooling down to room temperature the mixture was filtered through a plug of celite® and the filter cake was washed with ethylacetate. The filtrate was evaporated to dryness. The solid residue was dissolved in water, and the product was extracted by ethyl acetate for three times. The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. To the oily phase a small amount of diethylether was added and finally the product was precipitated by addition of pentane. The crystals are filtered off, washed with pentane and dried under vacuum over night. (Yield: 1.86 g, 33%).

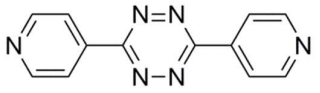
^{1}H-NMR (*$CDCl_3$*, 500 MHz):

δ (in ppm): 7.24 (m, 2 H), 7.30 (m, 2 H), 7.51 (s, 4 H), 7.88 (s, 2 H).

^{13}C-NMR (*DMSO-d_6*, 125 MHz):

δ (in ppm): 118.08 (CH), 121.49 (CH), 130.20 (CH), 130.02 (CH), 135.33 (Cq), 135.67 (CH).

3,6-bi(pyridin-4-yl)1,2,4,5-tetrazine (bpta)



A two necked round bottom flask was charged with 20.8 g (0.2 mol) 4-cyaopyridine in 39 ml (40.06 g, 0.8 mol, 4 eq) hydrazine monohydrate. This mixture was stirred for 5 h and then cooled to 0°C. The 1,4-dihydro-1,2,4,5-tetrazine precipitate, was filtered of and washed with diethyl ether. The solid was solved in 210 ml glacial acid/water (4:3) and the solution was cooled again to 0°C. Afterward 15.2 g (0.22 mol, 1.1 eq) sodium nitrite was carefully added. After 1 h additional stirring at 0°C the solution was neutralized with ammonia (25 wt.%). The resulting solid was filtered off and re-crystallized from ethanol (4.85 g, 21 %)

^{1}H-NMR (*$CDCl_3$*, 500 MHz):

δ (in ppm): 8.52 (d, 4 H), 8.97 (d, 4 H).

^{13}C-NMR (*$CDCl_3$*, 125 MHz):

δ (in ppm): 121.41 (CH), 138.63 (C_q), 151.31 (CH), 163.76 (C_q)

3. PXRD patterns

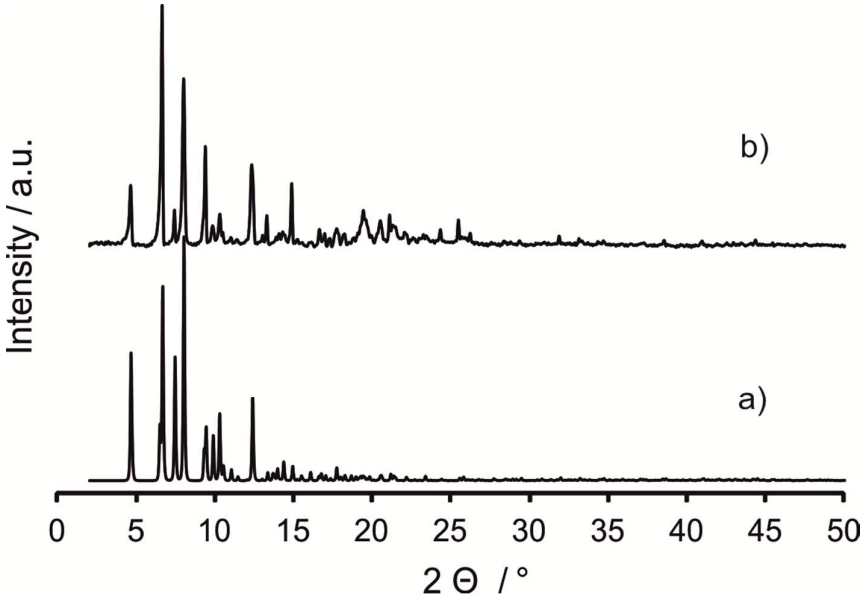


Figure S2. PXRD of DUT-71: a) calculated from the crystal structure: b) as made.

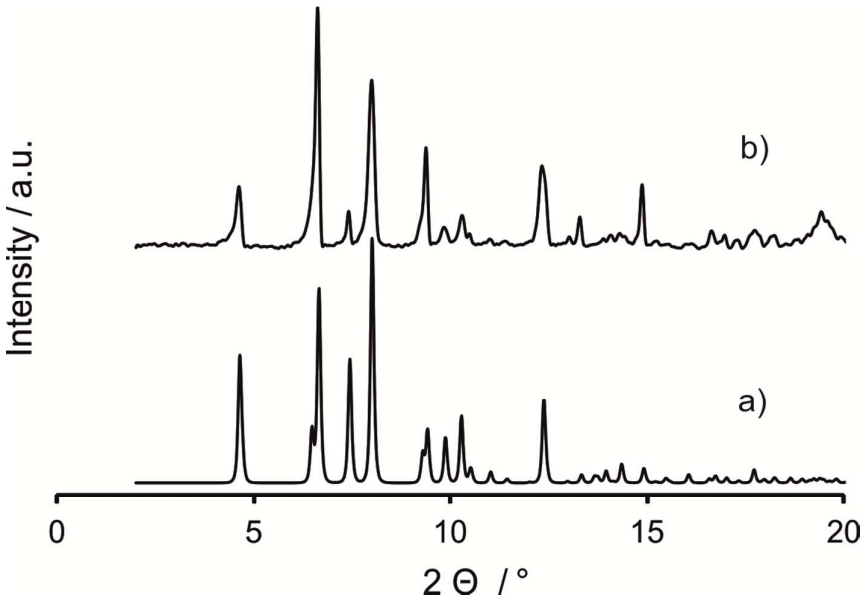


Figure S3. PXRD of DUT-71 a) calculated from the crystal structure: b) as made..

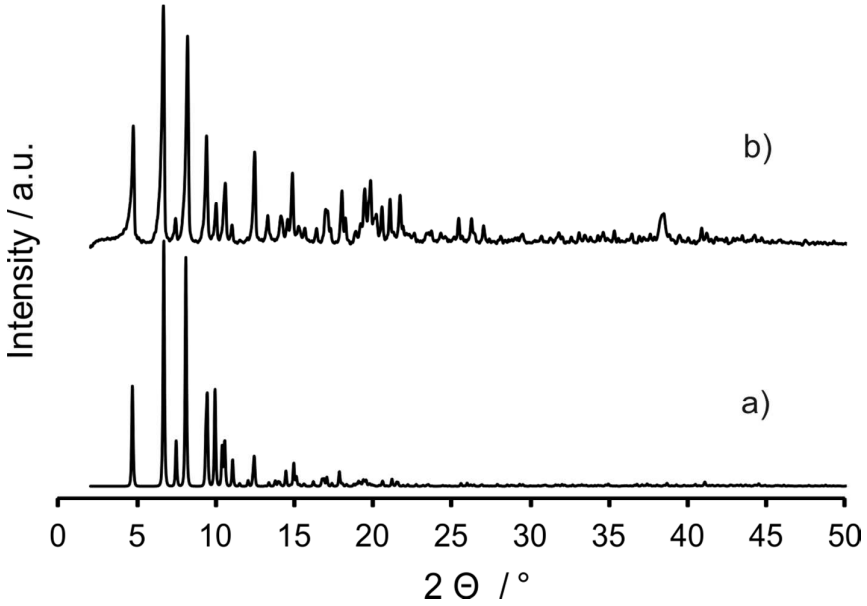


Figure S4: PXRD of DUT-72: a) calculated from the crystal structure: b) as made..

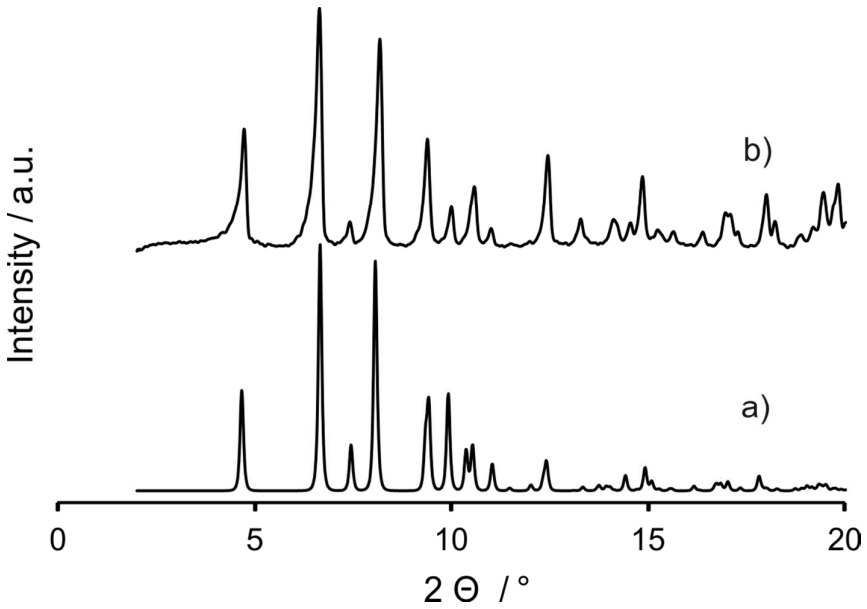


Figure S5: PXRD of DUT-72: a) calculated from the crystal structure: b) as made.

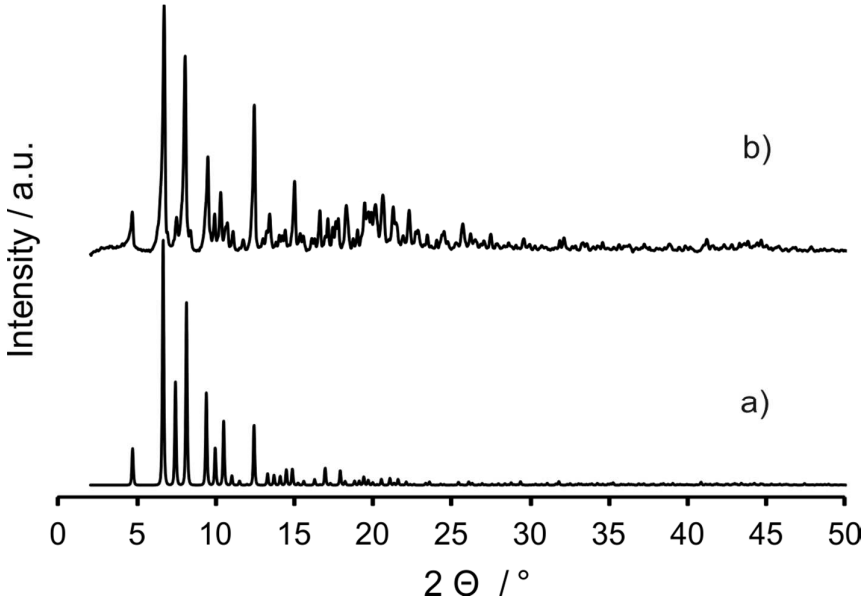


Figure S6. PXRD of DUT-73a a) calculated from the crystal structure: b) as made.

