Electronic Supporting Information

Insights into the water adsorption mechanism in the chemically stable zirconium-based MOF DUT-67 – a prospective material for adsorption-driven heat transformations

Volodymyr. Bon,[a*] Irena Senkovska,[a] Jack D. Evans,[a] Michelle Wöllner,[a,b] Markus Hölzel[c] and Stefan Kaskel[a,b]

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1. Pore size distribution in DUT-67(Zr)

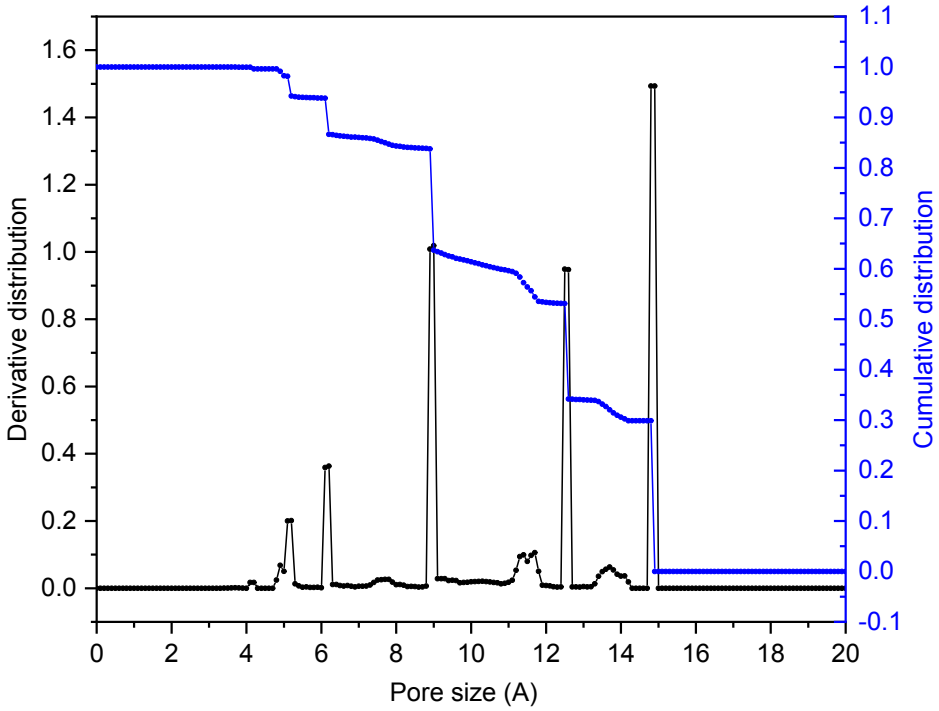
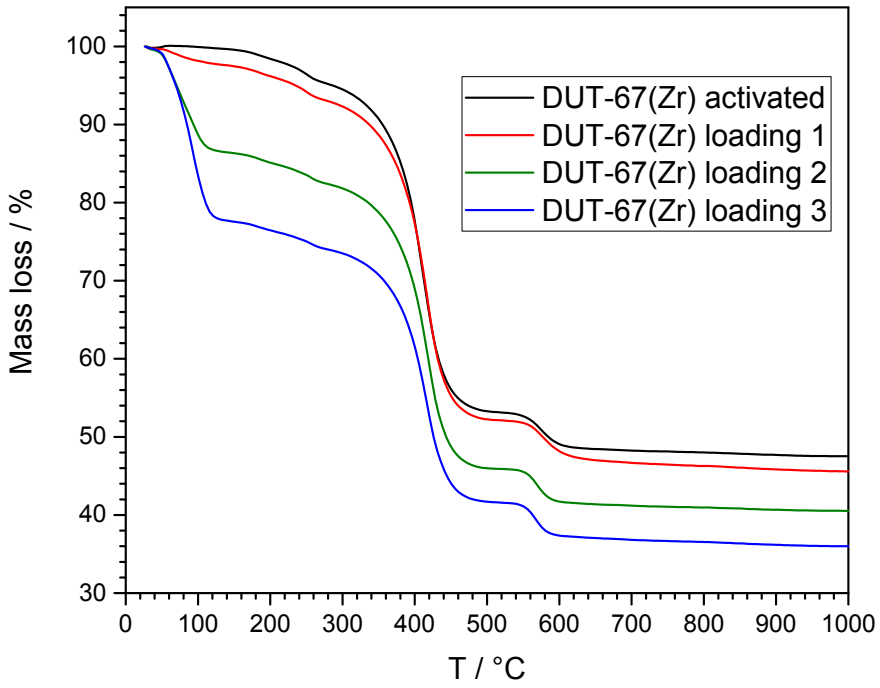


Figure S1. Pore size distribution and pore size fraction for DUT-67(Zr) calculated using Zeo++ software.

