Supporting Information

Water sorption performance of the zeolitic metal azolate framework MAF-7

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Experimental section

Synthesis of MAF-7

$[Zn(mtz)_2]_n$ (MAF-7, Hmtz = 3-methyl-1,2,4-triazole) was prepared following a method described in the literature, with some modifications. 5 mmol (407 mg) of ZnO and 10 mmol (831 mg) of Hmtz were dissolved in 10 mL of NH_4OH (25 %) in a 15 mL vial and stirred overnight at room temperature. The vial was left uncapped to allow the release of NH_3, which facilitated the progression of the reaction. The white precipitate was then filtered, washed with water, and air-dried (yield ~ 95 %).

Powder X-ray Diffraction

Powder X-ray diffraction experiments were conducted using microcrystalline samples on a Panalytical Empyrean diffractometer (40 kV, 40 mA, Cu $K\alpha_{1,2}$, λ = 1.5418 Å) at room temperature with a range of $5° < 2\theta < 40°$.

Thermogravimetric Analysis (TGA)

TGA for all the compounds were carried out under N_2 atmosphere in a TA instruments Q50 thermal analyzer between room temperature and 500 °C with a constant heating rate of 10 °C min^{-1}.

Dynamic water vapor sorption experiments

Water vapor sorption measurements were conducted using the Adventure dynamic vapour sorption (DVS) instrument manufactured by Surface Measurement Systems. This instrument gravimetrically measures water vapour uptake using air as the carrier gas. Digital mass flow controllers regulate the flows of dry and saturated gases. The saturated flow is created by passing dry air through a pure water bubbler. Desired relative humidity (RH) is then generated by precisely mixing dry and saturated gas flows in calibrated flow ratios. A total gas flow rate of 400 sccm min^{-1} was used for the measurements. The mass of each sample was determined by comparison to an empty reference pan and recorded by a high-resolution microbalance with a precision of 0.1 µg. For each RH data point, $dm/dt < 0.05$ % min^{-1} for a minimum of 10 min was used as criteria of reaching equilibrium. Prior to measurement, each sample was activated *in-situ* in dry air at 40 °C for 1 h using the built-in preheater and consequently cooled to the sorption temperature.

Water sorption isotherm measurements were performed on approximately 10 mg of sample powder across the range of 0 - 95 % RH at 15, 25, 35 and 45 °C. Kinetic measurements were carried out on approximately 7 mg of sample powder. The adsorption RH was set at 60 or 90 % at 25 °C and the

desorption RH was set at 0 % at 25, 30 or 40 °C. The recyclability test was performed at 25 °C, altering between 60 % RH (30 min) and 0 % RH (30min) for 10 cycles (600 min in total).

Molecular Simulations

Molecular simulations were performed using the reported single crystal structure of MAF-7 (refcode: EMAPAK). Water molecules in the original structure were carefully examined and manually selected based on reasonable atom distances. The uncoordinated N atom of mtz is treated indiscriminately with the neighbouring CH group to keep the crystal system in the cubic *I43m* space group. Further optimization of water locations was carried out in Materials studio using the Forcite module (task: geometry optimization, quality: ultra-fine, algorithm: smart; forcefield: universal). Only the positions of oxygen atoms in H_2O are optimized, as the hydrogen atoms exhibit two- or four-fold disorder depending on their specific locations in the cubic *I43m* space group.

Table S1. Water sorption recyclability test results for MAF-7.

	Target	**Water uptake (wt%)**		**Working capacity (wt%)**
	% RH	**Sorption**	**Desorption**	
Cycle 1	0.0	0.00	2.91	35.72
	60.0	38.63	38.63	
Cycle 2	0.0	2.91	3.18	35.76
	60.0	38.94	38.94	
Cycle 3	0.0	3.18	3.09	35.89
	60.0	38.98	38.98	
Cycle 4	0.0	3.09	2.99	35.78
	60.0	38.77	38.77	
Cycle 5	0.0	2.99	3.06	35.72
	60.0	38.78	38.78	
Cycle 6	0.0	3.06	2.89	35.68
	60.0	38.57	38.57	
Cycle 7	0.0	2.89	2.94	35.66
	60.0	38.60	38.60	
Cycle 8	0.0	2.94	3.00	35.52
	60.0	38.52	38.52	
Cycle 9	0.0	3.00	2.96	35.45
	60.0	38.41	38.41	
Cycle 10	0.0	2.96	2.86	35.45
	60.0	38.31	38.31	

