

Supplementary Information for

Impact of molecular clustering inside nanopores on desorption processes

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Experimental Procedures

General Considerations.

All reagents and solvents were purchased from commercial sources and used without further purification. Microwave syntheses were performed in a Biotage Initiator 2.5 microwave with a maximum irradiation power of X W.

Preparation of $\text{Cu}_3(\text{btc})_2$ (HKUST-1). The preparation of ref. 1 was adapted. Copper(II) nitrate trihydrate (41.0 mg, 0.17 mmol) was dissolved in 10 mL of butanol in a 20 mL Pyrex microwave vial. The mixed solution was heated with a heat-gun until a transparent solution was obtained. Benzene-1,3,5-tricarboxylic acid (H_3btc , 20 mg, 0.095 mmol) was added, and the mixture was heated by microwave irradiation at 413 K for 60 min. The resulting blue powder was isolated by centrifugation and washed with ethanol (3×10 mL).

Preparation of $\text{Zn}(\text{MeIm})_2$ (ZIF-8). The preparation of ref. 2 was adapted. Zinc nitrate hexahydrate (mg, mmol), 2-methylimidazole and DMF (20 mL) were charged to a 40 mL Pyrex microwave vial. The reaction mixture was briefly sonicated until complete dissolution of the solids to give a colorless solution. The vial was transferred to the microwave, and heated at 433 K for 20 min. The resulting pale yellow powder was isolated by centrifugation, and washed with DMF (3×5 mL) then methanol (3×5 mL).

QCM substrate preparation. Following solvent exchange, the samples were dried under vacuum for one day and then 5 mg were suspended in 2 mL dry methanol. After dispersing the sample by sonication the crystals were drop-casted to the substrate at 100 °C (by placing the substrate on a heating plate). Afterwards the substrates were thoroughly rinsed with methanol and a flow of compressed air to remove any weakly attached crystals. The deposited amount of PCP crystals was determined by QCM measurement and adjusted to an amount of 3000-7000 ng.

Powder X-ray diffraction. The solids obtained were dried for 1 h at 20 mbar at room temperature before analysis. The diffraction data were collected on a Bruker Model D8 Discover apparatus with GADDS equipped with a sealed tube X-ray generator producing Cu K α radiation ($\lambda = 1.54$ Å).

IR measurements. For infrared absorption spectra the $\text{Cu}_3(\text{btc})_2$ crystals were placed in an environment controlled Zn/Se flow cell, which is connected to the vapor flow cell of the QCM instrument. The flow cell was placed in a JASCO FT-IR 6200 spectrometer equipped with a TGS detector.

Dynamic light scattering (DLS) measurements. Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS from Malvern instruments equipped with a 4 mW He-Ne, 633 nm laser.

Volumetric sorption measurement. The sorption isotherms of $\text{Cu}_3(\text{btc})_2$ for methanol vapor at 298 K was recorded on a BELSORPmax volumetric-adsorption instrument from BEL Japan, Inc. The

measurement was performed after pretreatment at 403 K under vacuum condition for 12 hours.

QCM measurements. The sorption properties of heterogeneous PCP materials for volatile organic compounds (VOCs) were investigated by an environment-controlled BEL JAPAN QCM system. Prior to the measurement, the QCM sensors were activated in methanol at 40 °C for 3 h. During the additional pretreatment the QCM sensors were placed for 2h in He stream inside the QCM chamber. The He carrier gas flow was controlled by mass flow controllers with a total mass flow of 100 cm³ min⁻¹. The mass of deposited PCP material was estimated by the comparison of the fundamental frequency with the current frequency.

Quantitative mass change on quartz oscillator (Δm) was converted from frequency change (Δf) according to the Soubrey equation, which shown in equation 1,

$$\Delta f = (-2f_0^2 / A\sqrt{\mu\rho}) \times \Delta m \quad (1)$$

where f_0 is fundamental frequency of the oscillator, A is the surface area in cm², μ is shear modulus of quartz (2.95×10^{11} g cm⁻¹ s⁻²) and ρ is density of quartz (2.65 g cm⁻³).

According to the eq 1, sensitivity of the QCM substrate was calculated as 5.4 ng.Hz⁻¹.cm².

Relative vapor pressure in helium was controlled by three independent mass flow controllers (MFC) in the range of 0.0 – 85.0 %; A vapor saturated carrier gas was generated by passing through the solvent (301 K) and cooling to 298 K. The vapor saturated gas was then mixed with the dry helium in certain amount to obtain desired relative pressure. The frequency change-time dependency was monitored with continuously flowing of the analyte vapor. Mass uptake, M_t / M_e , is given by,

$$M_t / M_e = (f_i - f) / (f_e - f) \quad (2)$$

where M_t is the mass uptake at time t , M_e is the mass uptake at equilibrium, f_i is frequency of the oscillator at a time t , f is frequency of the oscillator at a $t = 0$ ($P/P_0 = 0$) and f_e is frequency of the oscillator at equilibrium.