2. TG curves for DUT-67(Zr)



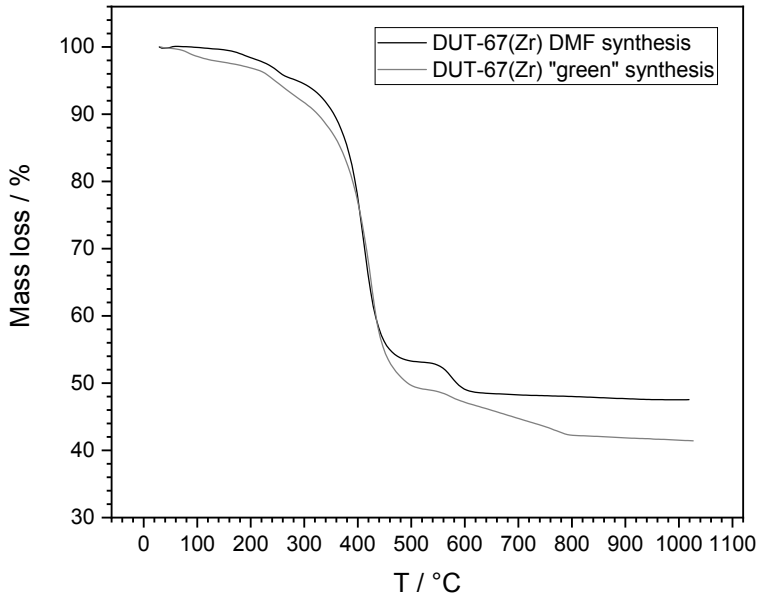


Figure S2. TG curves for activated and D_2O pre-loaded DUT-67(Zr) samples.

3. DRIFT spectra for DUT-67(Zr).

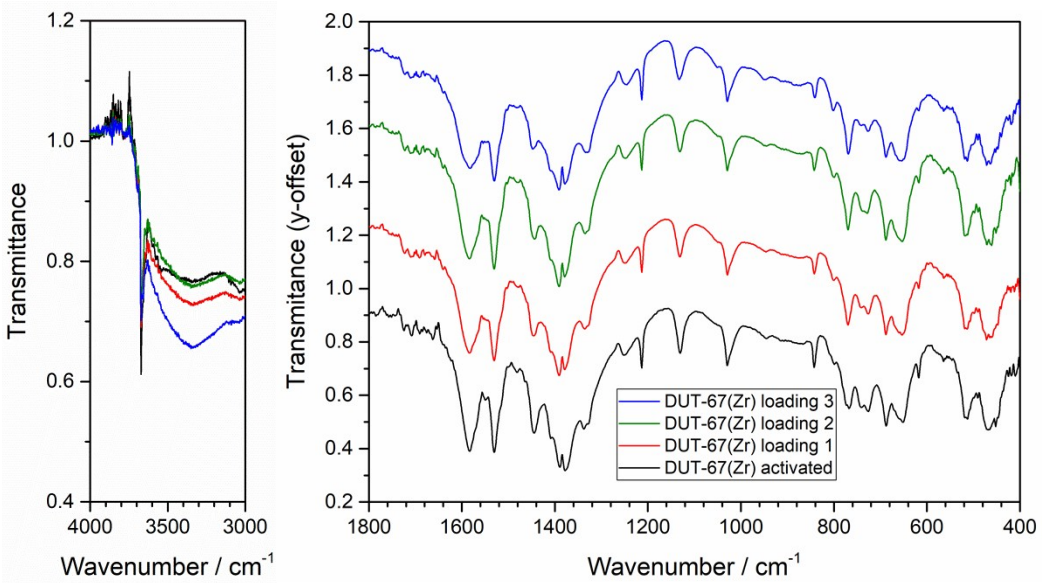


Figure S3. DRIFT spectra for DUT-67(Zr) samples.