Table S2. Water deliverability of MAF-7 under different desorption conditions (Working capacity of 35.66 wt% per cycle is used as default).

conditions	adsorption Temperature (°C)	adsorption Time (min)	desorption Temperature (°C)	desorption Time (min)	deliverability (L kg^{-1} d^{-1})
1	25	30	25	30	8.56
2	25	30	30	20	10.27
3	25	30	40	10	12.84

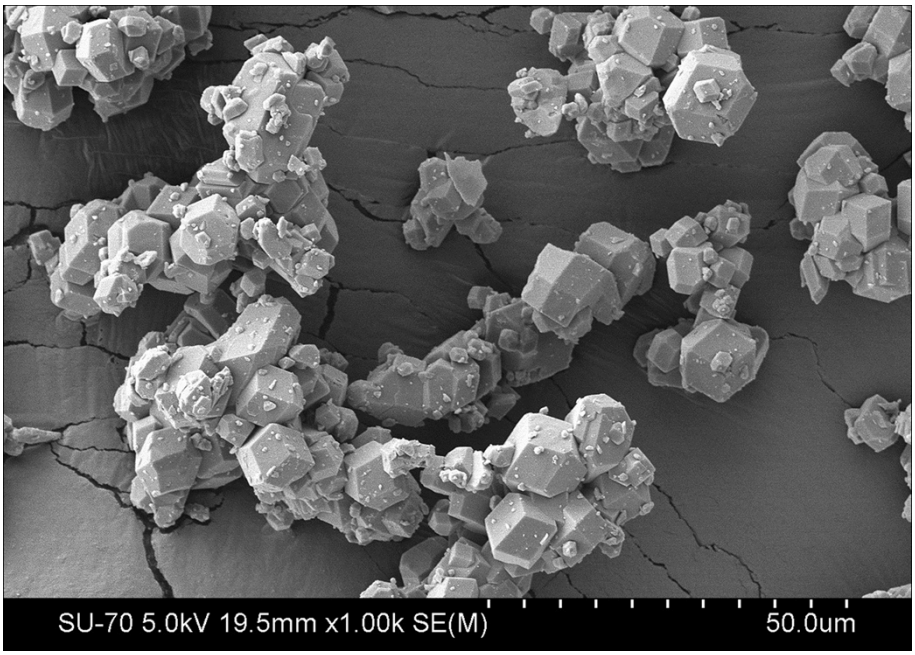

Figure S1. SEM image of MAF-7.

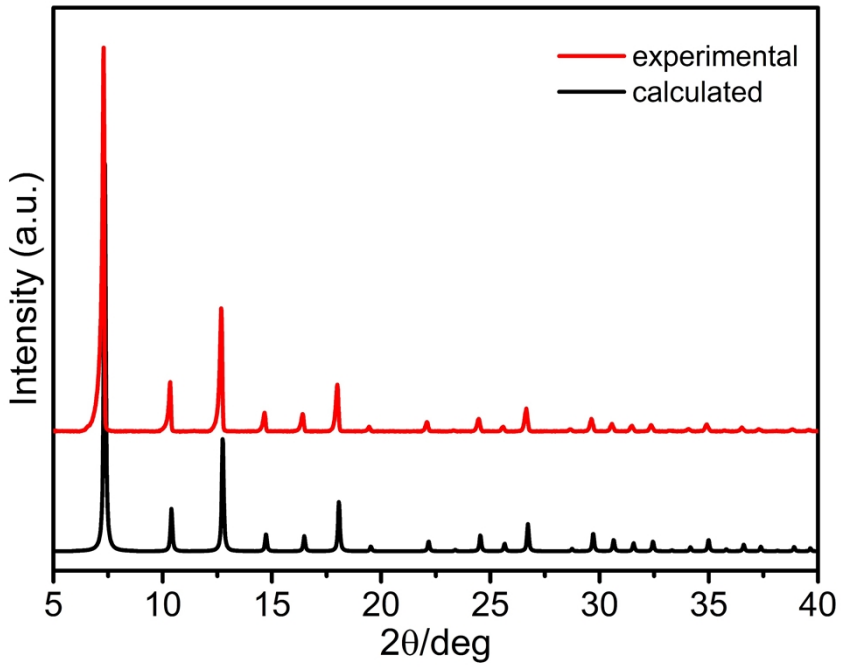

Figure S2. Calculated and experimental PXRD patterns of MAF-7.

