Supporting Information

Accessing accelerated molecular diffusion by nanopore alignment in MOF thin film

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General Information

Material

$Zn(NO_3)_2 \cdot 6H_2O$ (99.0 %) and 2-methylimidazole (2-mIm, 99.0 %) were purchased from Sigma-Aldrich (ACS grade). Anhydrous methanol, 1-propanol, 2-propanol were also purchased from sigma Aldrich. All chemicals were used as received without further purification. QCM Sensors (both 5MHz and 10MHz) were purchased from Open qcm.

Surface functionalization

10 MHz (SiO_2 coated) QCM-sensors and SiO_2/Si substrates were functionalized with $–NH_2$ end groups. Substrates were cleaned by isopropanol and then by UV-ozone cleaner, to remove organic impurities and to create free –OH groups on the surface. These treated substrates were dipped in a 20μM solution of APTES (3-aminopropyltriethoxysilane) in anhydrous toluene at 60° C for 2 h. Substrates were then thoroughly washed with absolute ethanol (99.99%), dried and then used for thin films synthesis.

To make –OH functionalized surface, 100 nm Au coated Si-substrate and 5 MHz (Au coated) QCM-sensors were dipped in an ethanolic solution (20 mM) of 11-mercapto-1-undecanol (MUD) for 24 h. Substrates were then thoroughly washed with absolute ethanol (99.99%), dried and then used for thin films synthesis.

Characterization

Powder X-ray diffraction (XRD) patterns of thin film and powder samples were recorded with a Rigaku XDS 2000 diffractometer using nickel-filtered Cu Kα radiation (λ= 1.5418 Å) in θ-

2θ geometry (step size – 0.001). The gravimetric adsorption profiles were measured using a quartz crystal microbalance (QCM) from Open qcm. To record vibrational Raman spectra Renishaw inVia Raman microscope (532 nm excitation) was used. The surface morphology and composition of the samples were characterized using field emission scanning electron microscopy (FESEM), JEOL JSM-7200F along with Energy-Dispersive X-ray spectroscopy (EDS).

QCM measurement

The samples were activated preceding the measurements by heating the QCM sensors at 65 °C for 12 h under vacuum (10^{-4} bar). QCM experiments were done using a flow controlling system having a mass flow controller with a flow rate of 50 sccm with a continuous dry nitrogen flow.

Procedure for the synthesis of ZIF-8 thin films

SiO_2 (10 MHz) and gold (5 MHz) coated QCM sensors were used as substrates for growing two different type of ZIF-8 thin films i.e ZIF-$8_{oriented}$ and ZIF-$8_{mixed\text{-}oriented}$. Before the use, the substrates were cleaned by isopropanol (sonication for 30 min), afterwards respective surface functionalisation has been done. Following an earlier developed method with slight modification,[1] the functionalized substrates were immersed in a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (25 mM) and of 2-methylimidazole (2-mIm) (50 mM) methanol solution for 30 and 45 min, for ZIF-$8_{oriented}$ and ZIF-$8_{mixed\text{-}oriented}$, respectively. By repeating the cycles, thicker ZIF-8 films were obtained.

Thickness calculation of the ZIF-8 thin film

$$d\ (g/cc) = \frac{Mass\ of\ the\ deposited\ MOF\ on\ qcm\ sensor\ (ug/cm2)}{l \times \pi r^2}$$

Where d is the density of ZIF-8 (0.95 g/cc), l is the thickness of the film and *r* is the radius of the QCM-chip (*r* = 7mm).