Field-emission scanning electron microscopy. The PCP crystals were coated with osmium prior to measurement. The images were obtained from a JEOL Model JSM-7001FA SEM system operating at 2.0 to 15.0 kV.

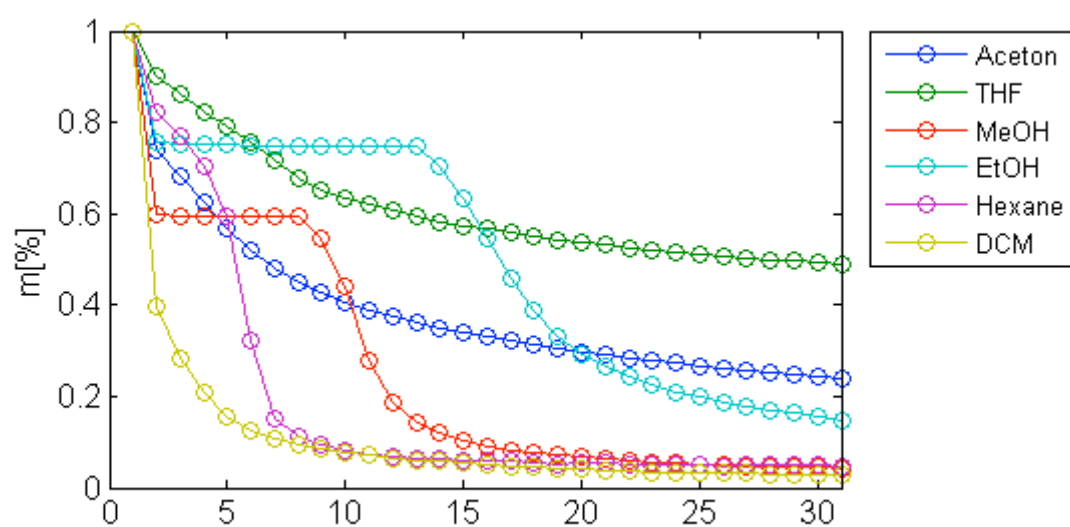


Figure S1. Desorption kinetics of acetone, tetrahydrofuran (THF), methanol, ethanol, hexane, dichloromethane.

Mathematical model. Our observations on the time-dependence of desorption rate and the IR spectrum of the methanol filled $\text{Cu}_3(\text{btc})_2$ indicate that the guest molecules can strongly interact with each other. In order to test the hypothesis that the metastable state results from strong guest-guest interactions, we considered a desorption model where the transport diffusion coefficient is a function of the local concentration of the guest molecules inside the material. We suppose that each $\text{Cu}_3(\text{btc})_2$ crystal is a one-dimensional element of unit length, which is initially uniformly filled with guest molecules. Each element has absorbing boundaries such that guest molecules that reach any of the two boundaries escape. As a PCP/QCM substrate contains a large number of PCP crystals, we suppose that the dynamics of desorption in the whole system can be represented by the dynamics of a single element (as fluctuations will be averaged out due to the large number of elements). It is well known that the concentration of guest molecules (or any fluid for the sake of argument) that are diffusing inside a one-dimensional space with absorbing boundaries, denoted by $c(\mathbf{x}, t)$, obeys the diffusion equation³

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D(c) \frac{\partial c}{\partial x} \right], \quad (1)$$

on the interval $\mathbf{x} \in (0, 1)$ (i.e. the volume of the host material is normalized to 1), where $D(c)$ is the concentration dependent transport diffusion coefficient, and the initial and boundary conditions are given by

$$\begin{aligned} c(\mathbf{x}, 0) &= 1, \\ c(0, t) &= c(1, t) = 0. \end{aligned} \quad (2)$$

As described in the main text, our results show that the rate of desorption strongly depends on the concentration of guest molecules, and gets very close to zero for molecules that are capable of forming hydrogen bonds. Therefore, we consider a concentration dependent diffusion coefficient that has a dip in the vicinity of a critical concentration c^* , and is given by the formula

$$D(c) = 1 - \left(1 + \frac{a}{\sqrt{2\pi b^2}} \right) e^{-(c-c^*)^2/2b^2} \quad (3)$$

Where a and b are parameters that determine how strongly intermolecular interactions affect the diffusion coefficient, and how quickly the diffusion coefficient changes in the vicinity of c^* , respectively. $D(c)$ is plotted in the inset of Figure 4 of the main manuscript with $c^* = 0.5$, $b = 0.1$

and $a = \{0, -0.025, -0.05, -0.075, -0.125\}$ such that the minimum value of $D(c)$ is approximately $\{0, 0.1, 0.2, 0.3, 0.5\}$, respectively. In this simple model, we envisage a coarse grained picture of the material without explicitly accounting for its inner structure. Therefore, our approach supposes that the prominent features of desorption kinetics can be described by a concentration dependent diffusion coefficient, although other properties of the material must have an effect on the kinetics as well. Note that Equation (3) is certainly not the only way of choosing the concentration dependent diffusion coefficient. We considered the form given in Equation (3) as it provides an appropriate mathematical description of our arguments above and is simple enough to be used in the numerical calculations.