4. Thermo PXRD on DUT-67(Zr)

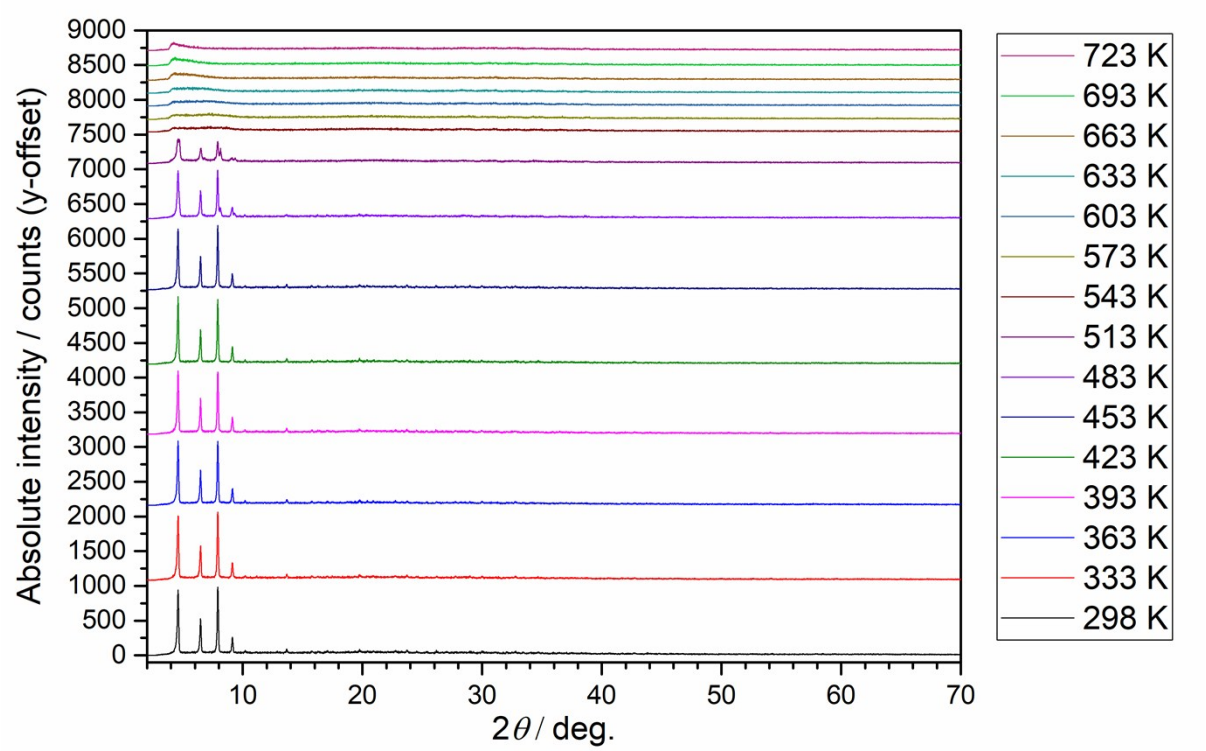


Figure S4. Thermo-PXRD experiments on the desolvated DUT-67(Zr) sample.

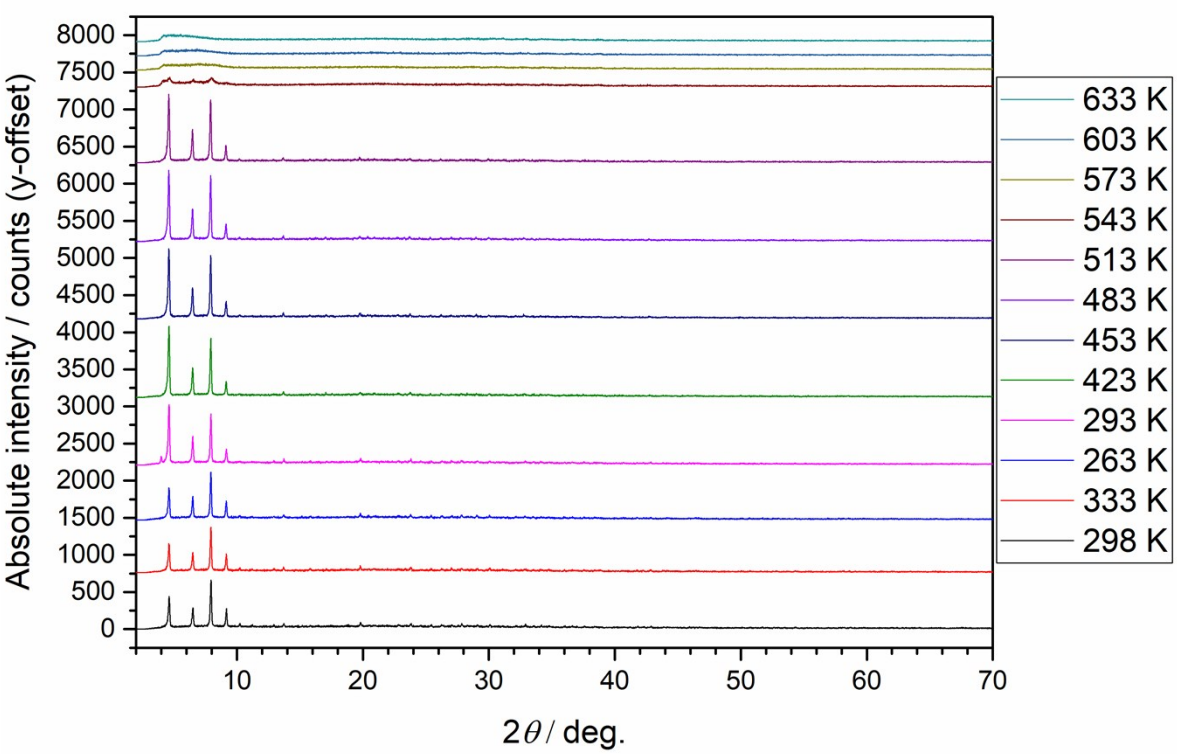


Figure S5. Thermo-PXRD experiments on the pre-loaded DUT-67(Zr) sample (3).