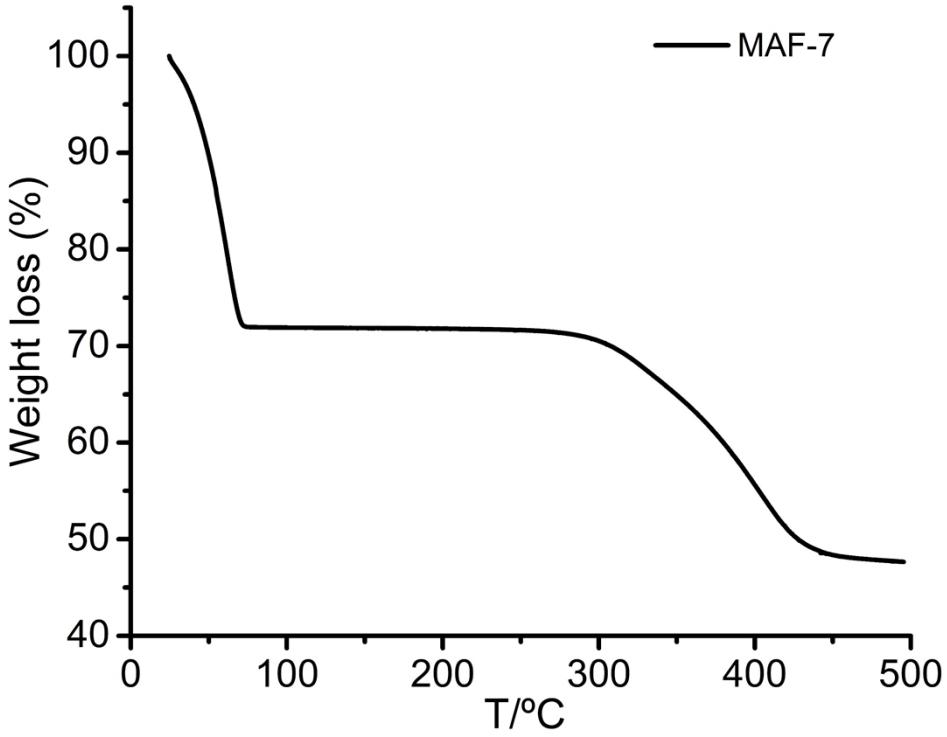

Figure S3. TGA curve of MAF-7.