In order to obtain the plotted curves in Figure 4 of the main text, we solved Equation (1) using a numerical algorithm based on the Euler's method, which is one of the standard ways of solving the diffusion equation.³

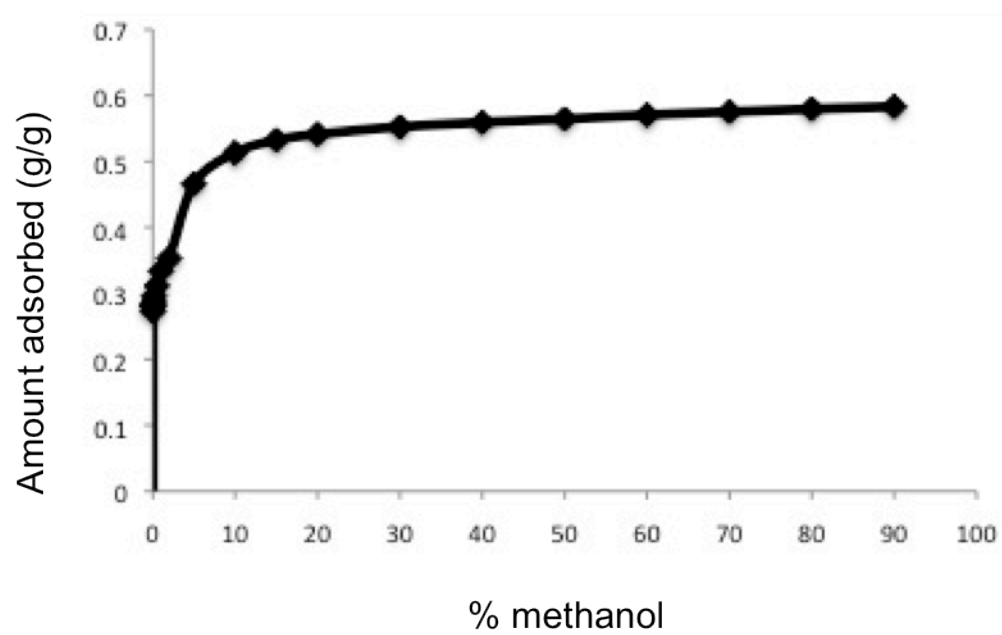


Figure S2. Methanol sorption isotherm measured by QCM