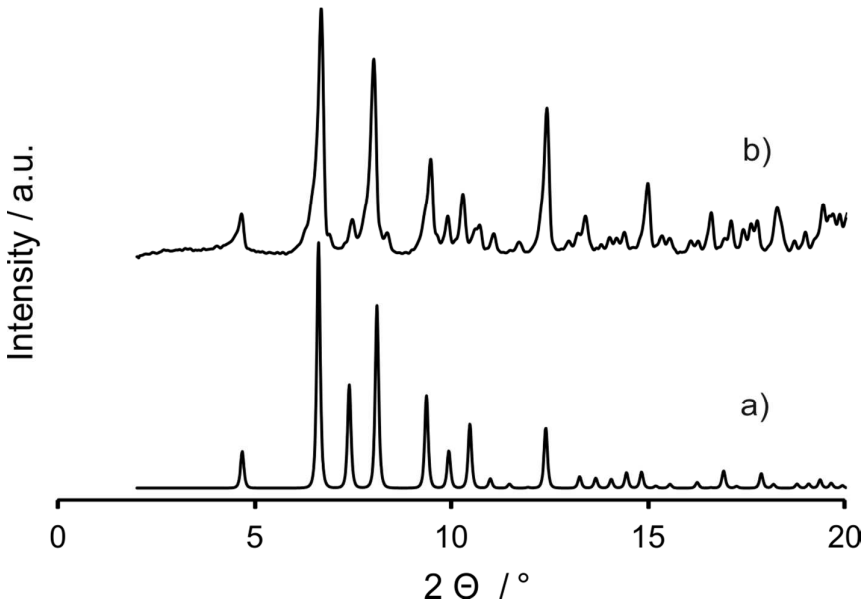


Figure S7. PXRD of DUT-73a: a) calculated from the crystal structure: b) as made..

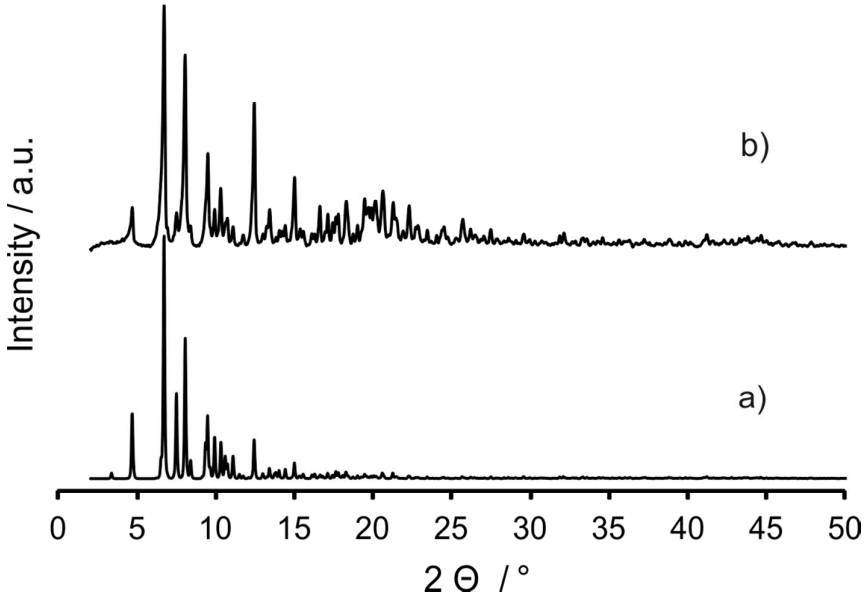


Figure S8. PXRD of DUT-73b: a) calculated from the crystal structure: b) as made..

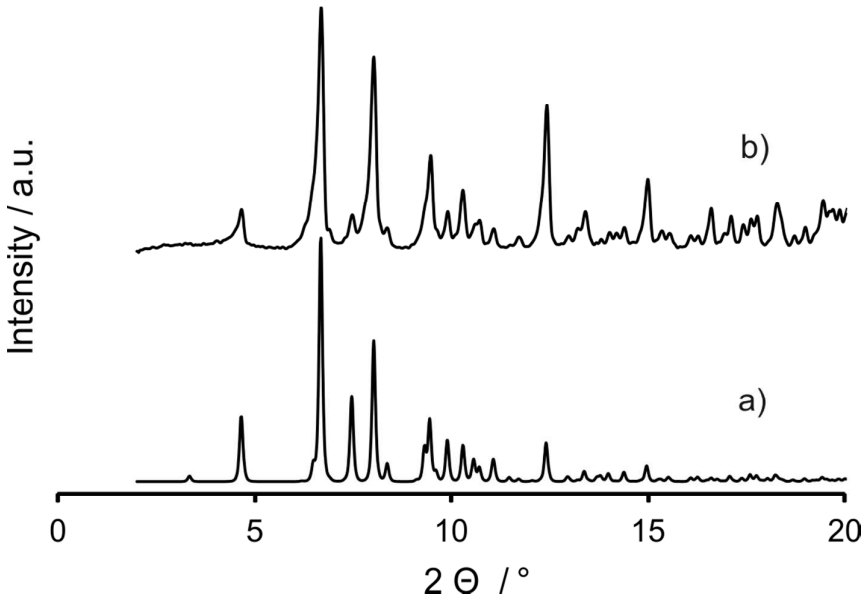


Figure S9. PXRD of DUT-73: b a) calculated from the crystal structure: b) as made.

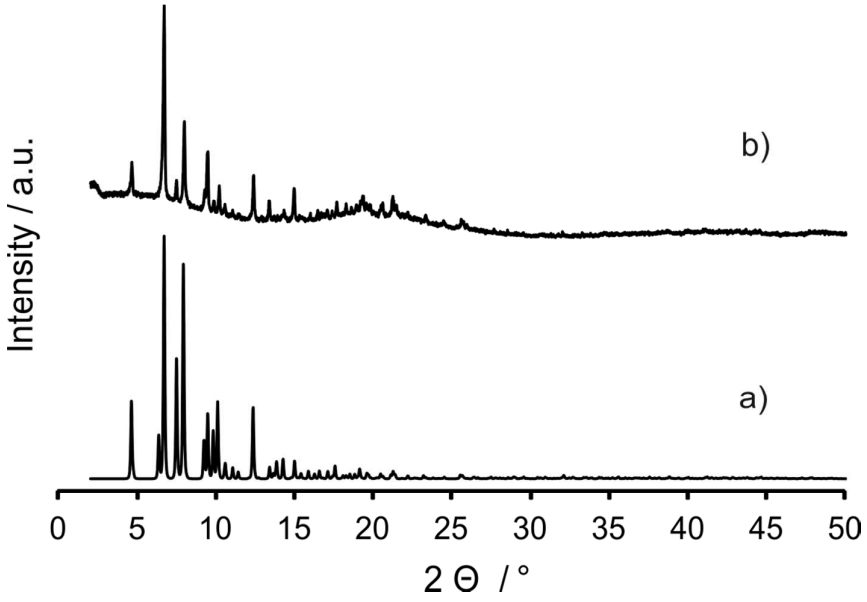


Figure S10. PXRD of DUT-74: a) calculated from the crystal structure: b) as made..

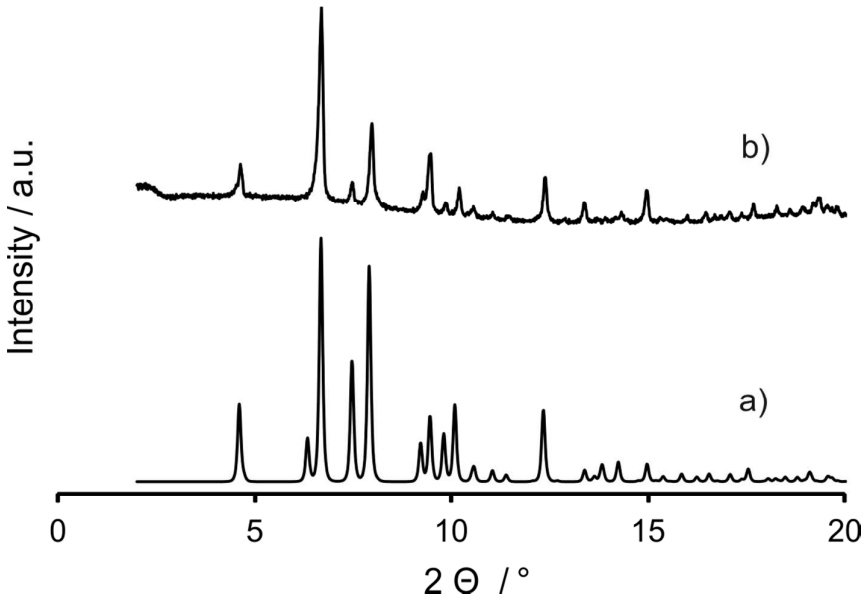


Figure S11. PXRD of DUT-74: a) calculated from the crystal structure: b) as made..

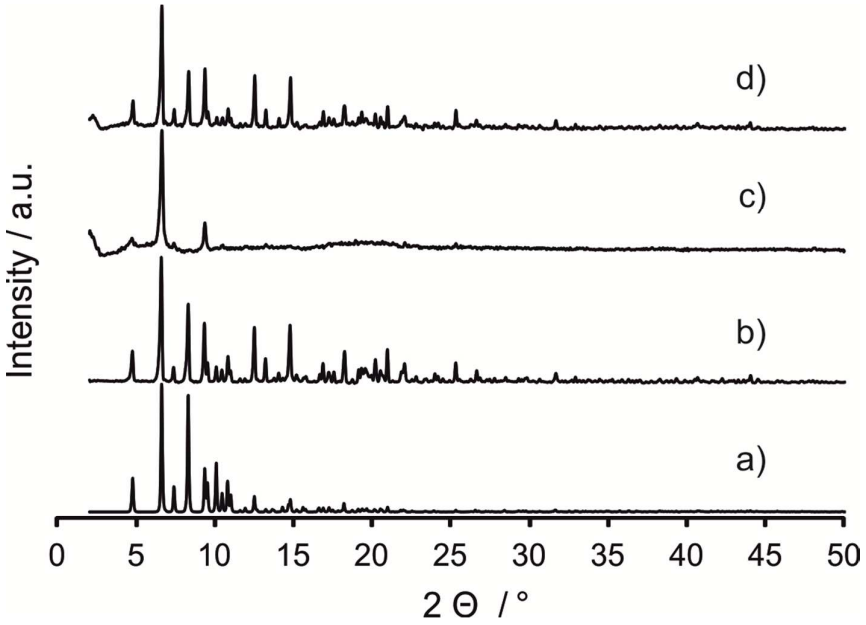


Figure S12. PXRD of DUT-90: a) calculated from the crystal structure; b) as made c) SCD dried; d) resolvated in DMF/EtOH.