5. Adsorption / desorption cyclization of water on DUT-67(Zr) using optical calorimetry

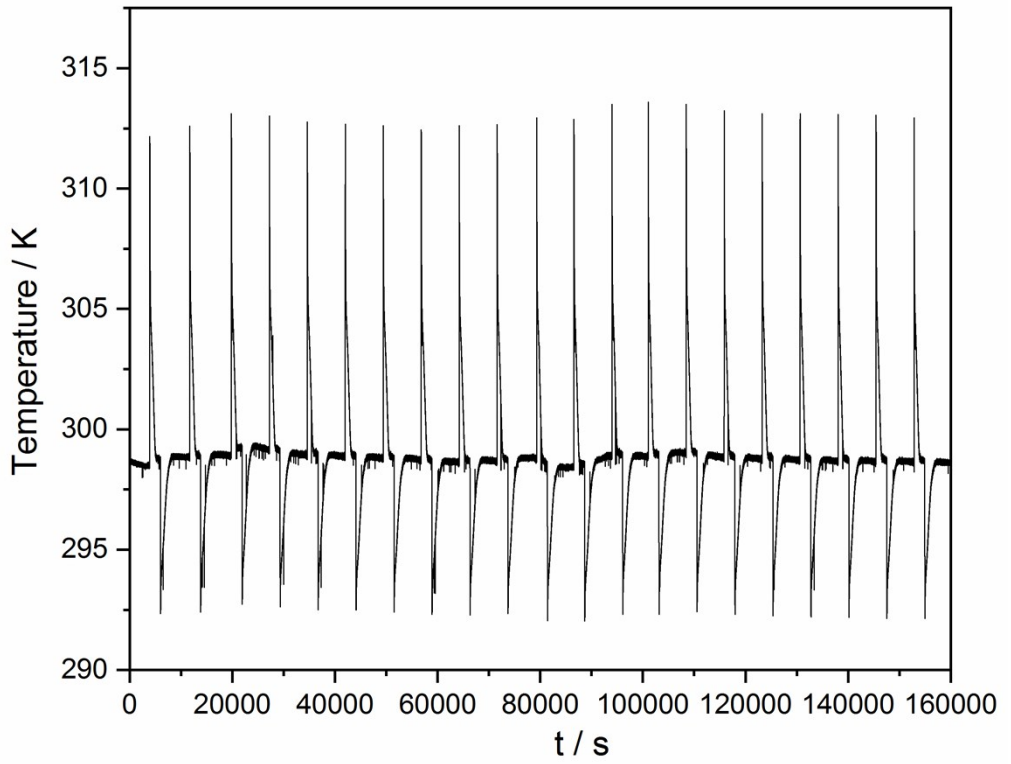


Figure S6. Thermal response during 20 adsorption / desorption cycles of water on DUT-67(Zr).

6. Water physisorption on DUT-67(Zr) at 298 K and 318 K

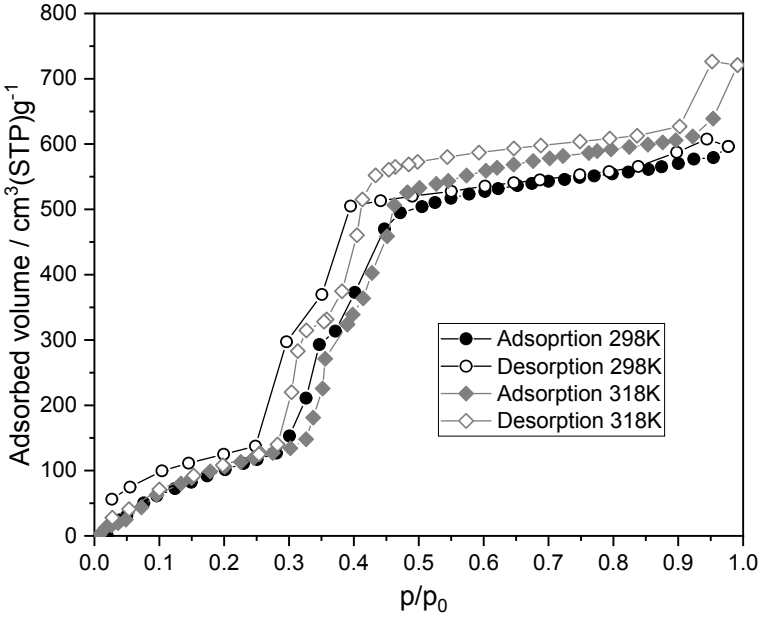


Figure S7. Water vapour adsorption isotherms on DUT-67(Zr) at 298 and 318 K.