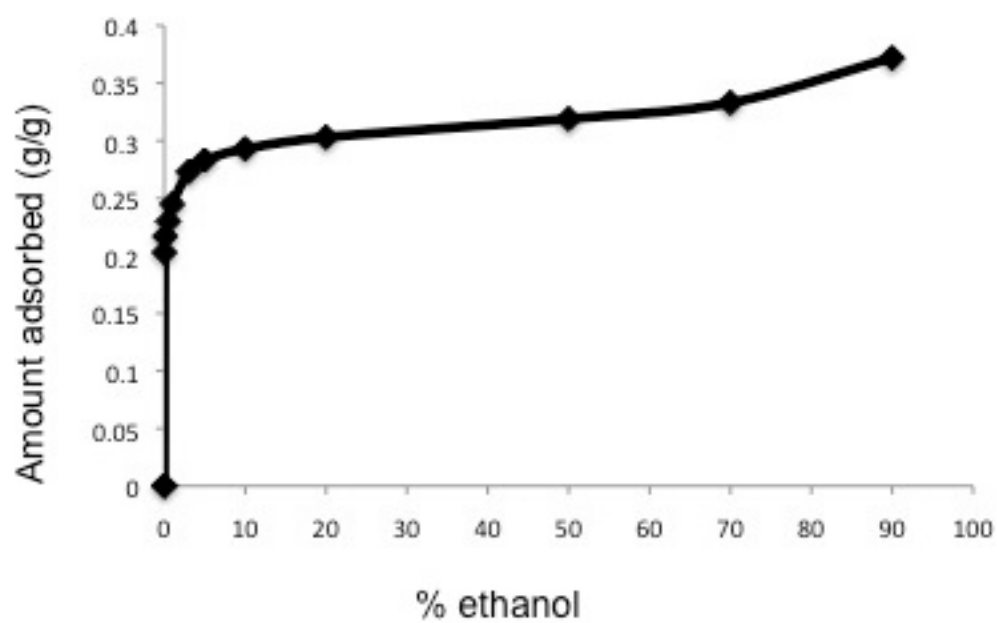


Figure S3. Ethanol sorption isotherm measured by QCM

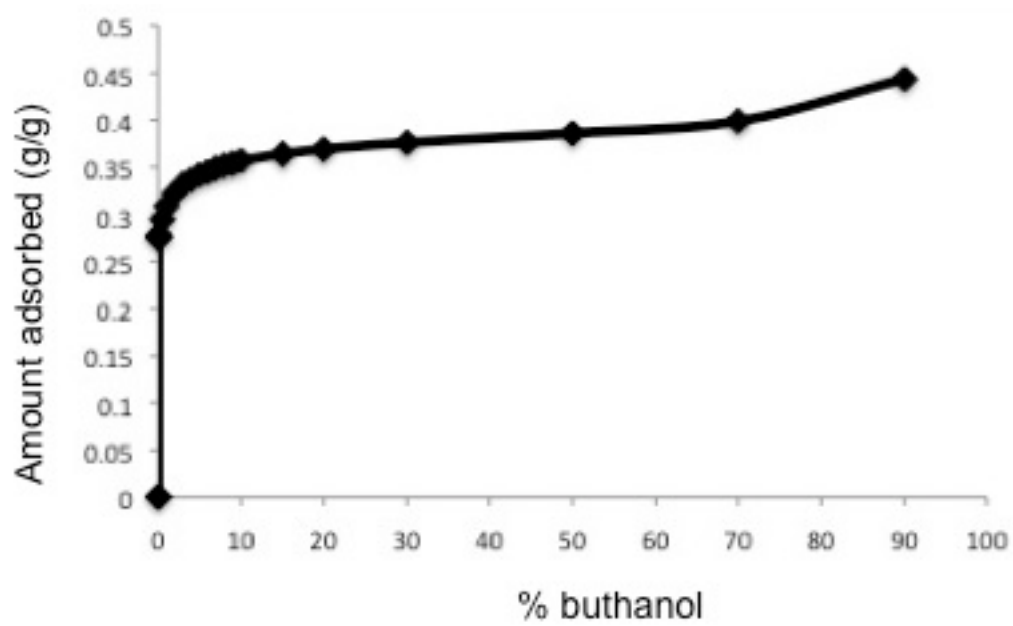


Figure S4. Butanol sorption isotherm measured by QCM.

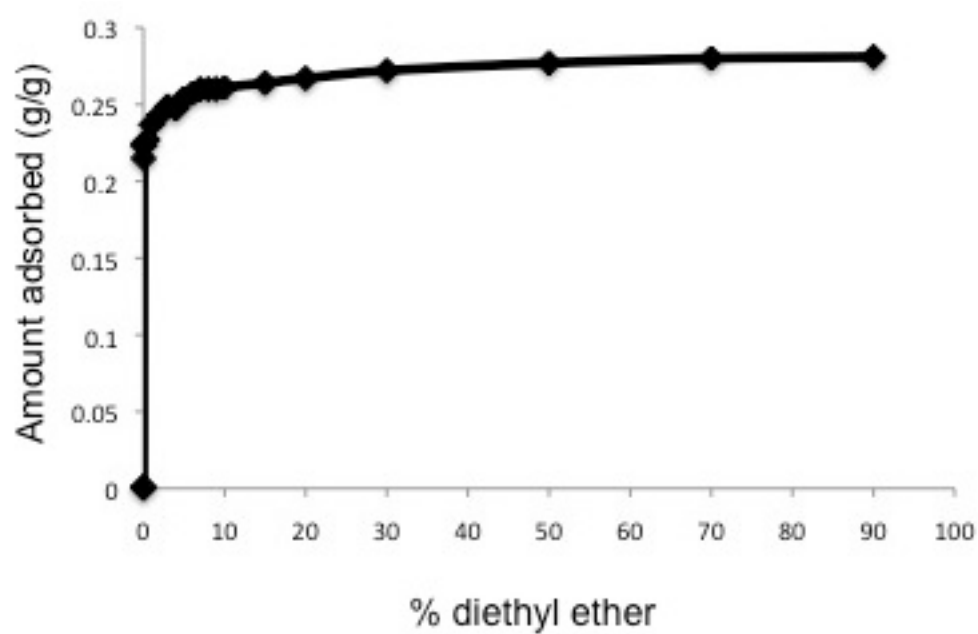


Figure S5. Diethyl ether sorption isotherm measured by QCM.