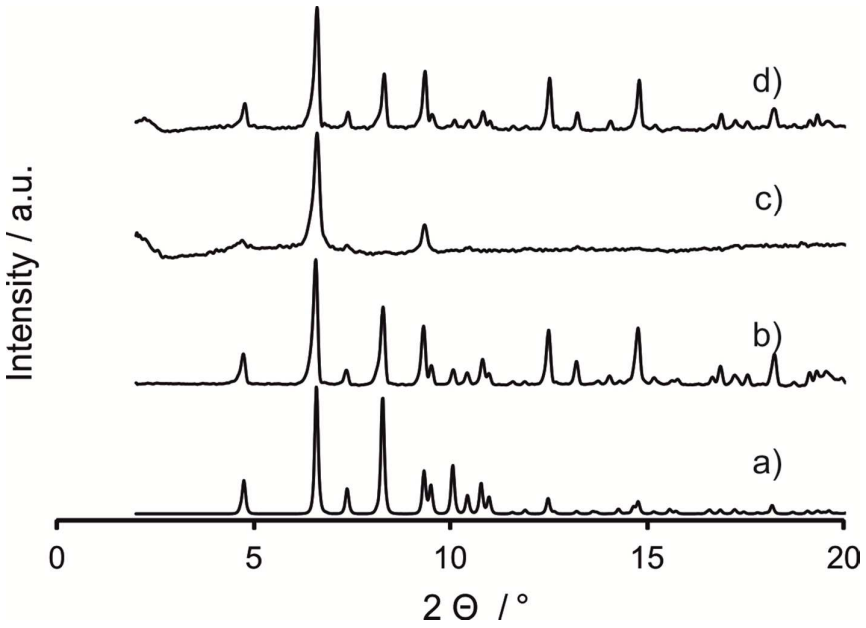


Figure S13. PXRD of DUT-90: a) calculated from the crystal structure; b) as made c) SCD dried; d) resolvated in DMF/EtOH.

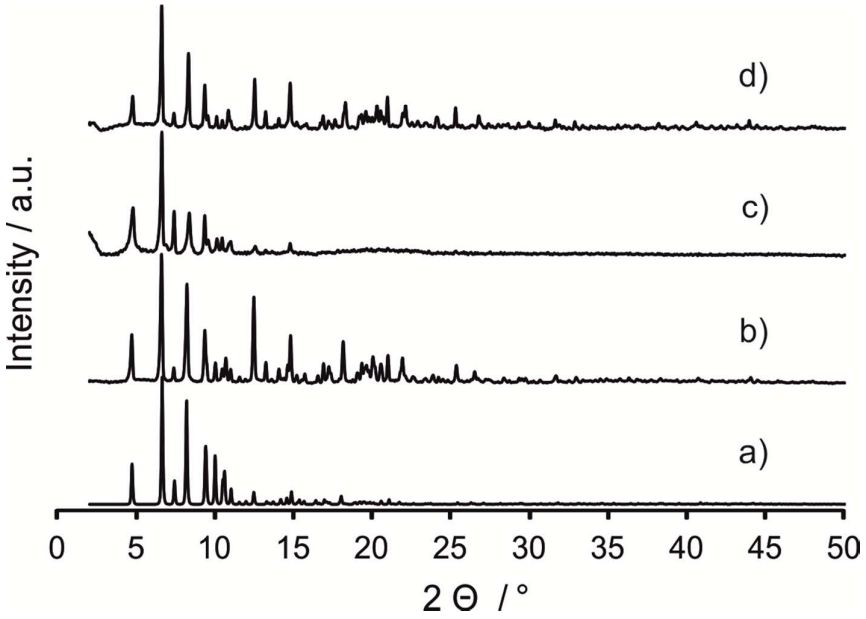


Figure S14. PXRD of DUT-91: a) calculated from the crystal structure; b) as made c) SCD dried; d) resolvated in DMF/EtOH.

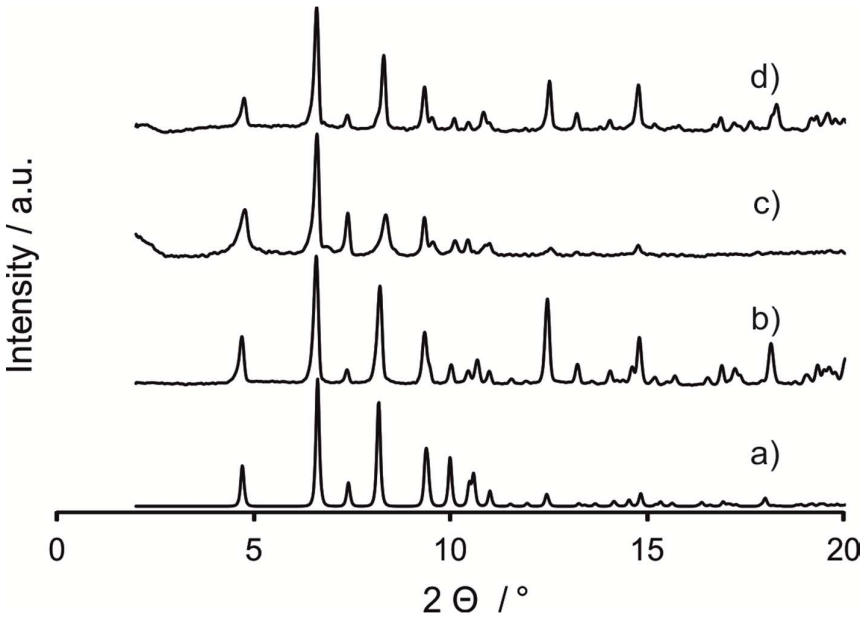


Figure S15. PXRD of DUT-91: a) calculated from the crystal structure; b) as made c) SCD dried; d) resolvated in DMF/EtOH..

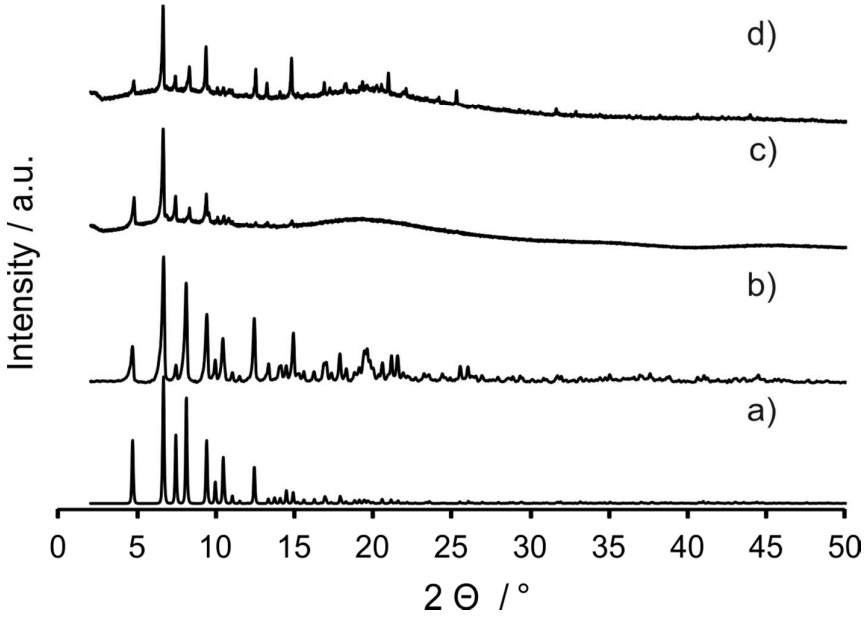


Figure S16. PXRD of DUT-95: a) calculated from the crystal structure; b) as made c) SCD dried; d) resolvated in DMF/EtOH.

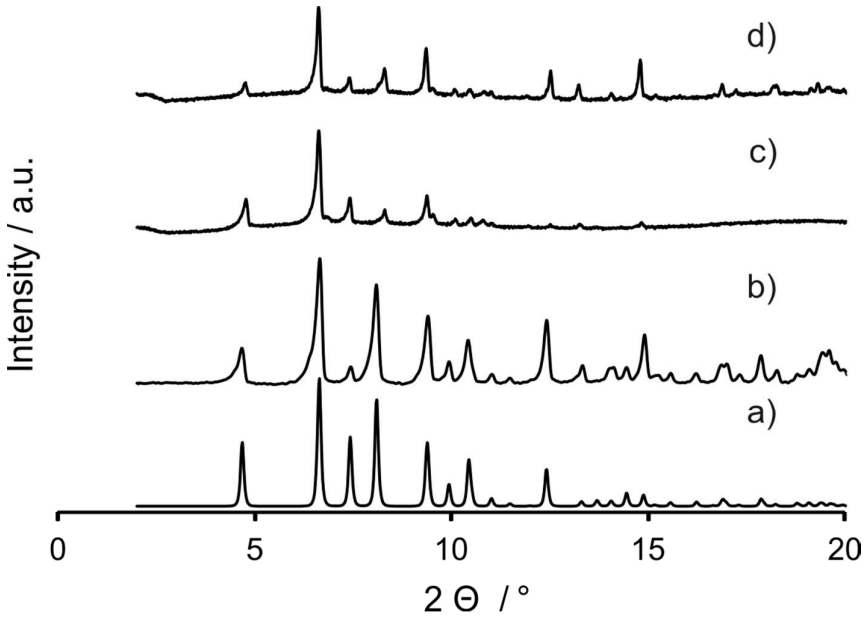


Figure S17. PXRD of DUT-95 : a) calculated from the crystal structure; b) as made; c) SCD dried; d) resolvated in DMF/EtOH.

4. Nitrogen physisorption at 77K

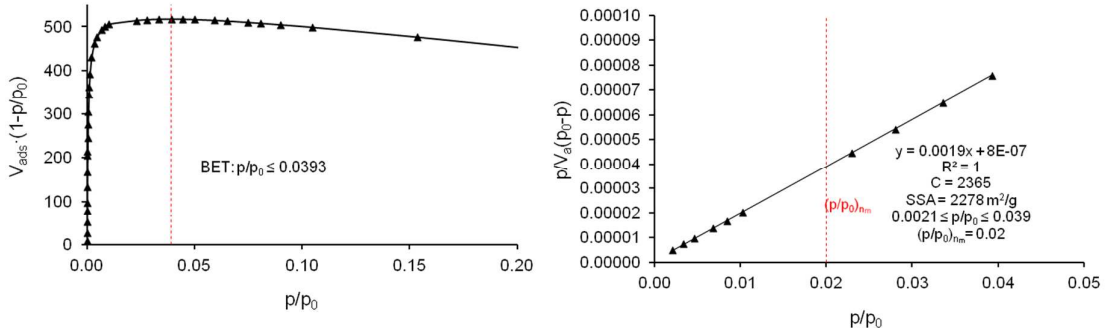


Figure S2. $V\cdot(1-p/p_o)$ vs. p/p_o for DUT-90 (left) and BET plot of DUT-90(right).