Analyses of Uptake Kinetics

Mass-frequency relationship at the QCM surface is given by Sauerbrey equation

$$\Delta m = -c\frac{\Delta f}{n}$$

Where n denotes the overtone order (n = 3, 5, and 7) and c is the mass sensitivity constant. For a 5 MHz crystal, c has value of 17.7ng.cm^{-2} and for a 10MHz its value is 4.4ng.cm^{-2}

We assume one dimensional diffusion in the direction perpendicular to the vapor/MOF film interface. We examine the data with the assumption of Fickian diffusion, that is, we assume a constant diffusivity, D, is independent of the vapour concentration.

$$\frac{M_f(t)}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-\frac{4D\pi^2 t(2m+1)^2}{L^2}\right)$$

Where M_f (t) is the uptake (µg) at time t, M_∞ is the uptake (µg) at infinite time (i.e., at equilibrium), D has units of m^2 /s, and L is the film thickness.

Diffusivity, D, can be obtained by fitting the mass uptake vs. the square root of adsorption time using this equation:

$$\frac{M_t(t)}{M_\infty} \approx \frac{8}{\sqrt{\pi}}\sqrt{\frac{Dt}{L^2}}$$

Characterization of the ZIF-8 thin films

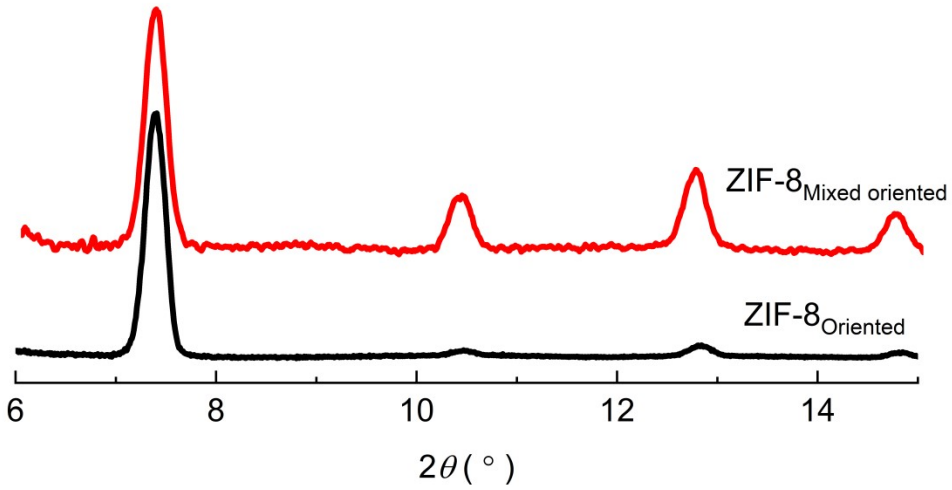

Fig. S1 Out-of-plane XRD patterns of the ZIF-$8_{oriented}$ and ZIF-$8_{mixed\text{-}oriented}$ films on the QCM substrates.

The degree of orientation is characterised using crystallographic preferred orientation (CPO) using the following equation[2]:

$$CPO\frac{X}{Y} = \frac{\frac{I_M^{(X)}}{I_M^{(Y)}} - \frac{I_P^{(X)}}{I_P^{(Y)}}}{\frac{I_P^{(X)}}{I_P^{(Y)}}}$$

Here, *I* stands for the intensity of a reflection X or Y and M and P belong to the ZIF-8 thin film (M) and the polycrystalline powder (P)