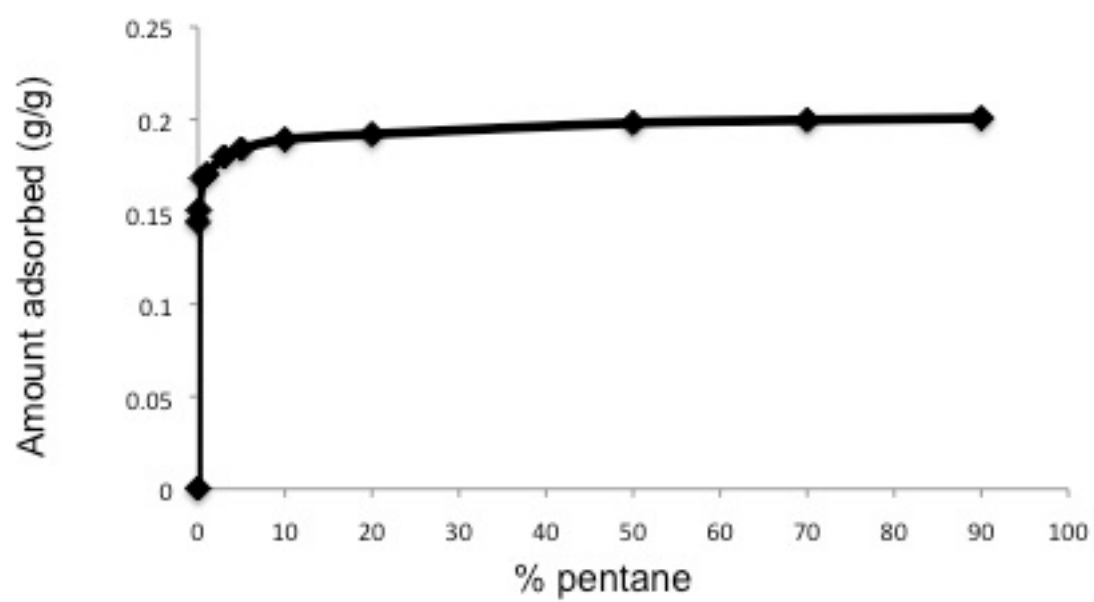


Figure S6. Pentane sorption isotherm measured by QCM

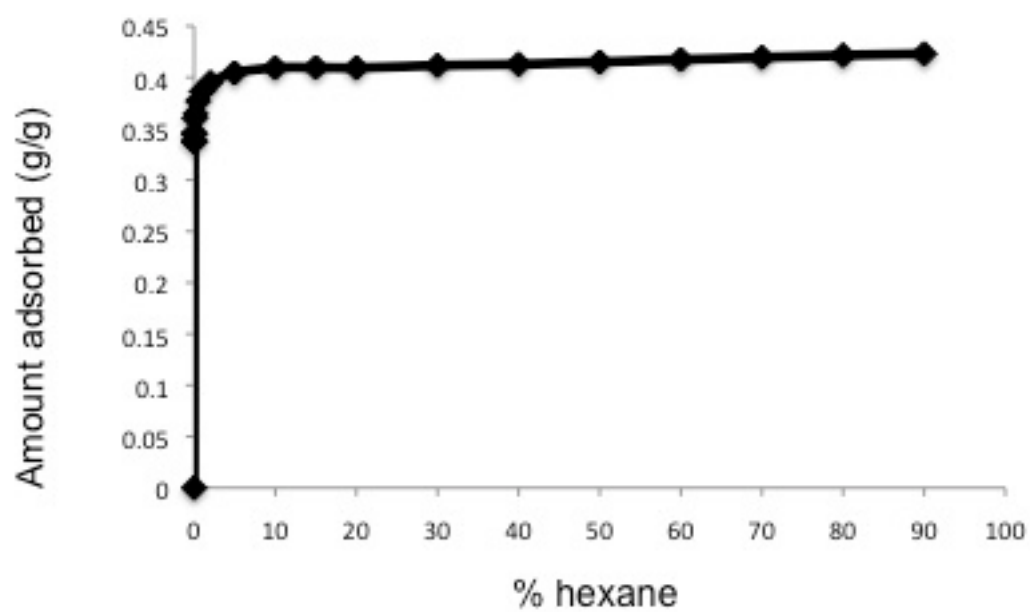


Figure S7. Hexane sorption isotherm measured by QCM.