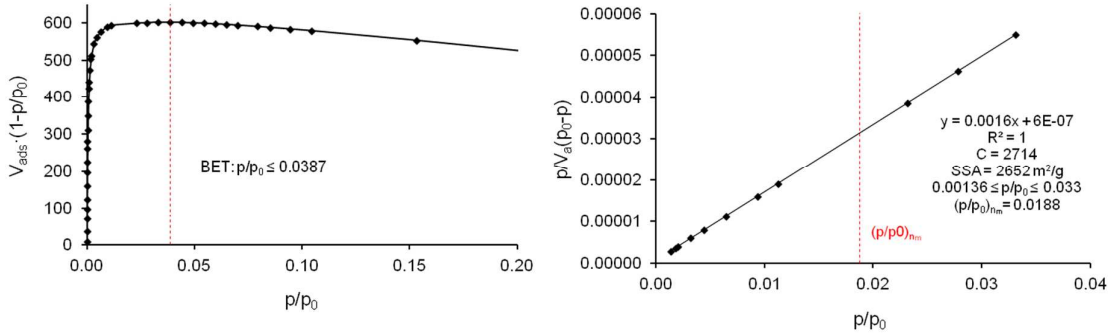


Figure S19. $V\cdot(1-p/p_o)$ vs. p/p_o for DUT-91 (left) and BET plot of DUT-91 (right).

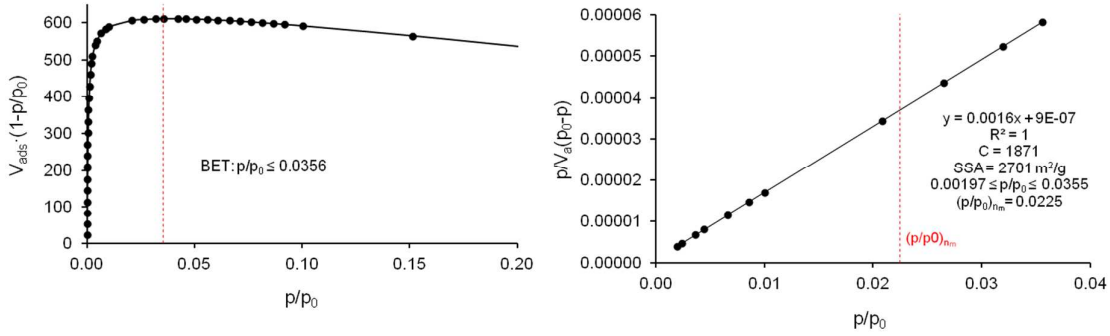


Figure S20. $V\cdot(1-p/p_o)$ vs. p/p_o for DUT-95 (left) and BET plot of DUT-95 (right).

5. Thermogravimetric analysis (TGA)

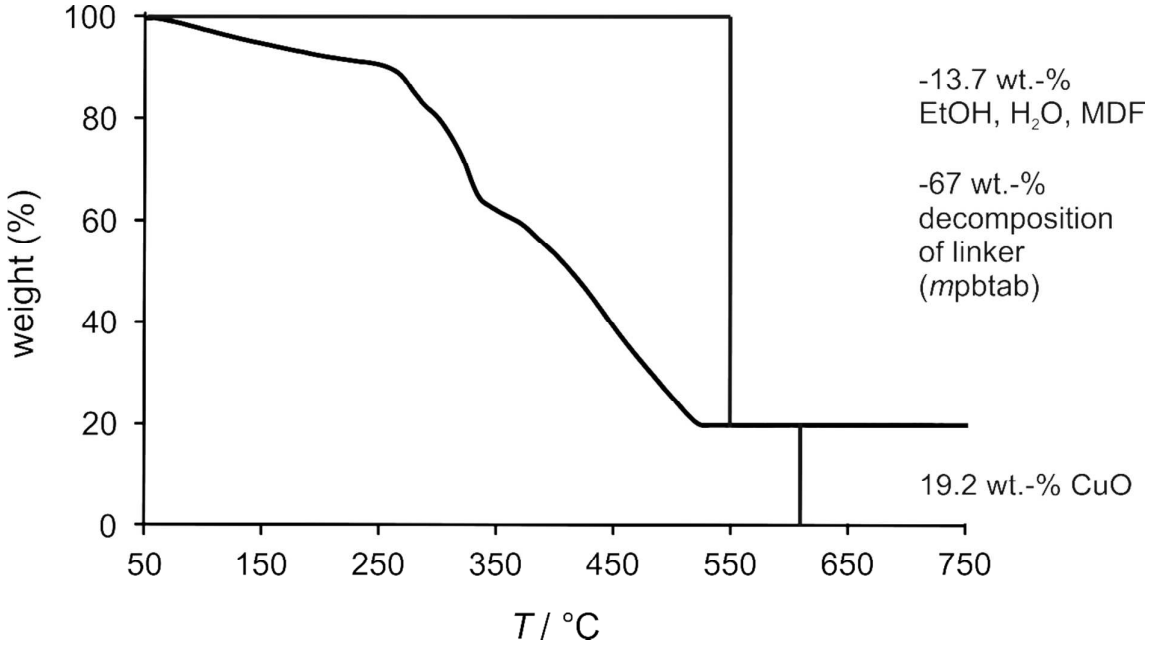


Figure S3. TGA of DUT-71 under air.

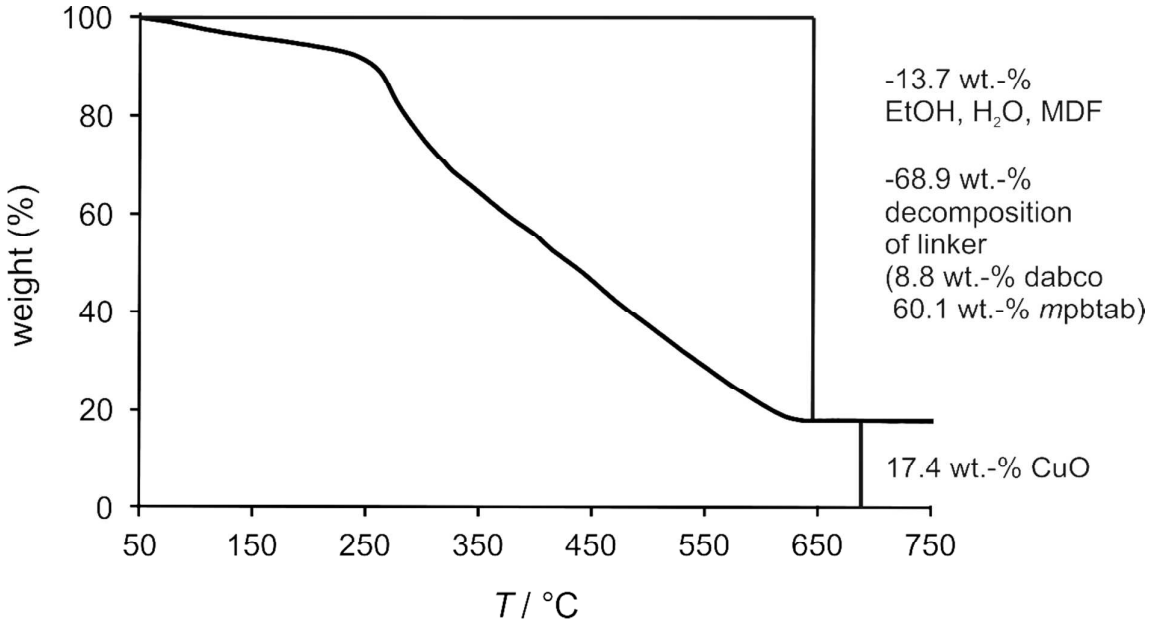


Figure S22. TGA of DUT-72 under air.

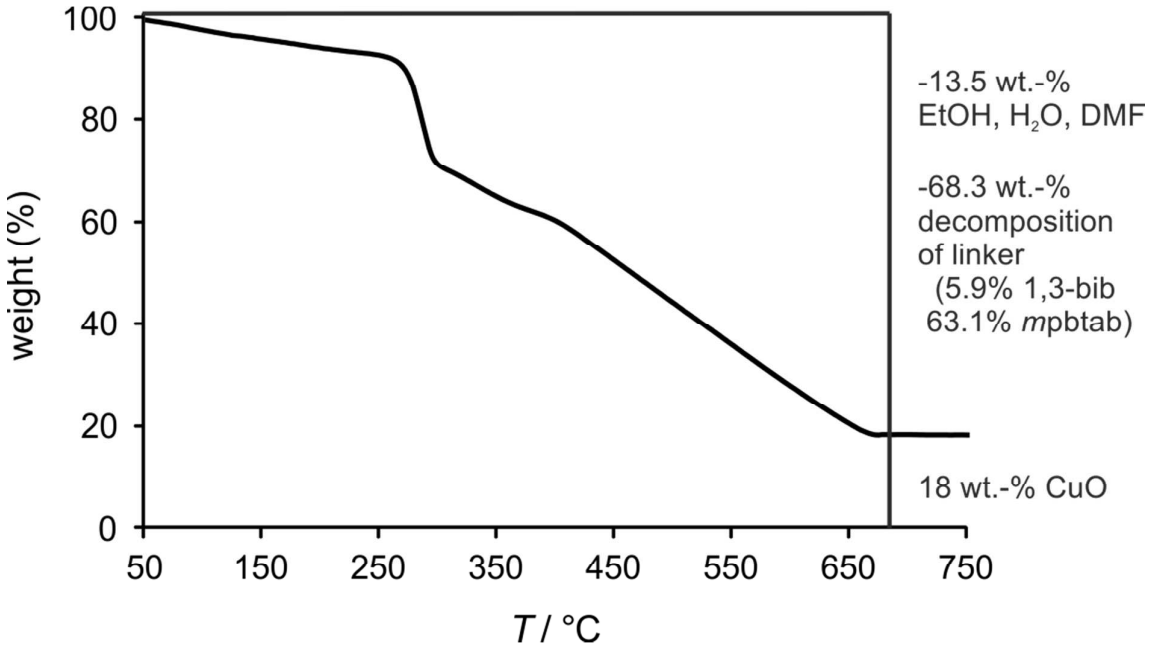


Figure S23: TGA of DUT-73a under air.