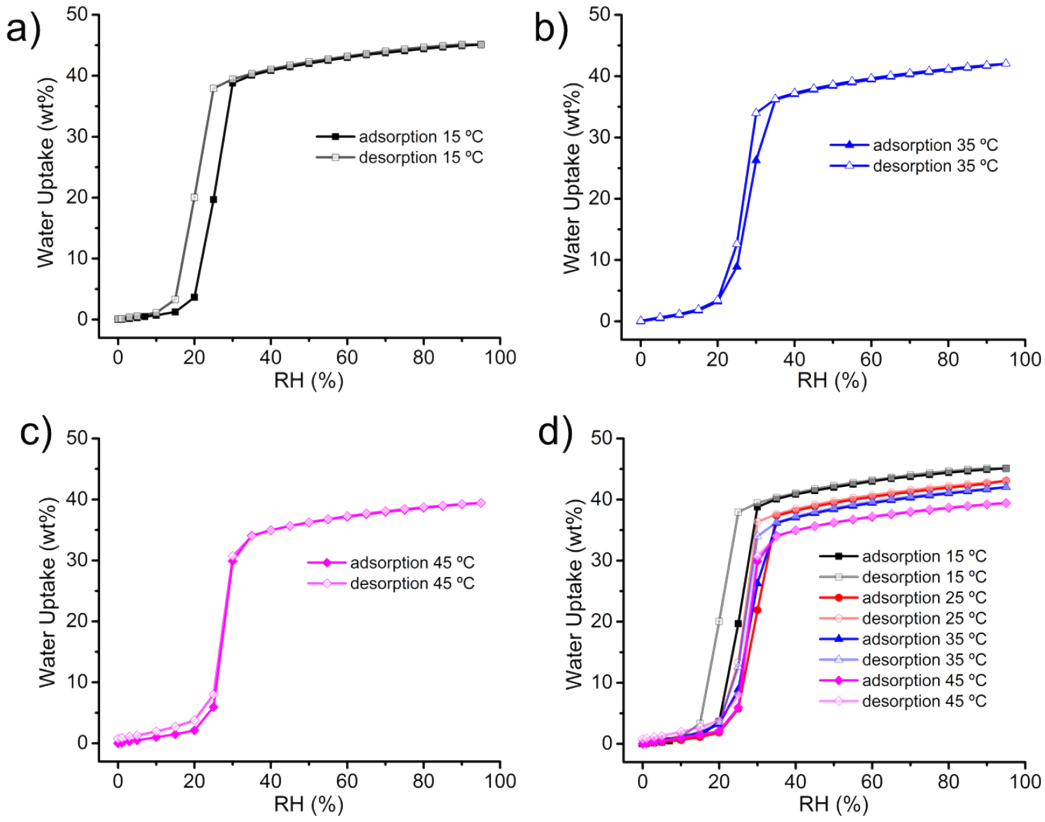

Figure S4. Water vapor sorption isotherms for MAF-7 under 15 - 45 °C.

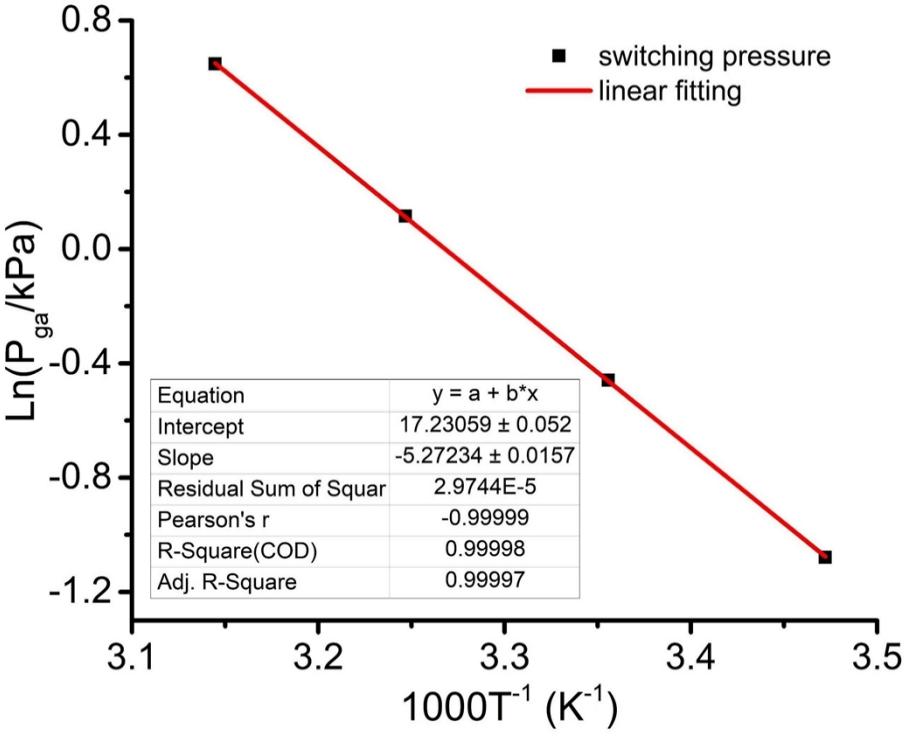

Figure S5. Linear fitting of the switching pressures at different temperatures.