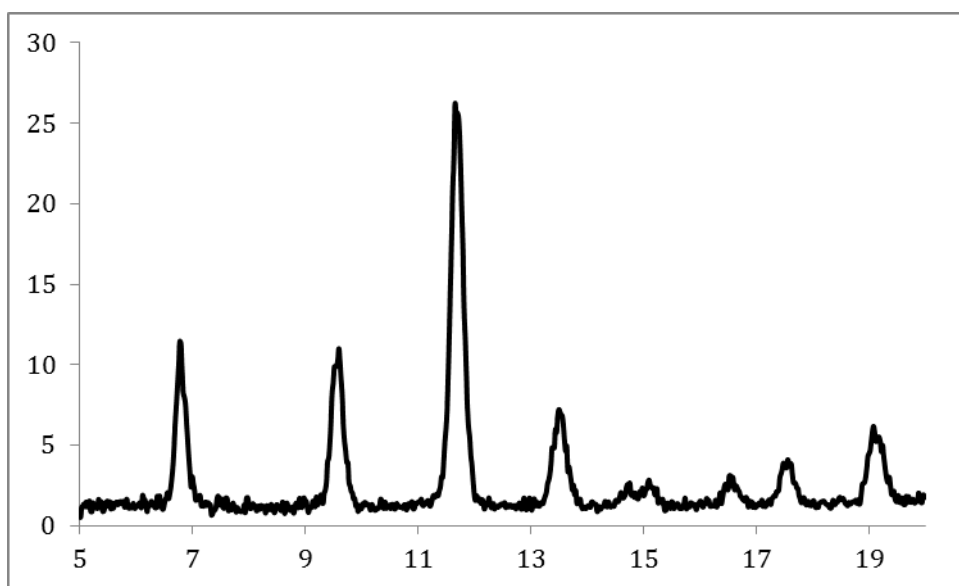


Figure S8. PXRD pattern of the $\text{Cu}_3(\text{btc})_2$ sample

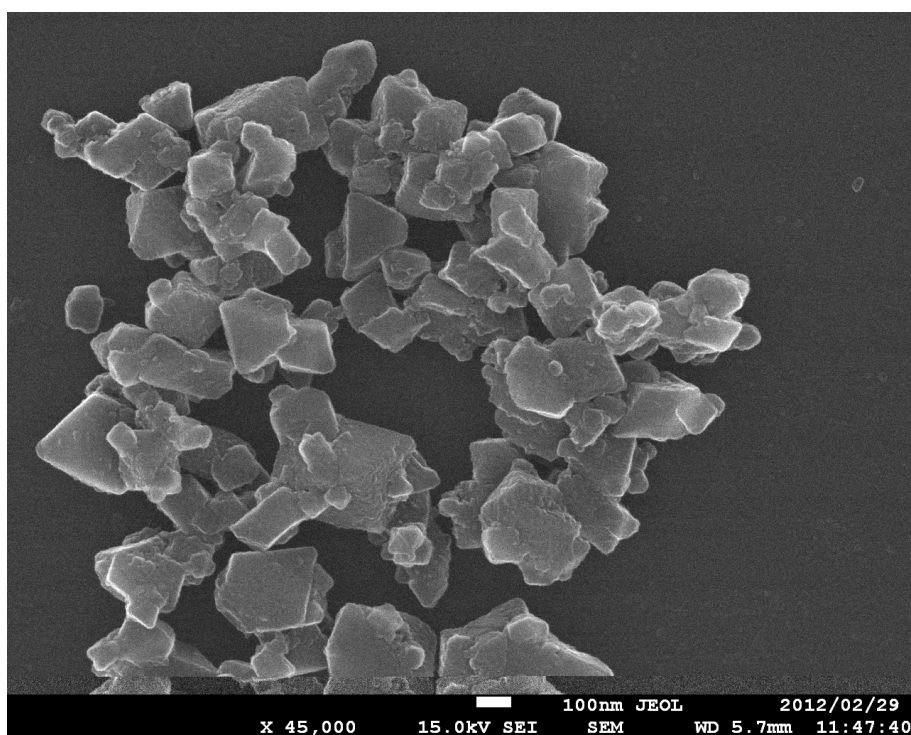


Figure S9. Scanning electron microscopy image of the $\text{Cu}_3(\text{btc})_2$ sample.

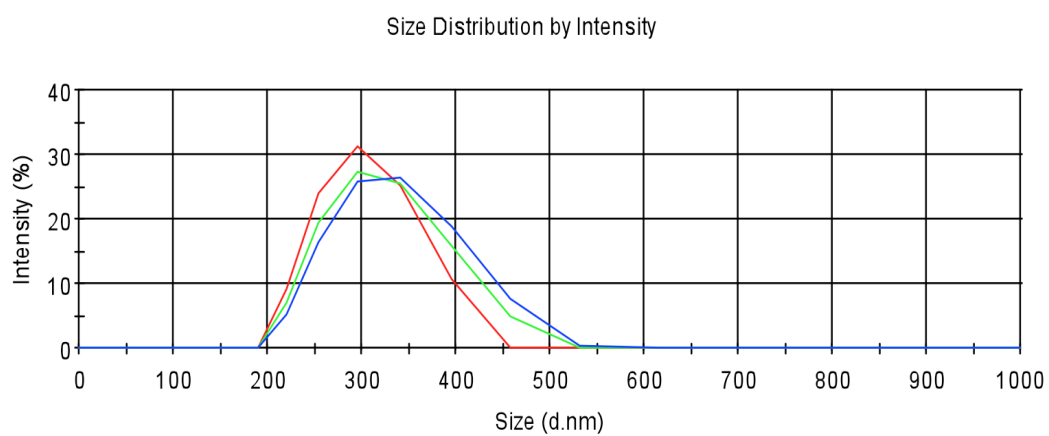


Figure S10. Dynamic light scattering (DLS) measurement of the $\text{Cu}_3(\text{btc})_2$ sample. The sample was sonicated in dry methanol before the measurements. The sample was measured three times (corresponding to the red, green and blue graphs).