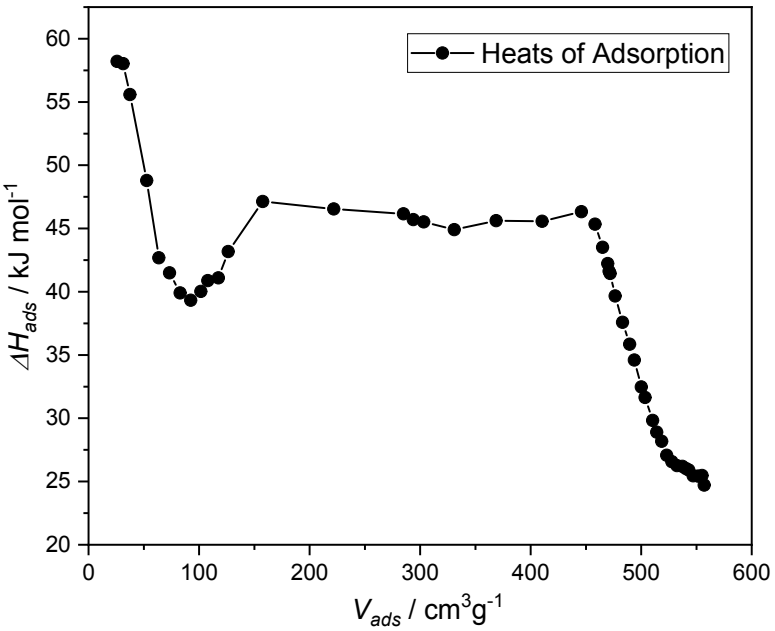


Figure S8. Adsorption enthalpy calculated from water adsorption isotherms in Fig.S7 using Clausius-Clapeyron equation.

7. Rietveld plots of NPD data

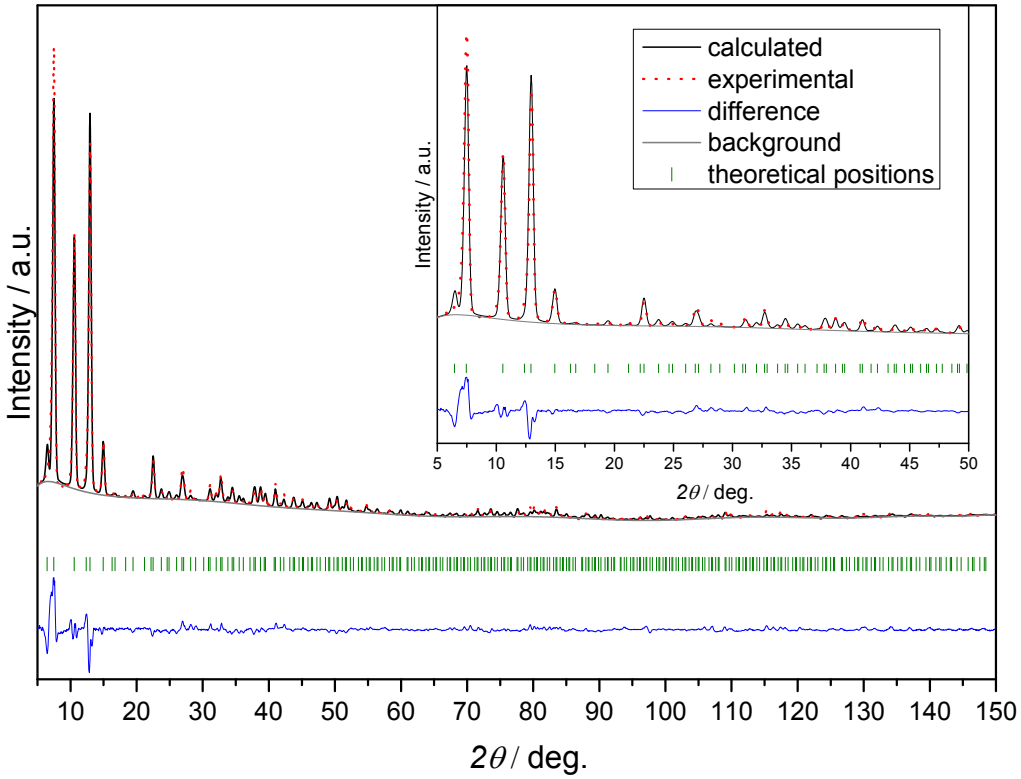


Figure S9. Rietveld plot for desolvated DUT-67(Zr).