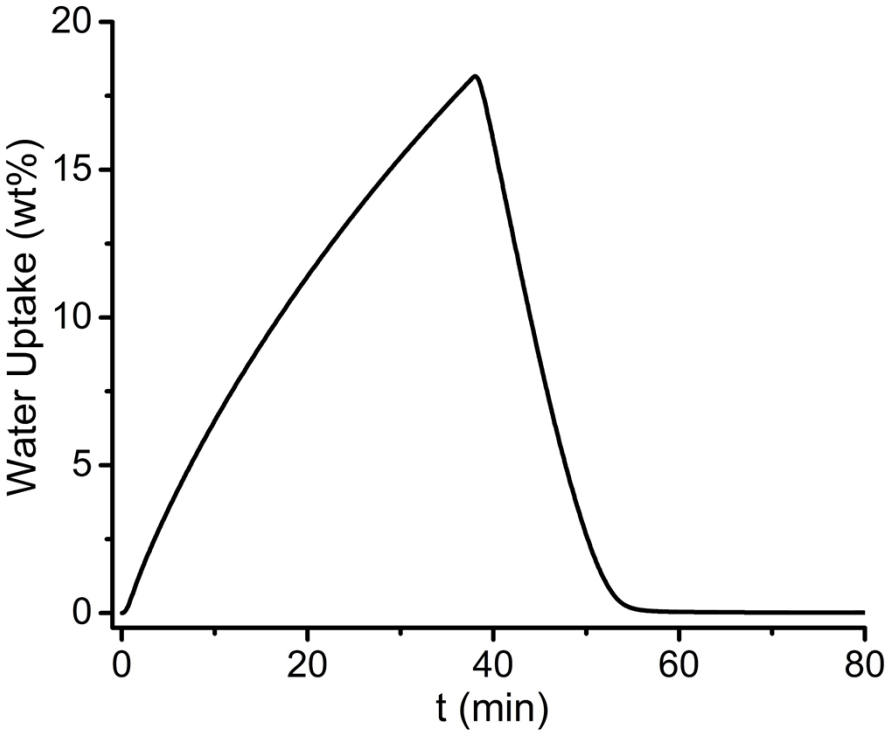

Figure S6. Water sorption kinetics tests under 30 - 0 % RH at 25 °C.

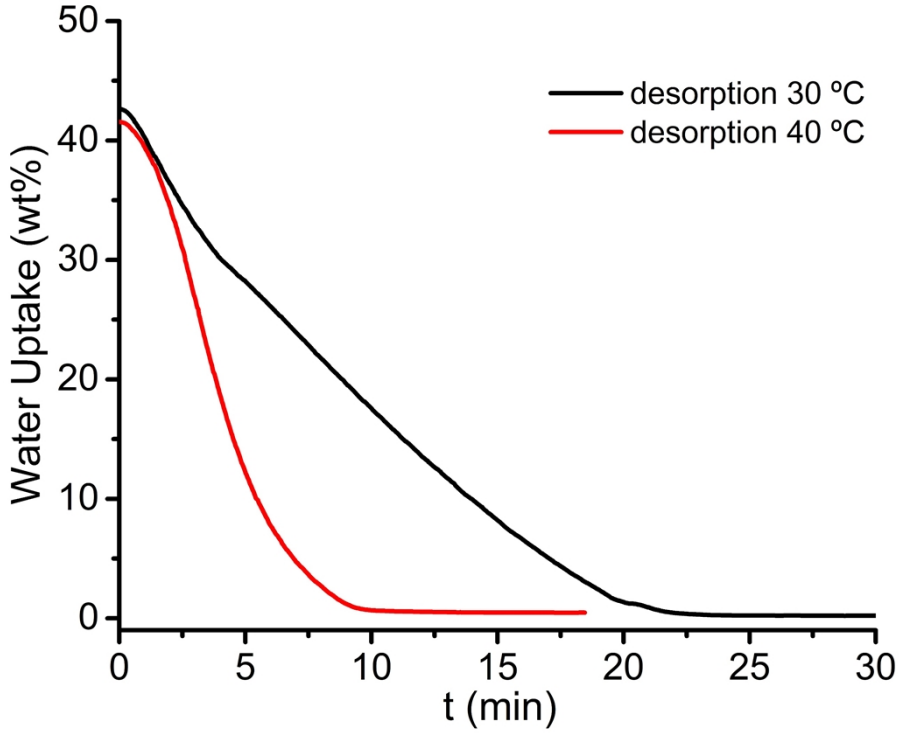

Figure S7. Water desorption kinetics at 30 and 40 °C.