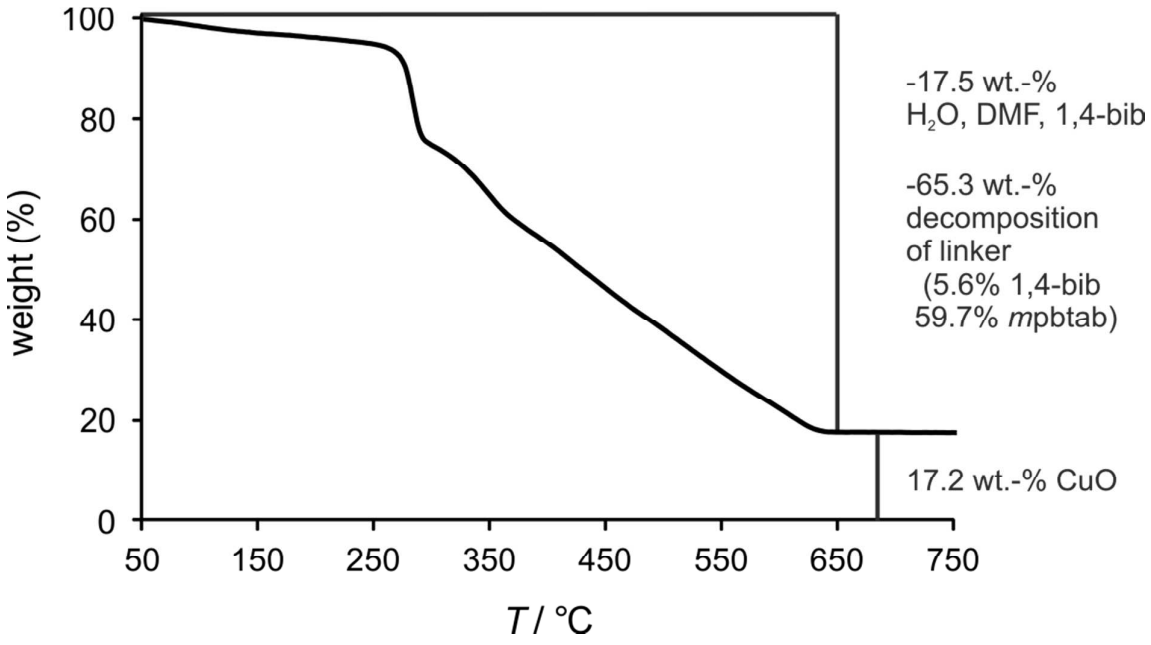


Figure S24: TGA of DUT-73b under air.

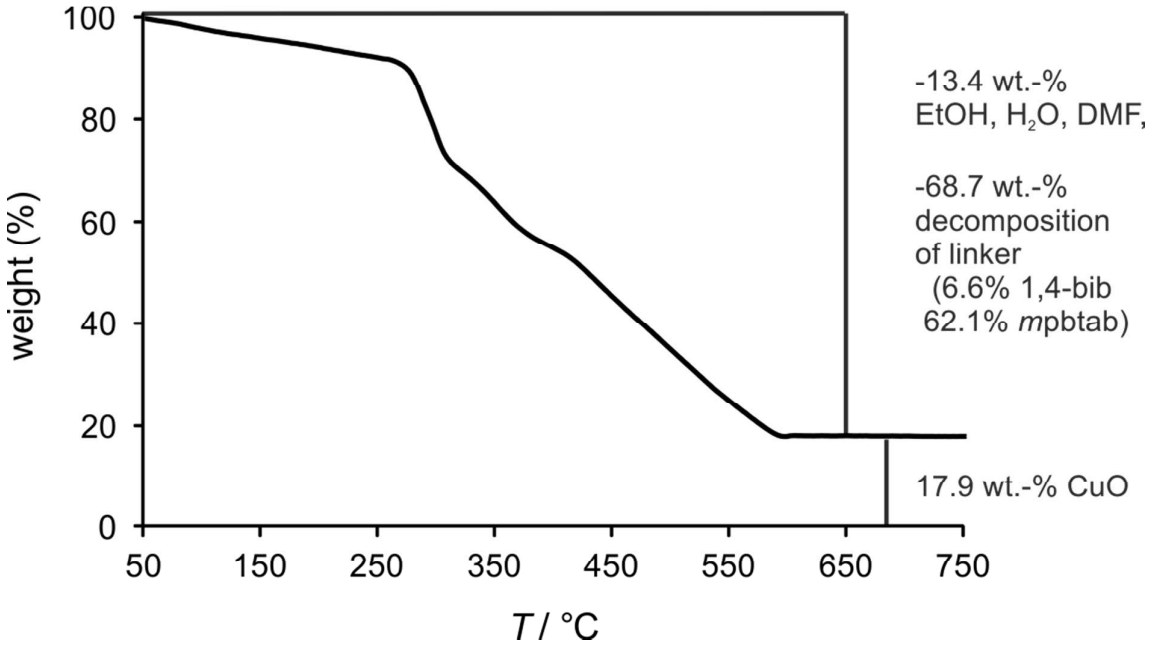


Figure S25: TGA of DUT-74 under air.

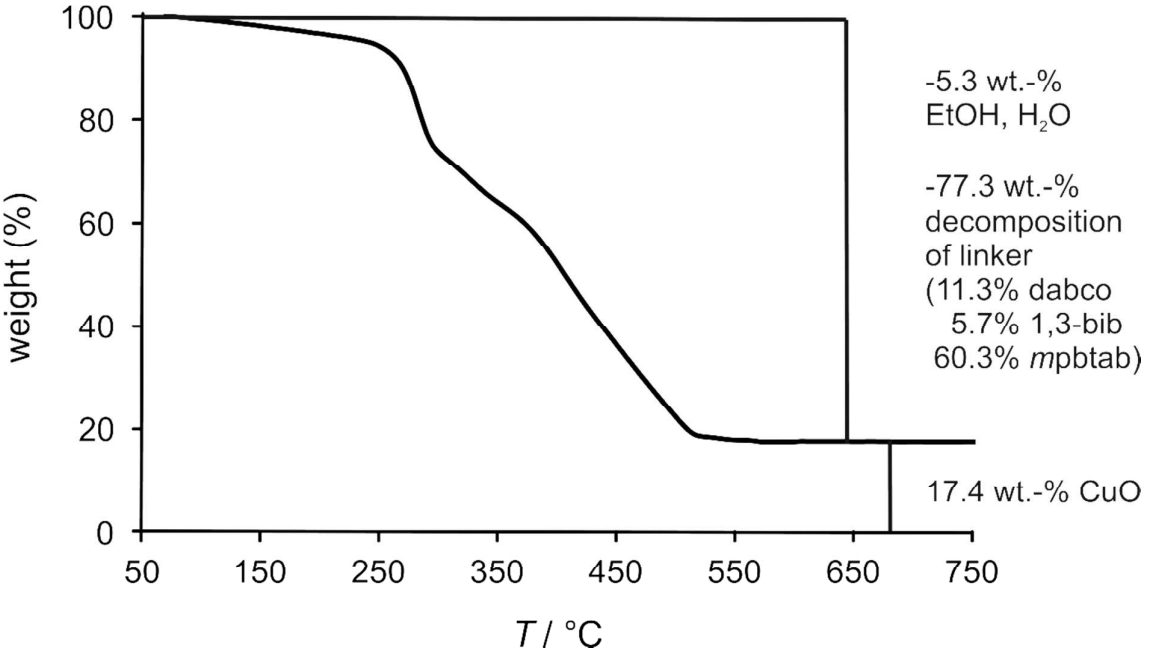


Figure S26. TGA of DUT-90 under air.

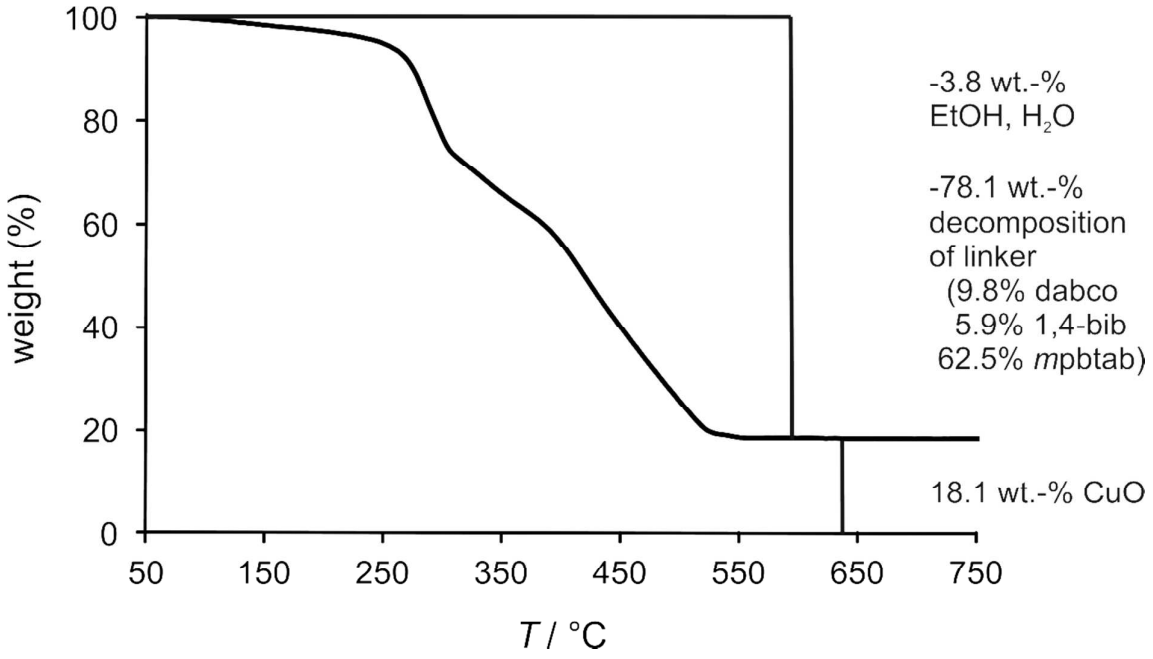


Figure S27. TGA of DUT-91 under air.