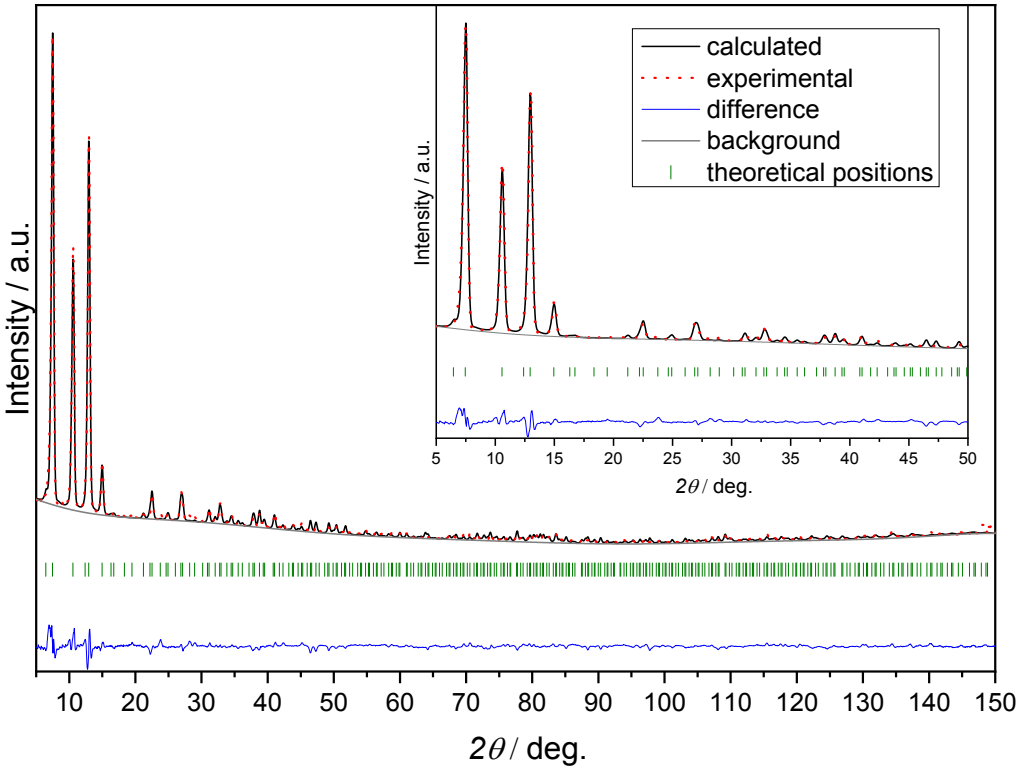


Figure S10. Rietveld plot for DUT-67(Zr) loading 1.

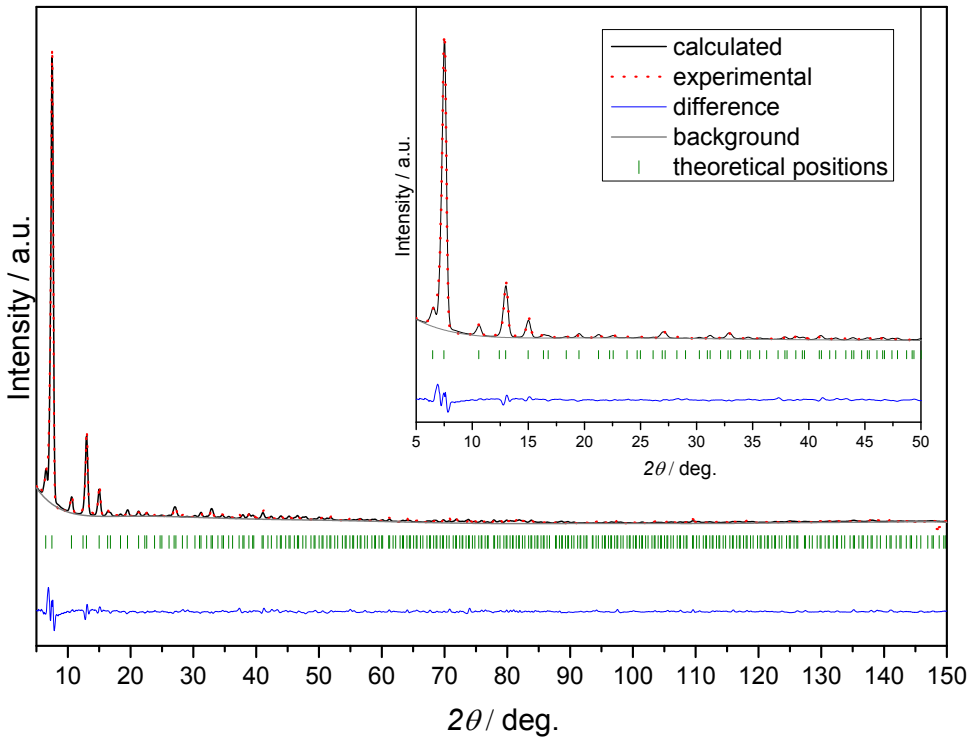


Figure S11. Rietveld plot for DUT-67(Zr) loading 2.