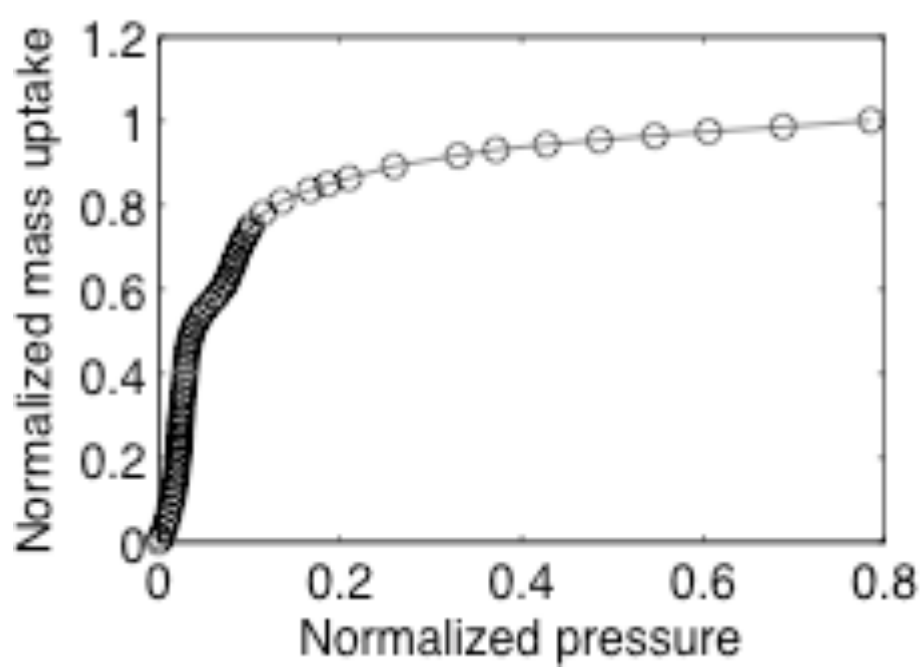


Figure S11. Volumetric sorption experiment of the $\text{Cu}_3(\text{btc})_2$ sample for methanol vapor.

Desorption kinetics of methanol from Zn(MeIm)₂ (ZIF-8)

ZIF-8 has been studied as an additional compound for comparison with the data collected for Cu₃(btc)₂. In contrast to Cu₃(btc)₂, ZIF-8 features a single type of pore that is hydrophobic owing to the organic units forming the bulk of the solvent-accessible pore surface. The desorption trace of methanol as measured starting with a relative methanol vapor pressure of 40% is shown in Fig. S12. Here, the desorption occurs very rapidly once the guest molecules begin to be released, which is indicative of the low affinity of methanol toward the hydrophobic pores. This provides further support the observations of the Cu₃(btc)₂ work, since the hydrophobic nature of the pores of ZIF-8 (in a manner similar to the small hydrophobic pores in Cu₃(btc)₂) do not facilitate a stable environment for the hydrogen-bonded methanol clusters to remain adsorbed. This result further underscores the importance of the chemical nature of the pore surface in determining whether or not the desorption process proceeds through a metastable state.