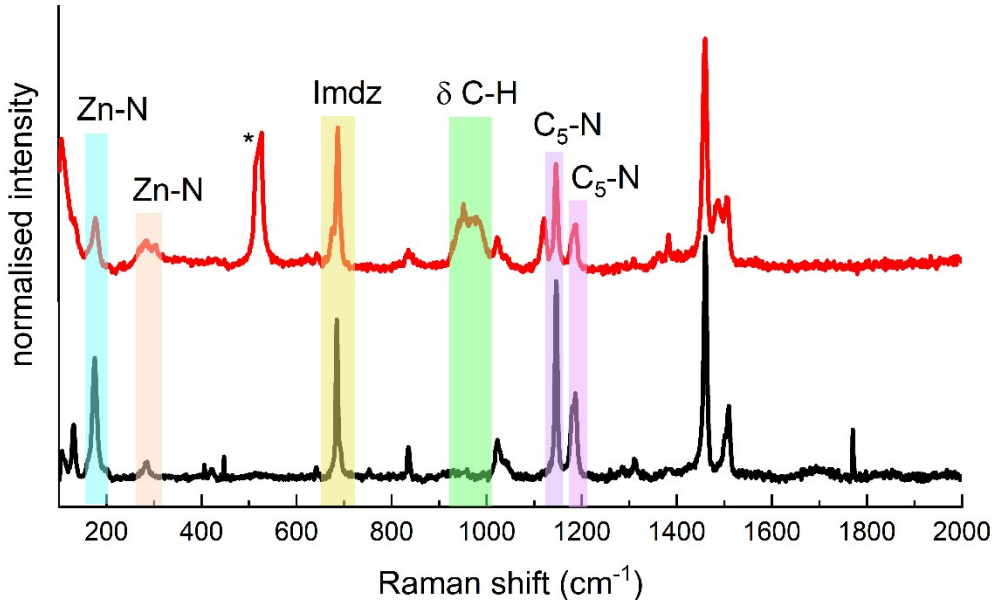

Fig. S2 Showing Raman spectra of the ZIF-$8_{oriented}$ thin film and the bulk powder.[3] (* indicates peak for Si-O of silicon wafer)