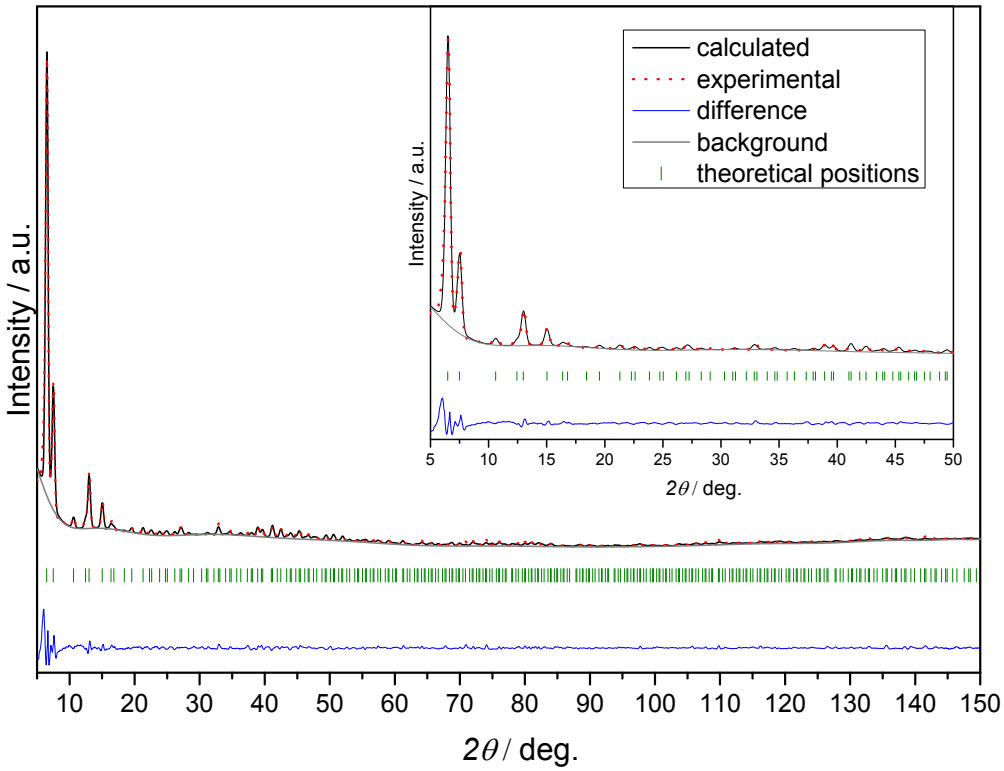


Figure S12. Rietveld plot for DUT-67(Zr) loading 3.

8. Experimental data for Rietveld refinement

Table S1. Experimental data on Rietveld refinement of desolvated DUT-67(Zr) and D_2O@DUT-67(Zr) samples.

	DUT-67(Zr) desolvated	D_2O@DUT-67(Zr) loading 1	D_2O@DUT-67(Zr) loading 2	D_2O@DUT-67(Zr) loading 3
Formula	$C_{32}H_{24}O_{32}S_4Zr_6$	$C_{32}H_{24}O_{32}S_4Zr_6$ x $0.62D_2O$	$C_{32}H_{24}O_{32}S_4Zr_6$ x $2.09D_2O$	$C_{32}H_{24}O_{32}S_4Zr_6$ x $3.87D_2O$
Molecular weight	1595.32	1607.72	1637.12	1672.72
Symmetry, space group	Cubic, $Fm\bar{3}m$			
a, Å	38.9954(20)	38.9621(12)	38.8762(25)	38.8181(28)
V, Å^3	59298.01(24)	59146.23(15)	58755.89(27)	58492.86(31)
z	24			
Profile function	Thompson-Cox-Hastings			
U	0.05198	0.06586	0.04100	0.08028
V	-0.12642	-0.17541	-0.18195	0.02079
W	0.17240	0.15275	0.20186	0.18342
X	0.06781	0.11622	0.37756	0.13968
Y	0.05433	0.09664	0.05558	0.06084
Zero line shift	-0.004	-0.005	-0.007	0.001
Berar-Baldinozzi asymmetry correction ($2\vartheta_{max}$ = 90°)				
P1	-0.00596	-0.02116	-0.02800	-0.00072
P2	-0.00318	-0.00637	-0.00671	-0.00136
P3	-0.03241	-0.06401	-0.06728	-0.01314
P4	-0.00611	-0.01212	-0.01353	-0.00254
Refined motioned groups	8	2	5	9
Refined degrees of freedom	20	12	30	56
Final R_{wp}	0.0433	0.0413	0.0459	0.0391
Final R_p	0.0275	0.0301	0.0310	0.0250