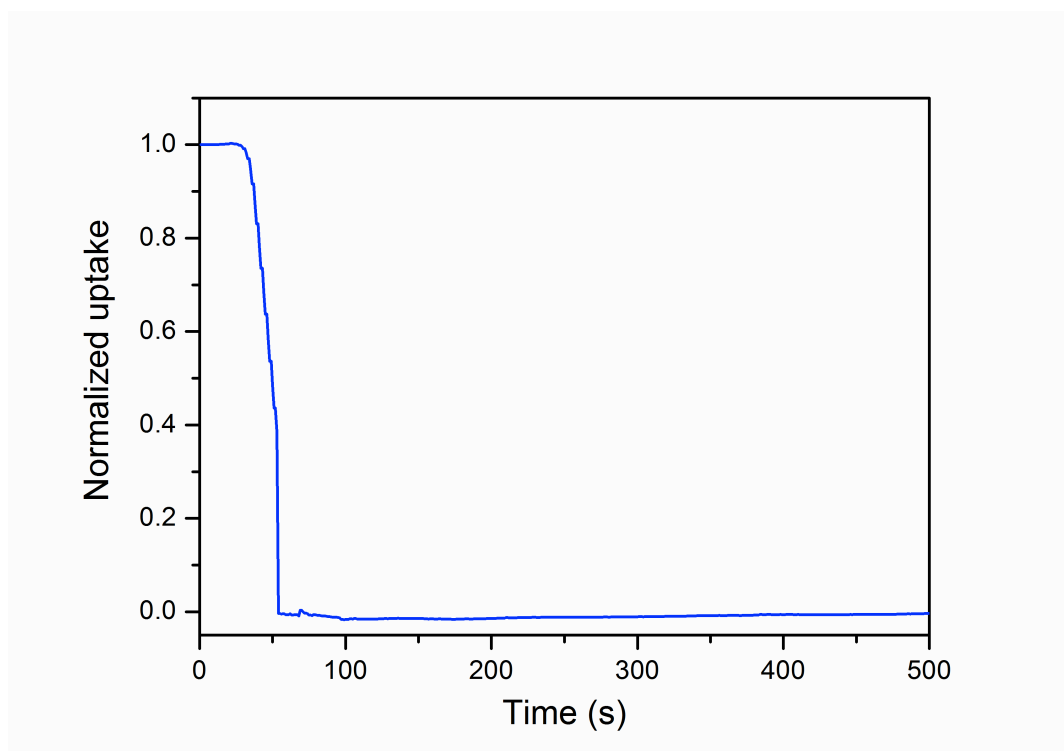


Figure S12. Desorption kinetics of methanol from the pores of ZIF-8 collected using a relative methanol vapor pressure of 40%. The uptake at this pressure of methanol was 0.20 g/g.

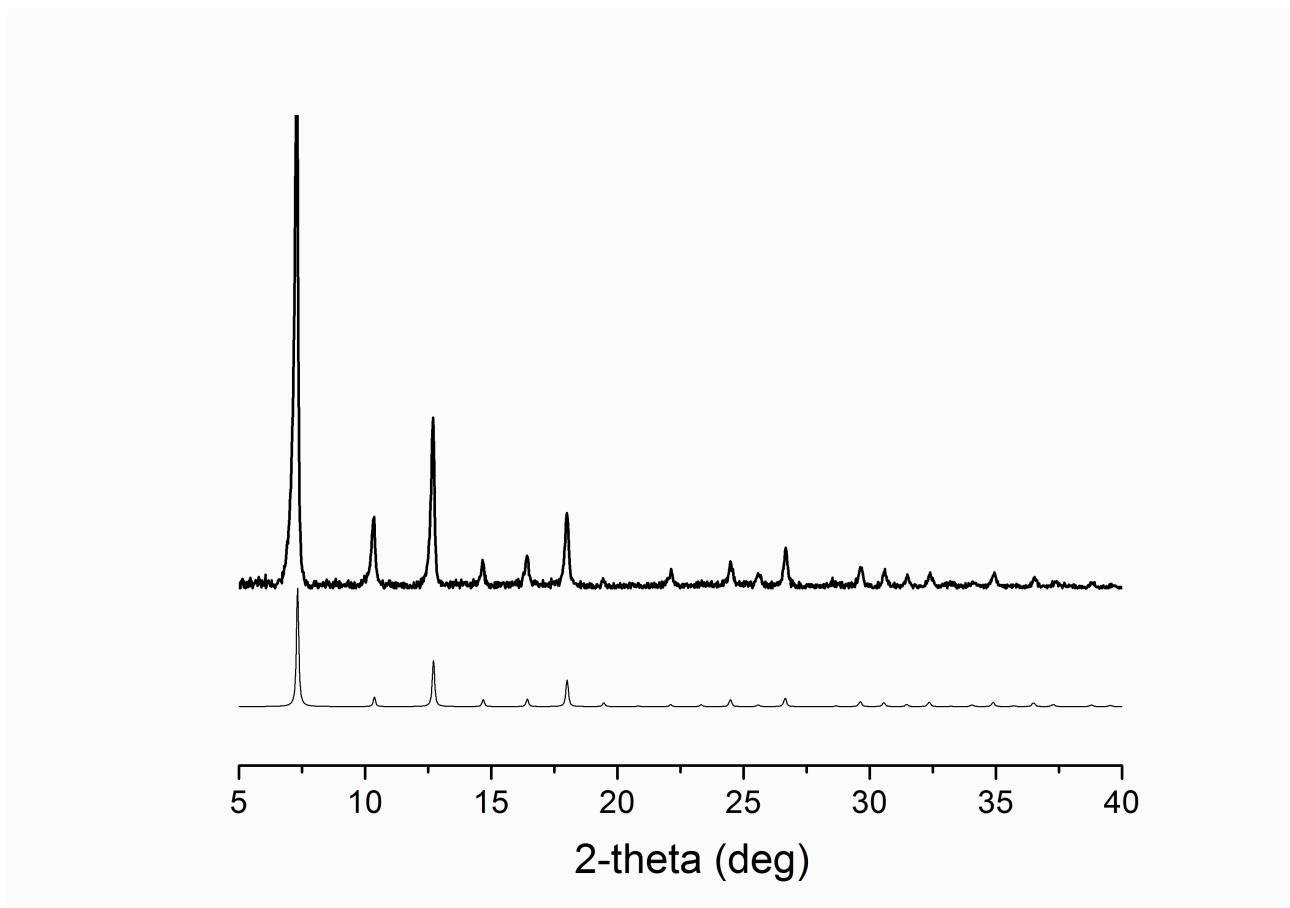


Figure S13. PXRD patterns for the ZIF-8 sample employed in the QCM measurement (upper) and simulated from the single-crystal X-ray structure (lower).

References

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- [3] J. Crank, 1980. *The Mathematics of Diffusion*. 2nd ed. Oxford University Press, USA