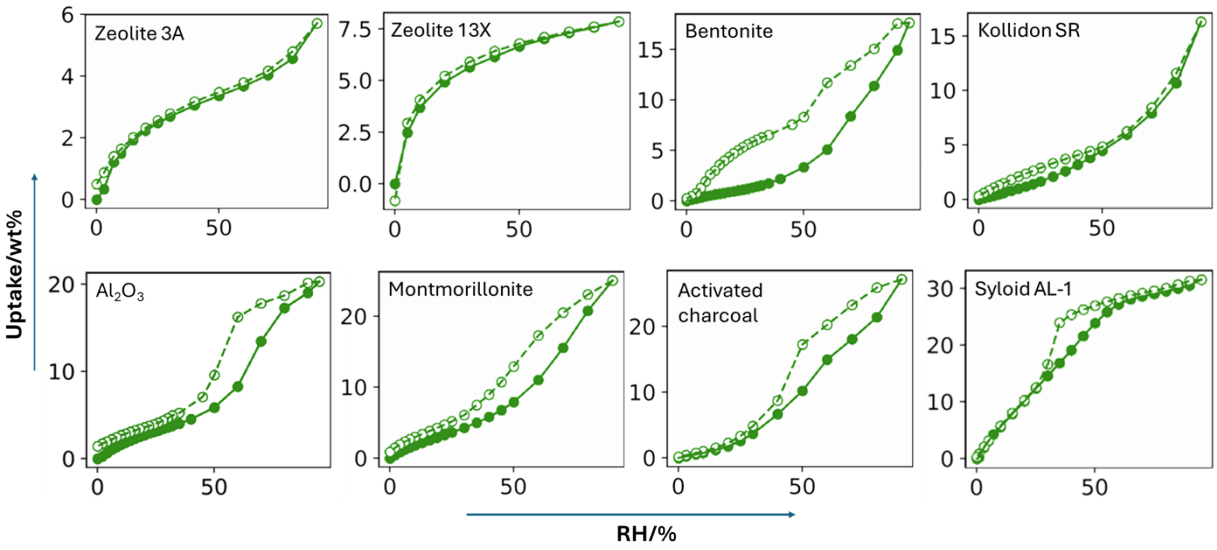

Figure S8. Water vapor sorption isotherms for selected commercial dessicants at 25/27 °C (ref 34).

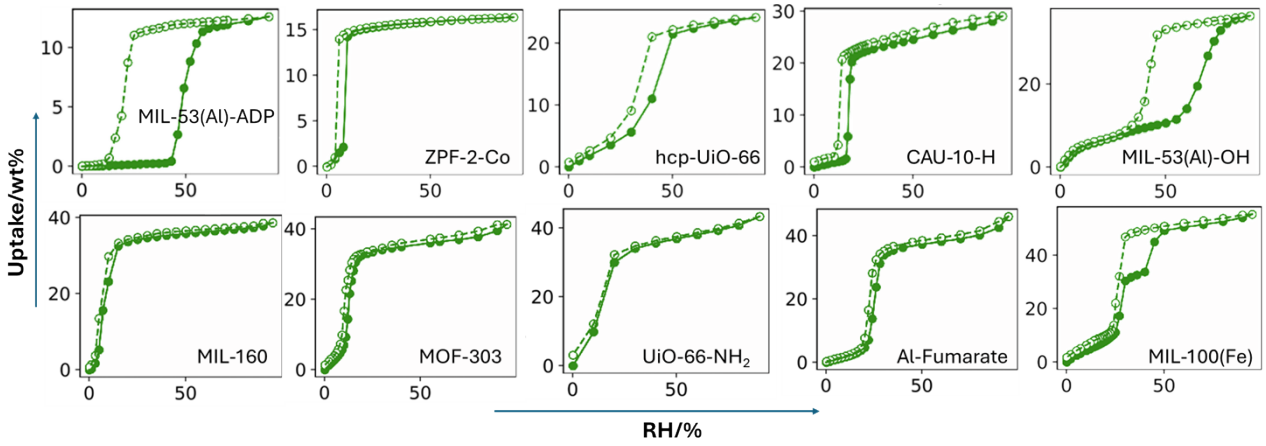

Figure S9. Water vapor sorption isotherms for selected MOFs at 25/27 °C (ref 34).