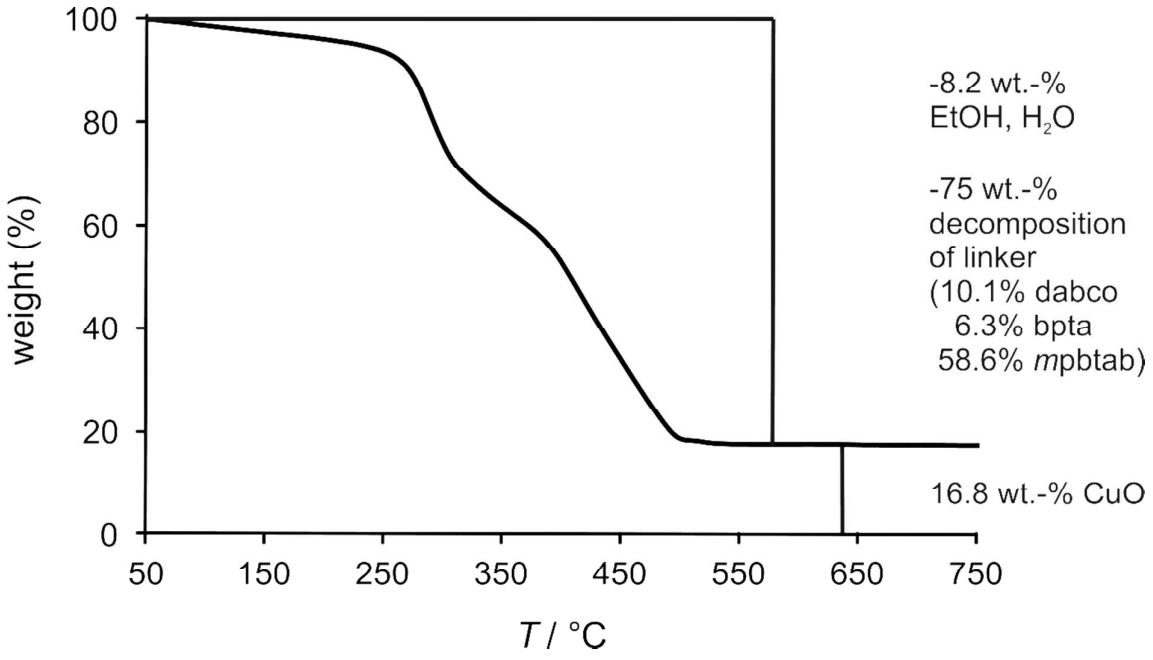


Figure S28. T TGA of DUT-95 under air.

6. UV/Vis experiments

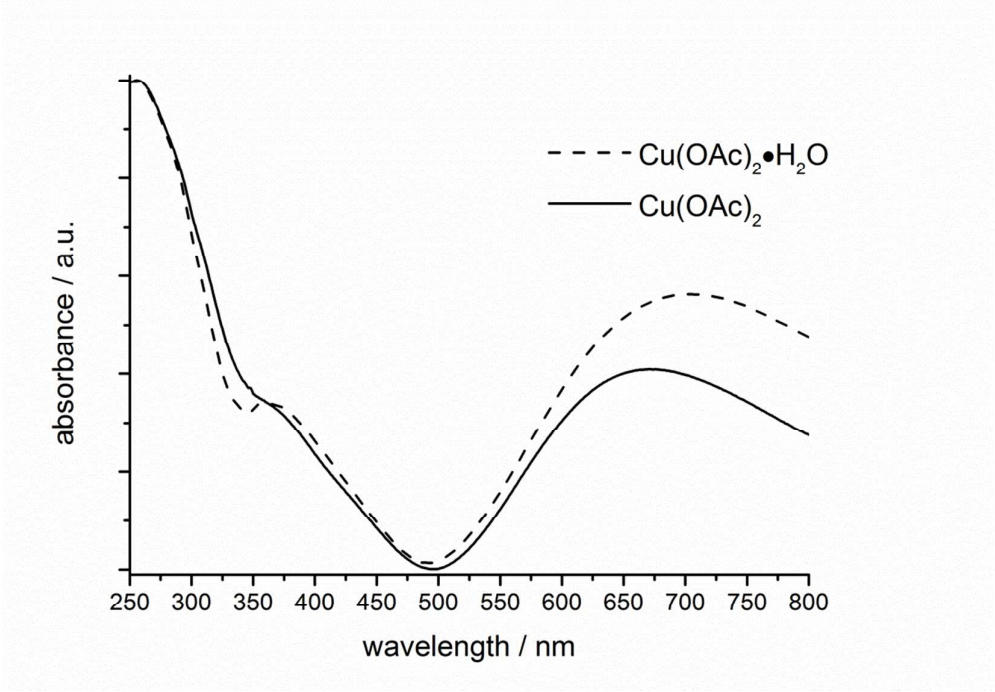


Figure S29. UV/Vis spectra of $Cu(OAc)_2 \cdot H_2O$ and $Cu(OAc)_2$ in KBr.

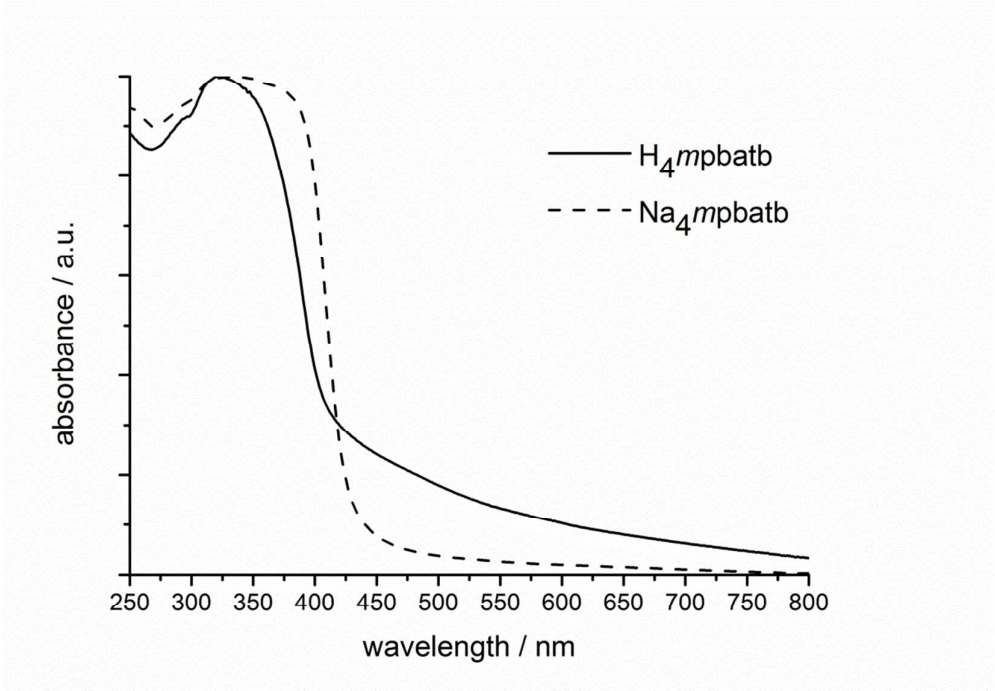


Figure S4. UV/Vis spectra of H_4*m*pbatb and Na_4*m*pbatb in KBr.

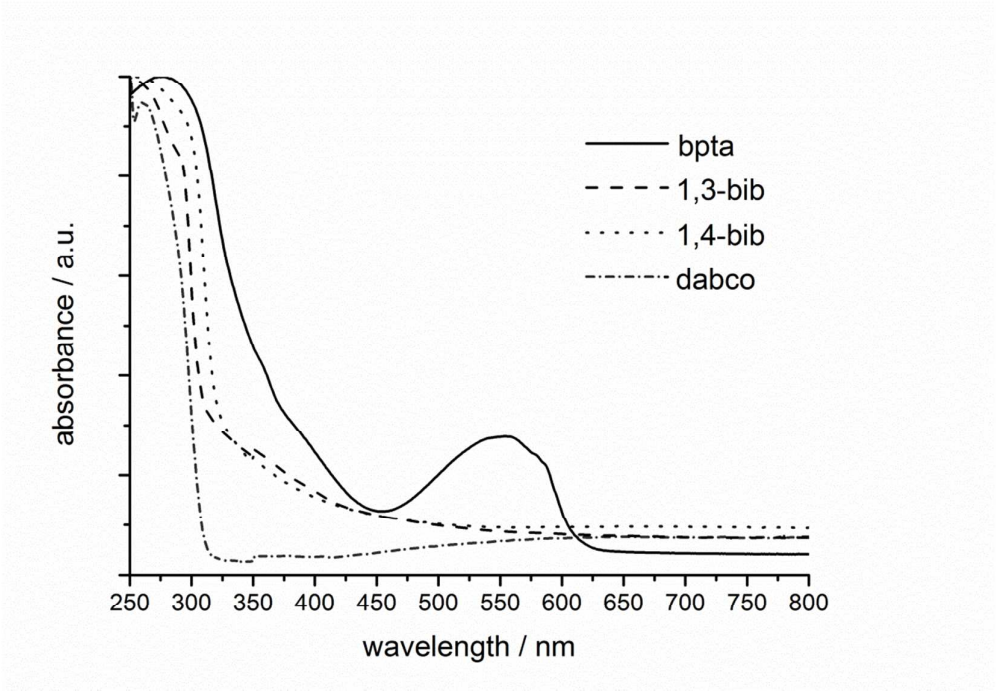


Figure S5. UV/Vis spectra of bpta, 1,3-bib, 1,4-bib and dabco in KBr.

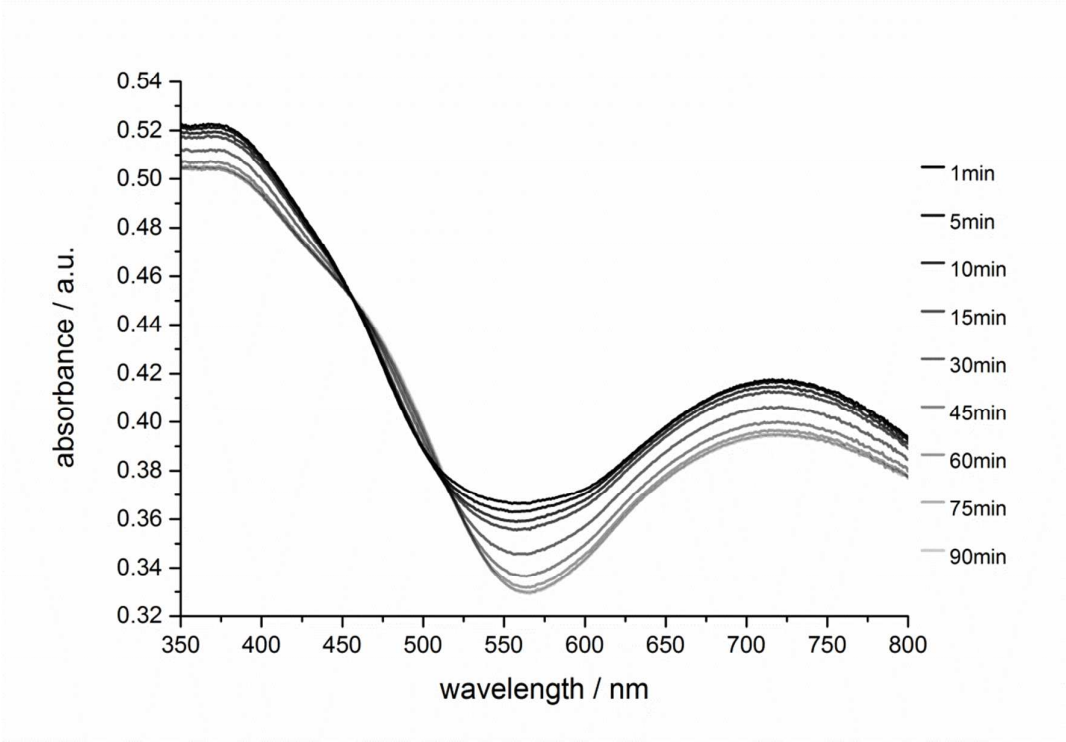


Figure S6. Kinetic study of ethanol adsorption on DUT-90 at 400 ppm.