9. Vapour adsorption isotherms

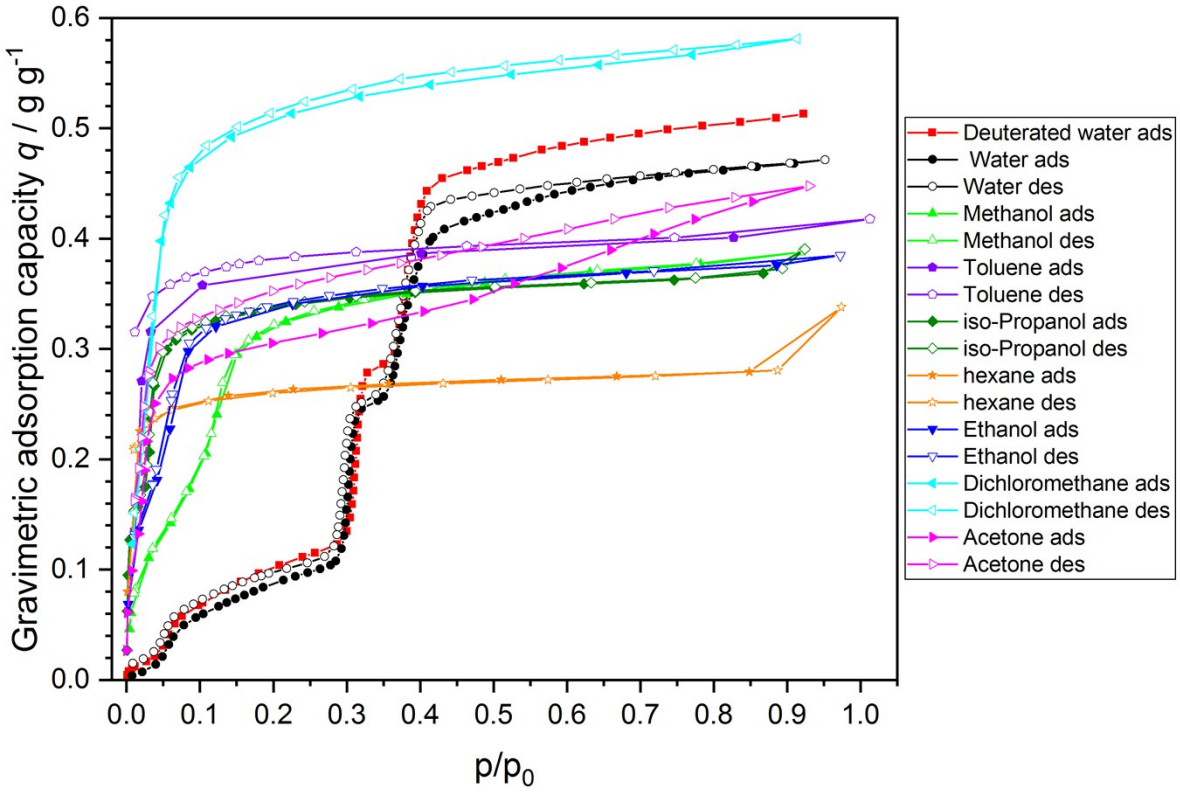


Figure S13. Gravimetric solvent adsorption capacity of DUT-67(Zr).

10. Scanning electron microscopy

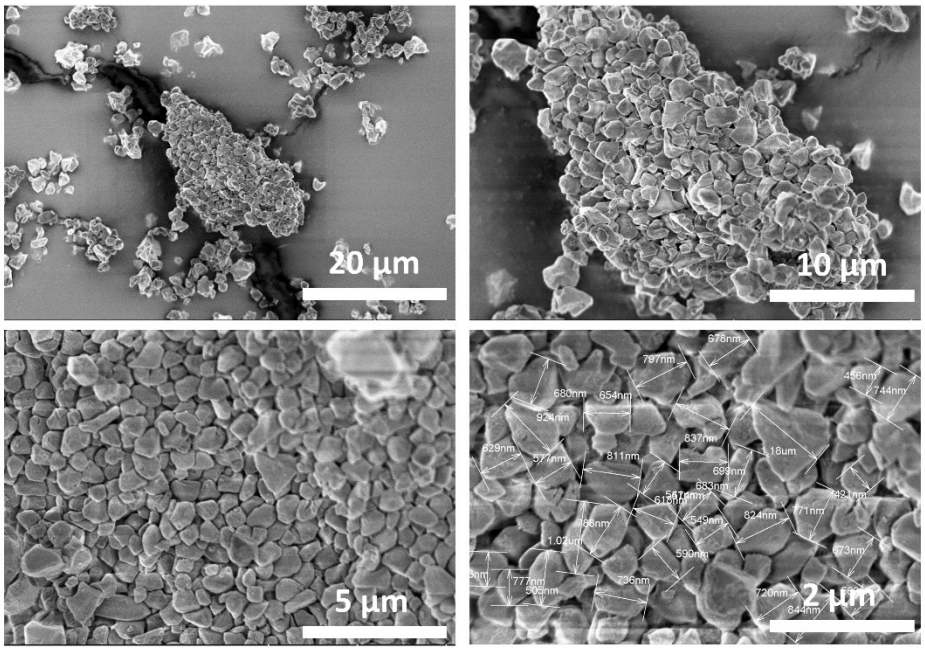


Figure S14. SEM images of DUT-67(Zr).