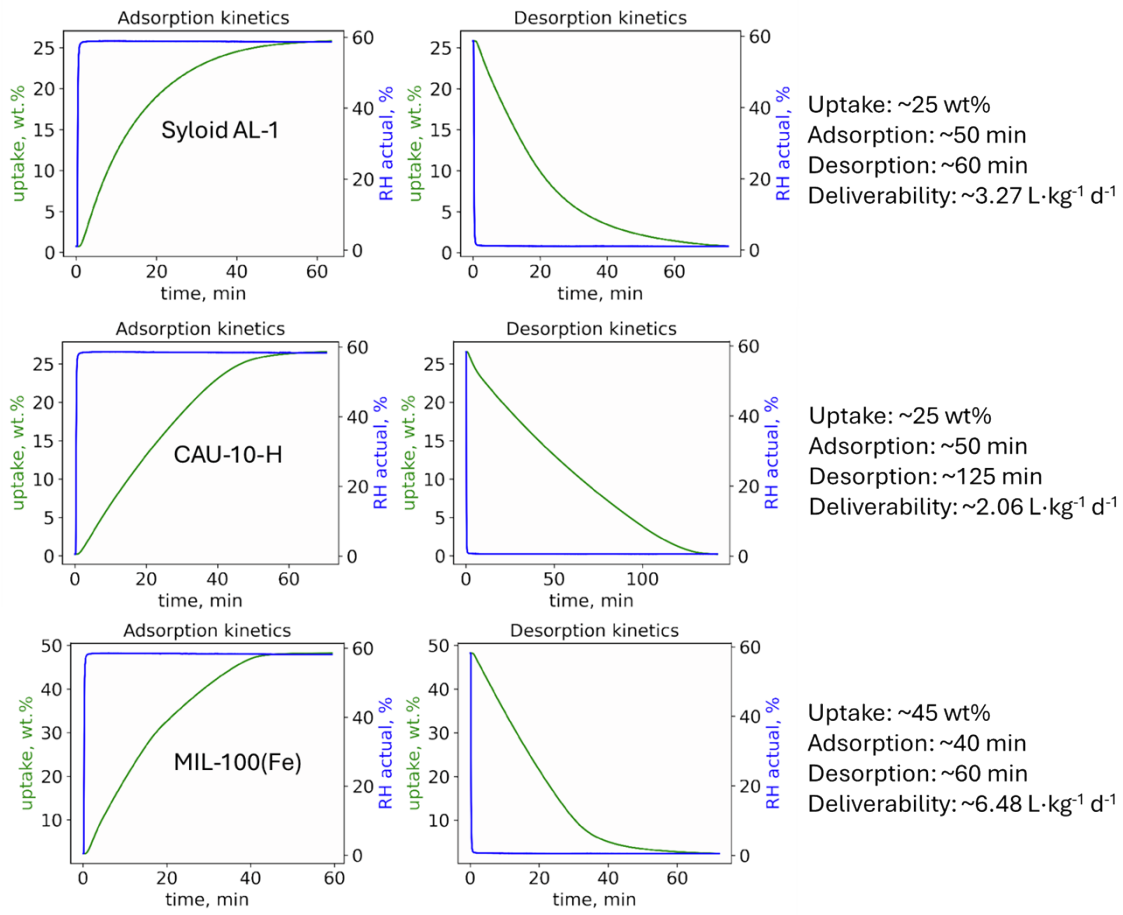

Figure S10. Water vapor sorption kinetics for selected adsorbents between 60-0 % RH at 25/27 °C (ref 34).