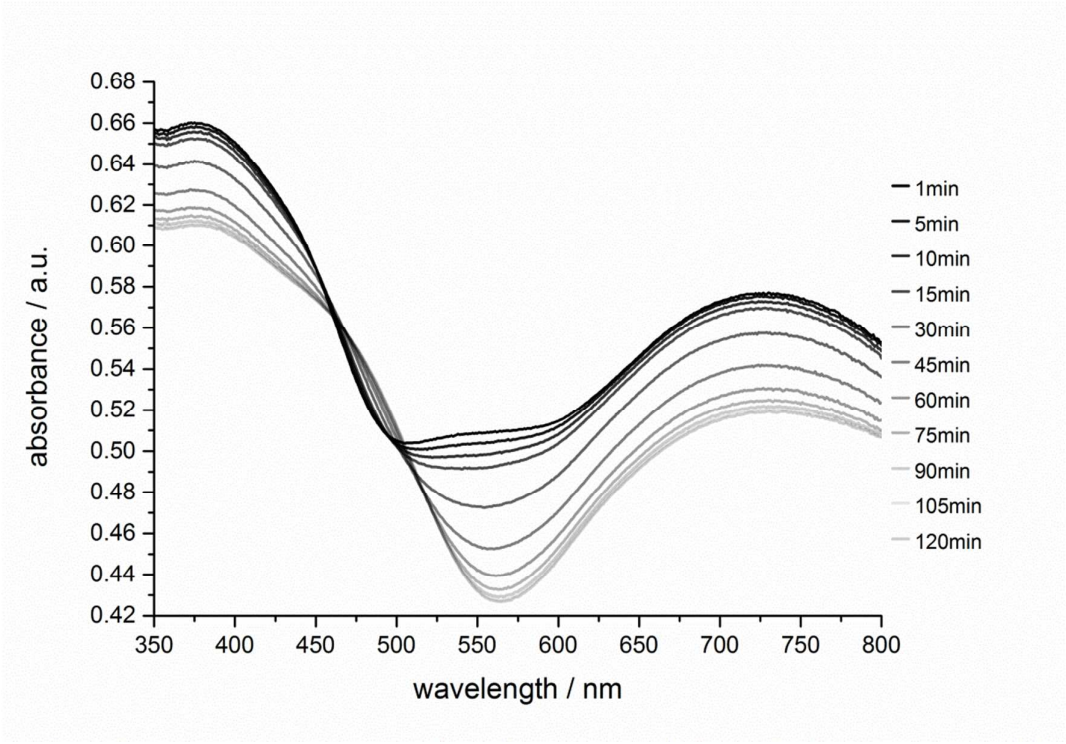


Figure S7. Kinetic study of ethanol adsorption on DUT-91 at 400 ppm.

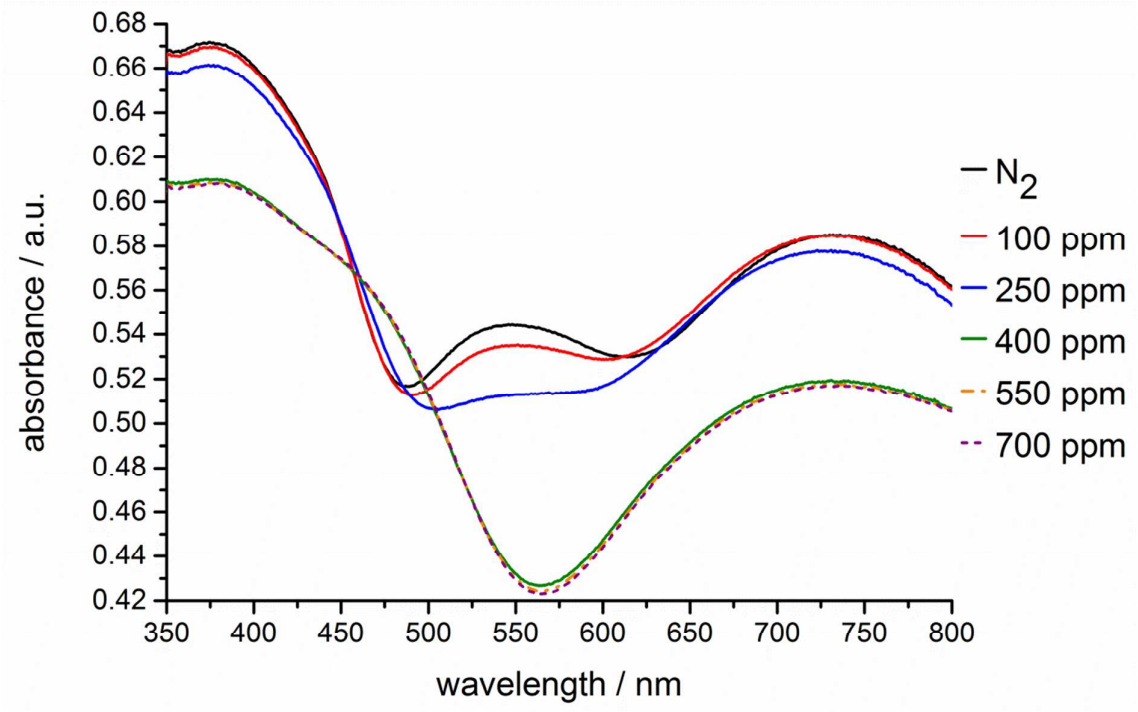


Figure S34. Ethanol adsorption on DUT-91 monitored by UV/Vis.

7. Ethanol physisorption

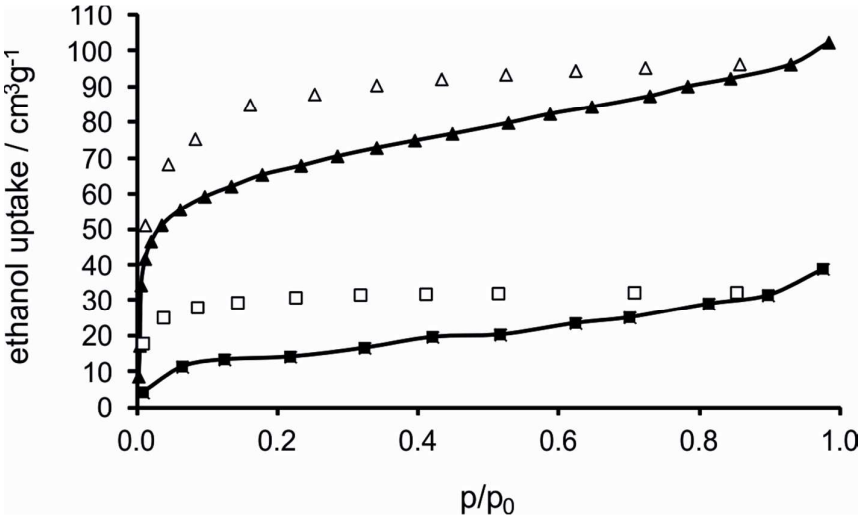


Figure S35. Ethanol adsorption isotherms of DUT-90: fresh SCD dried sample (triangles); second adsorption run with additional activation at room temperature after first adsorption cycle (squares).

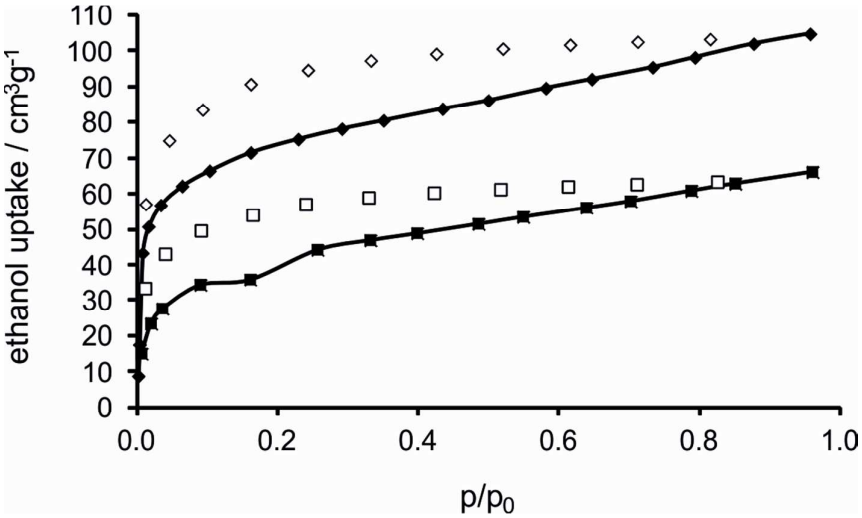


Figure S36. Ethanol adsorption isotherms of DUT-91: fresh SCD dried sample (diamonds); second adsorption run with additional activation at room temperature after first adsorption cycle (squares).

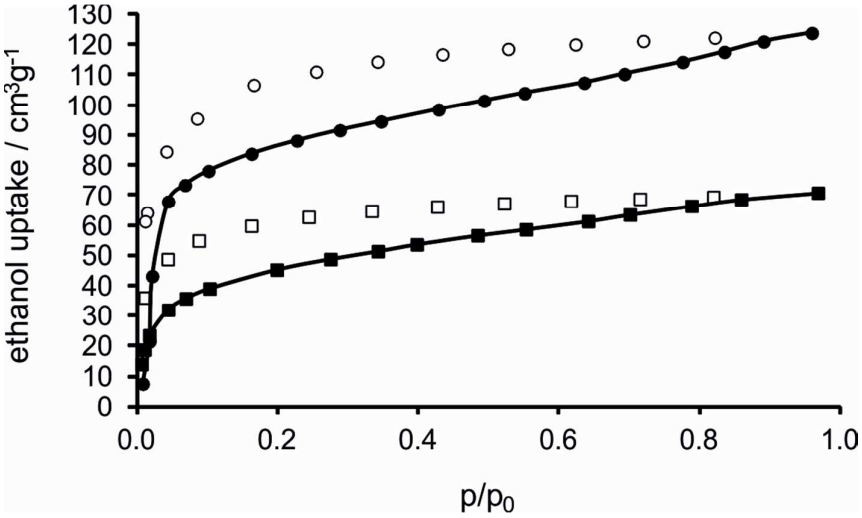


Figure S37. Ethanol adsorption isotherms of DUT-95, fresh SCD dried sample (circles); second adsorption run with additional activation at room temperature after first adsorption cycle (squares).

8. Correlation between intensity of characteristic absorption peak and ethanol uptake

Table S2. DUT-90.

EtOH concentration/ ppm	p/p_0	absorbance at 562 nm / a. u.	1/absorbance	EtOH uptake / g/cm^3
100 for 45 min	0.00128	0.3833	2.6089	
147	0.00189			8.7
250 for 45 min	0.00321	0.3685	2.7137	
272	0.00350			17.2
400 for 45 min	0.00541	0.3367	2.9700	
400 for 90 min	0.00541	0.3291	3.0378	
414	0.00533			34.3
550 for 45 min	0.00707	0.3266	3.0618	
700 for 30 min	0.009	0.3265	3.0628	
858	0.01104			41.7
1511	0.01944			46.6

Table S3. DUT-91.

EtOH concentration/ ppm	p/p_0	absorbance at 562 nm / a. u.	1/absorbance	EtOH uptake / g/cm^3
100 for 45 min	0.00128	0.5340	1.8723	
138	0.00184			8.8
250 for 45 min	0.00321	0.5136	1.9470	
260	0.00350			17.5
400 for 45 min	0.00541	0.4532	2.2062	
400 for 120 min	0.00541	0.4266	2.3436	
550 for 30 min	0.00707	0.4243	2.3567	
610	0.00787			43.3
700 for 30 min	0.009	0.4231	2.3631	
1264	0.0162			50.8

Table S4. DUT-95.

EtOH concentration/ ppm	p/p_0	absorbance at 562 nm / a. u.	1/absorbance	EtOH uptake / g/cm³
100 for 45 min	0.00128	0.5618	1.7799	
205	0.00269			8.6
250 for 45 min	0.00321	0.5525	1.8099	
400 for 45 min	0.00541	0.5339	1.8730	
400 for 180 min	0.00541	0.4627	2.1612	
421	0.00546			17.2
550 for 45 min	0.00707	0.4351	2.2983	
617	0.00796			43.2
700 for 30 min	0.009	0.4332	2.3083	
850 for 15 min	0.0109	0.4329	2.3100	
1172	0.0150			51.324

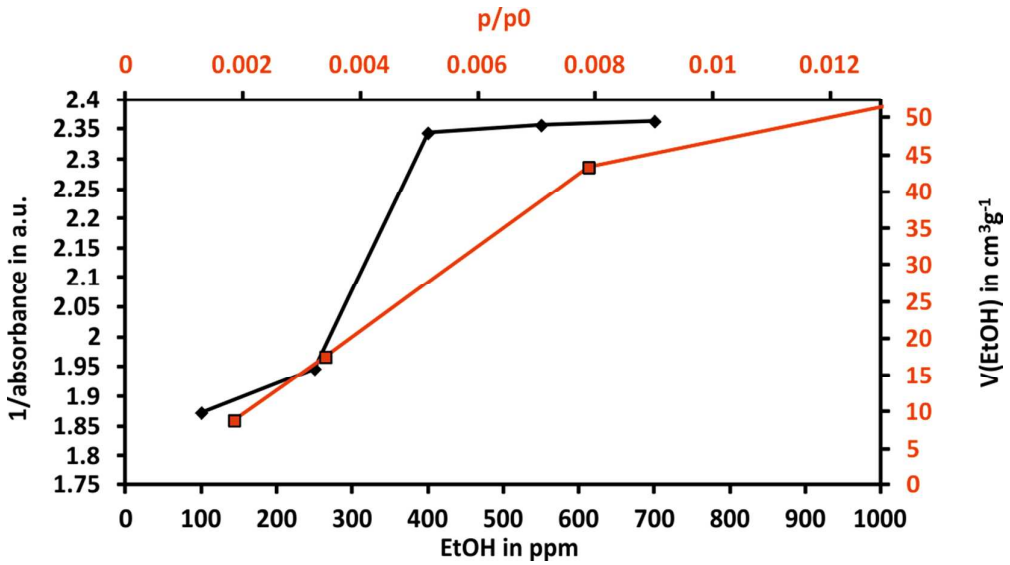


Figure S388. Correlation between ethanol loading (red graph) and 1/absorbance at 566 nm from UV/Vis experiments (black graph) in DUT-91 at 298 K..

9. Crystallographic data

Single crystal structure determination

All single crystals were prepared in the glass capillary with 0.3 mm wall thickness with some amount of solvent. The capillaries were sealed with melted wax. The datasets were measured 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 $U_{iso}(H)$=1.2$U_{iso}(C)$. Because of the high symmetry of the crystal system, it was impossible to model the lattice solvent molecules in the pores. On this ground, the SQUEEZE procedure was used to correct reflection intensities, corresponding to disordered solvent molecules.[4] CCDC-1033164 – 1033171 contain the supplementary crystallographic data for DUT-71, DUT-72, DUT-73a, DUT-73b, DUT-74, DUT-90, DUT-91 and DUT-95. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S5: Experimental data of DUT-71 and DUT-72 single crystal X-ray diffraction.

	DUT-71	**DUT-72**
Empirical formula	$C_{68}\ H_{40}\ O_{20}\ N_4\ Cu_4$	$C_{89}\ H_{38}\ O_{16}\ N_{11}\ Cu_4$
Formula weight	1487.20	1815.82
Crystal system, space group	tetragonal, P_4/mnc	tetragonal, P_4/mnc
Unit cell dimensions, Å	a = 26.600(4) c = 27.120(5)	a = 26.540(4) c = 27.010(5)
Volume, Å^3	19189(7)	19025(7)
Z	4	4
Calculated density, g/cm^3	0.515	0.635
Absorption coefficient, 1/mm	0.839	0.855
F(000)	3008 (after SQUEEZE)	3748 (after SQUEEZE)
θ range, deg	3.4 – 34.1	3.5 – 34.1
Limiting indices	$0 \le h \le 33$ $1 \le k \le 33$ $0 \le l \le 29$	$0 \le h \le 33$ $0 \le k \le 33$ $0 \le l \le 34$
Reflections collected / unique	18273 / 9443	17686 / 9373
R(int)	0.02	0.016
Data / parameters	9443 / 225	9373 / 317
GooF on F^2	1.08	1.12
Final R indices [I>2σ(I)]	$R1$ = 0.0634	$R1$ = 0.0509
R indices (all data)	$wR2$ = 0.2249	$wR2$ = 0.1737
Largest diff. peak / hole, eÅ^{-3}	0.43 / -0.29	0.93 / -0.44

Table S6: Experimental data of DUT-73a and DUT-73b single crystal X-ray diffraction.

	DUT-73a	**DUT-73b**
Empirical formula	$C_{74}\ H_{45}\ O_{19}\ N_6\ Cu_4$	$C_{81}\ H_{55}\ O_{18}\ N_9\ Cu_4$
Formula weight	1576.32	1696.54
Crystal system, space group	tetragonal, P_4/mnc	orthorhombic, *Pccn*
Unit cell dimensions, Å	a = 26.700(4) c = 26.720(5)	a = 37.441(7) b = 37.449(7) c = 27.250(5)
Volume, Å^3	19048(7)	38198(16)
Z	4	8
Calculated density, g/cm^3	0.550	0.590
Absorption coefficient, 1/mm	0.848	0.849
F(000)	3196 (after SQUEEZE)	6912
θ range, deg	3.6 – 34.1	3.2 – 34.1
Limiting indices	$0 \le h \le 33$ $0 \le k \le 33$ $0 \le l \le 33$	$0 \le h \le 47$ $0 \le k \le 47$ $0 \le l \le 29$
Reflections collected / unique	19435 / 10102	38807 / 36949
R(int)	0.027	0.042
Data / parameters	10102 / 297	36949 / 986
GooF on F^2	1.11	1.74
Final R indices [I>2σ(I)]	$R1$ = 0.0614	$R1$ = 0.0975
R indices (all data)	$wR2$ = 0.2218	$wR2$ = 0.2779
Largest diff. peak / hole, eÅ^{-3}	0.59 / -0.60	0.89 / -0.57

Table S7: Experimental data of DUT-74 and DUT-90 single crystal X-ray diffraction.

	DUT-74	**DUT-90**
Empirical formula	$C_{72}\ H_{42}\ O_{19}\ N_6\ Cu_4$	$C_{89}\ H_{75}\ O_{16}\ N_{11}\ Cu_4$
Formula weight	1549.28	1808.76
Crystal system, space group	tetragonal, P_4/mnc	tetragonal, P_4/mnc
Unit cell dimensions, Å	a = 26.450(4) c = 27.880(5)	a = 26.810(4) c = 25.860(5)
Volume, Å^3	19505(7)	18588(7)
Z	4	4
Calculated density, g/cm^3	0.528	0.646
Absorption coefficient, 1/mm	0.827	0.875
F(000)	3136 (after SQUEEZE)	3720 (after SQUEEZE)
θ range, deg	2.8 – 32.0	3.3 – 34.1
Limiting indices	$0 \le h \le 31$ $0 \le k \le 31$ $0 \le l \le 33$	$0 \le h \le 33$ $0 \le k \le 33$ $0 \le l \le 32$
Reflections collected / unique	15041 / 7988	19354 / 10065
R(int)	0.025	0.02
Data / parameters	7988 / 258	10065 / 369
GooF on F^2	0.92	1.11
Final R indices [I>2σ(I)]	$R1$ = 0.072	$R1$ = 0.0581
R indices (all data)	$wR2$ = 0.2326	$wR2$ = 0.2079
Largest diff. peak / hole, eÅ^{-3}	0.77 / -0.84	0.72 / -0.47

Table S8: Experimental data of DUT-91 and DUT-95 single crystal X-ray diffraction.

	DUT-91	**DUT-95**
Empirical formula	$C_{89}\ H_{75}\ O_{16}\ N_{11}\ Cu_4$	$C_{89}\ H_{74}\ O_{16}\ N_{12}\ Cu_4$
Formula weight	1808.80	1821.80
Crystal system, space group	tetragonal, P_4/mnc	tetragonal, P_4/mnc
Unit cell dimensions, Å	a = 26.690(4) c = 26.380(5)	a = 26.610(4) c = 26.810(5)
Volume, Å^3	18792(7)	18984(7)
Z	4	4
Calculated density, g/cm^3	0.639	0.637
Absorption coefficient, 1/mm	0.866	0.858
F(000)	3720 (after SQUEEZE)	3744 (after SQUEEZE)
θ range, deg	1.3 – 35.1	1.3 – 32.7
Limiting indices	-28 ≤ h ≤ 27 -33 ≤ k ≤ 33 -33 ≤ l ≤ 21	-32 ≤ h ≤ 30 -32 ≤ k ≤ 26 -29 ≤ l ≤ 25
Reflections collected / unique	74017 / 10508	64712 / 8721
R(int)	0.041	0.076
Data / parameters	10508 / 340	8721 / 324
GooF on F^2	1.03	1.07
Final R indices [I>2σ(I)]	$R1$ = 0.0661	$R1$ = 0.0612
R indices (all data)	$wR2$ = 0.2613	$wR2$ = 0.2302
Largest diff. peak / hole, eÅ^{-3}	0.72 / -0.83	0.42 / -0.89

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