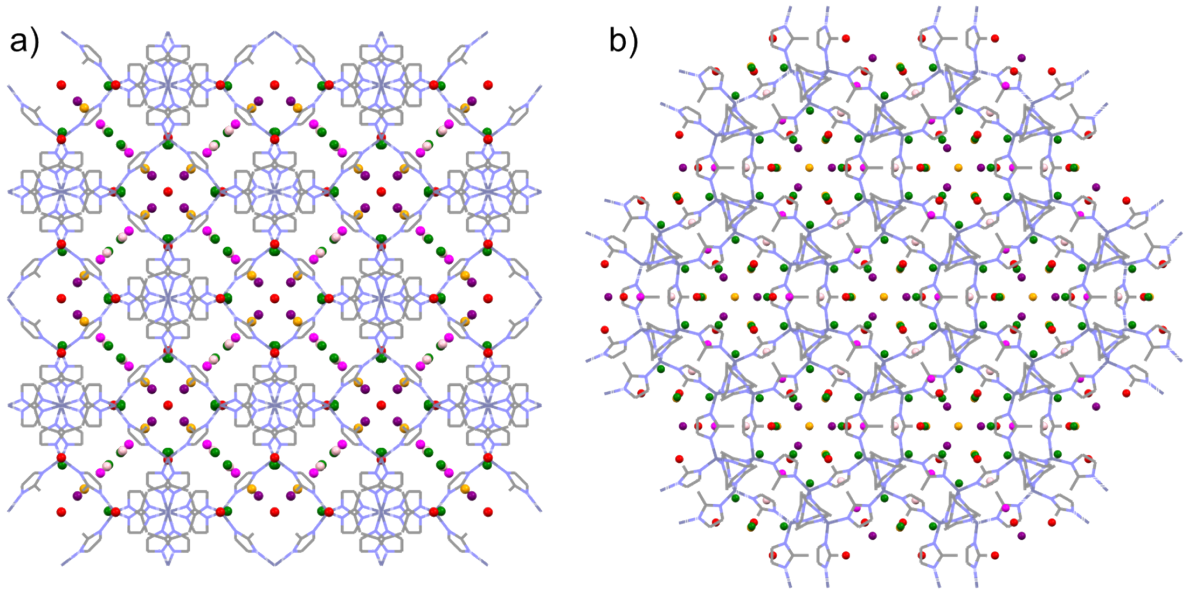

Figure S11. Six independent water locations within the structure of MAF-7 (2 × 2 × 2 cell), viewed along a) the four-member ring window and b) the six-member ring window. H_2O color code and numbers per unit-cell: red (12), green (24), purple (8), orange (8), magenta (8), pink (8).

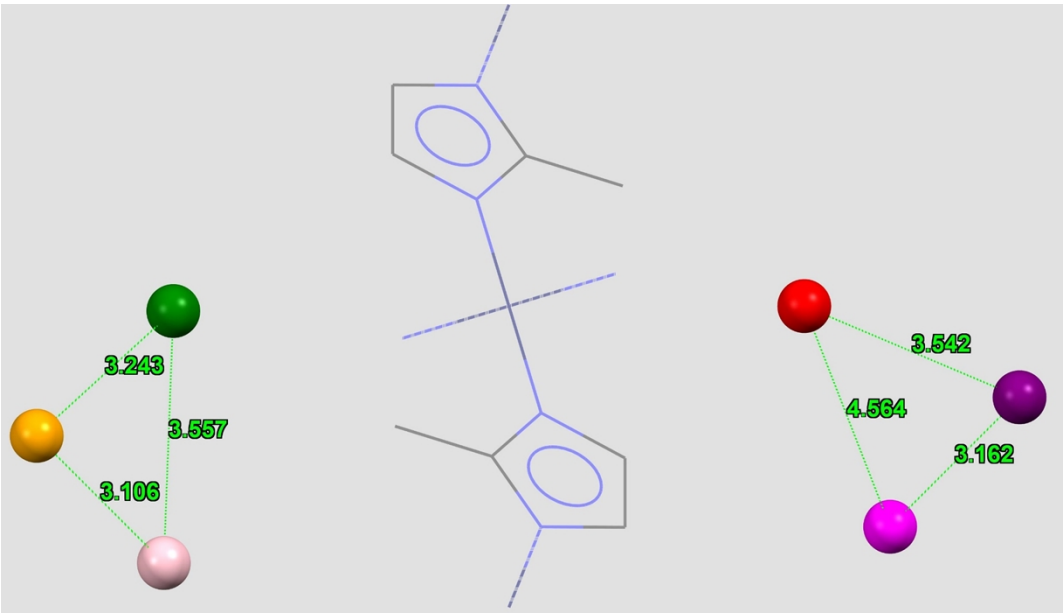

Figure S12. The six independent water molecules form two water clusters in the asymmetric unit with O···O distances of 3.106 - 4.564 Å.