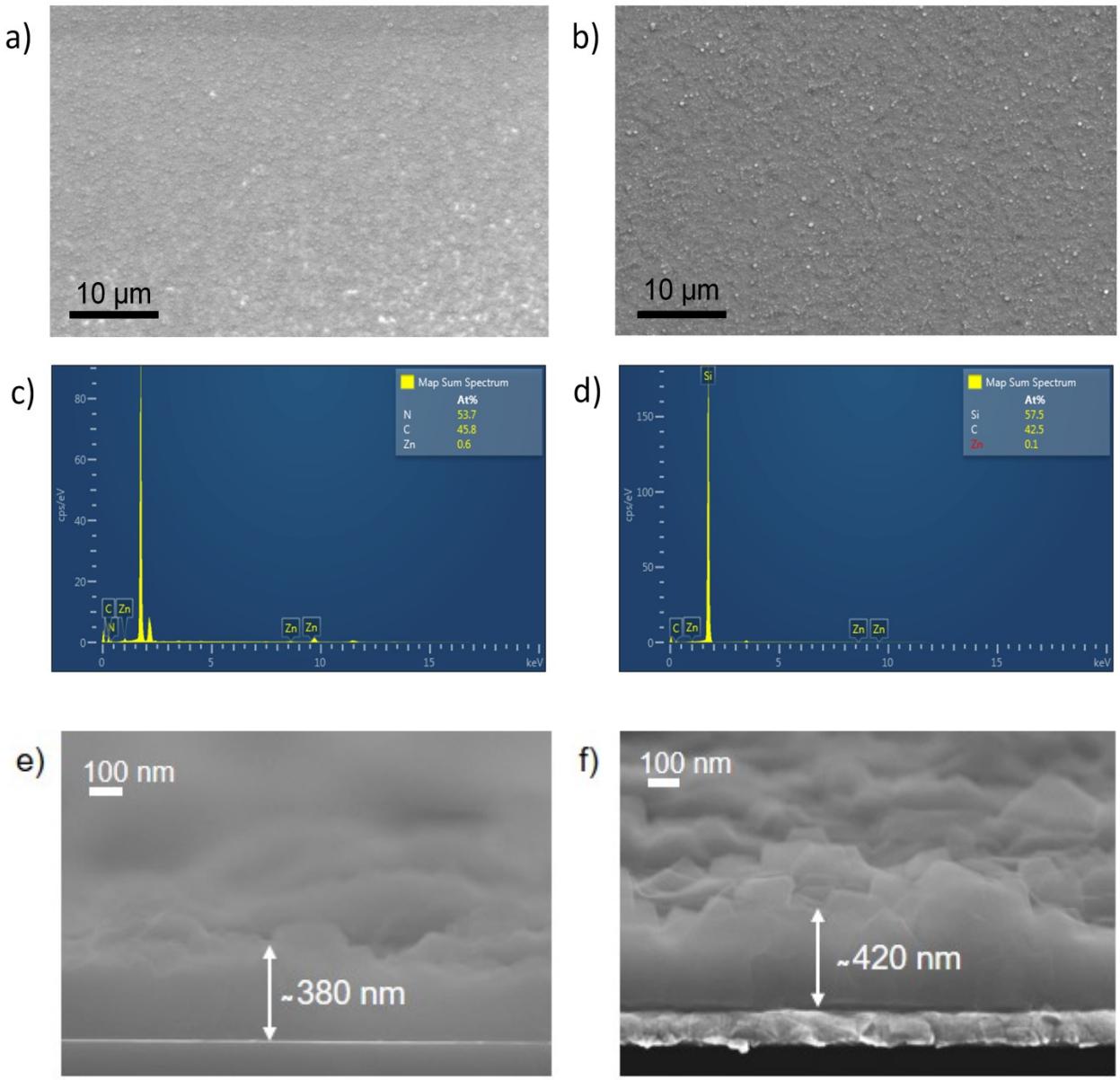

Fig. S3 SEM images and Elemental analyses (a), (c) and (e) for ZIF-$8_{oriented}$ and (b), (d) and (f) for ZIF-$8_{mixed\text{-}oriented}$.

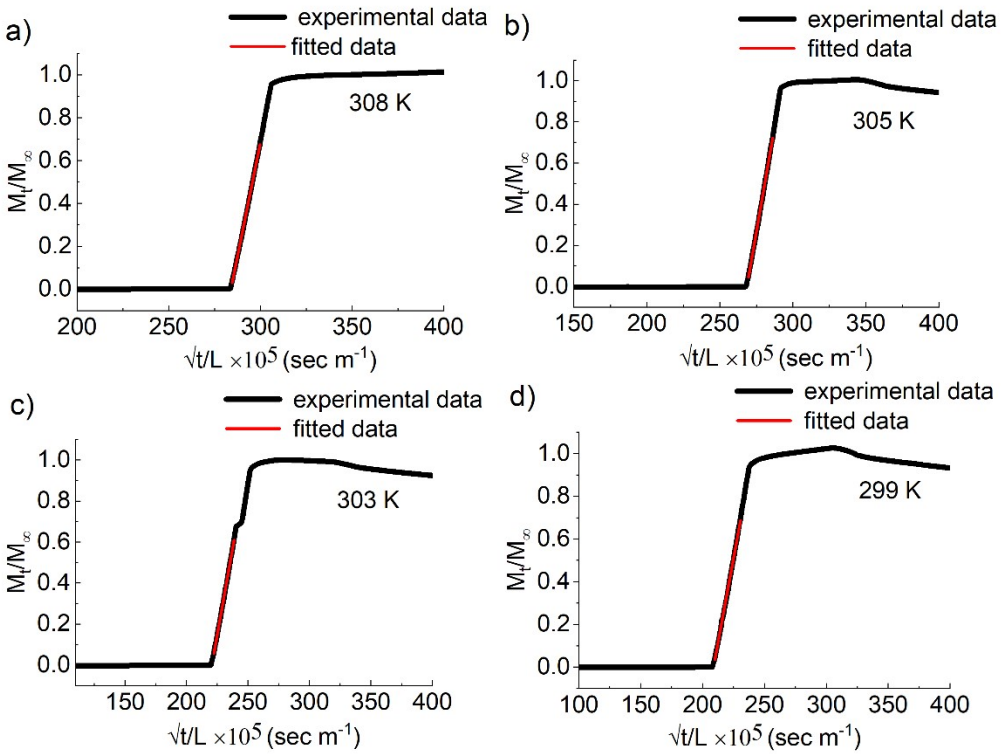

Fig.S4 Methanol uptake profiles at different temperature for ZIF-$8_{oriented}$.

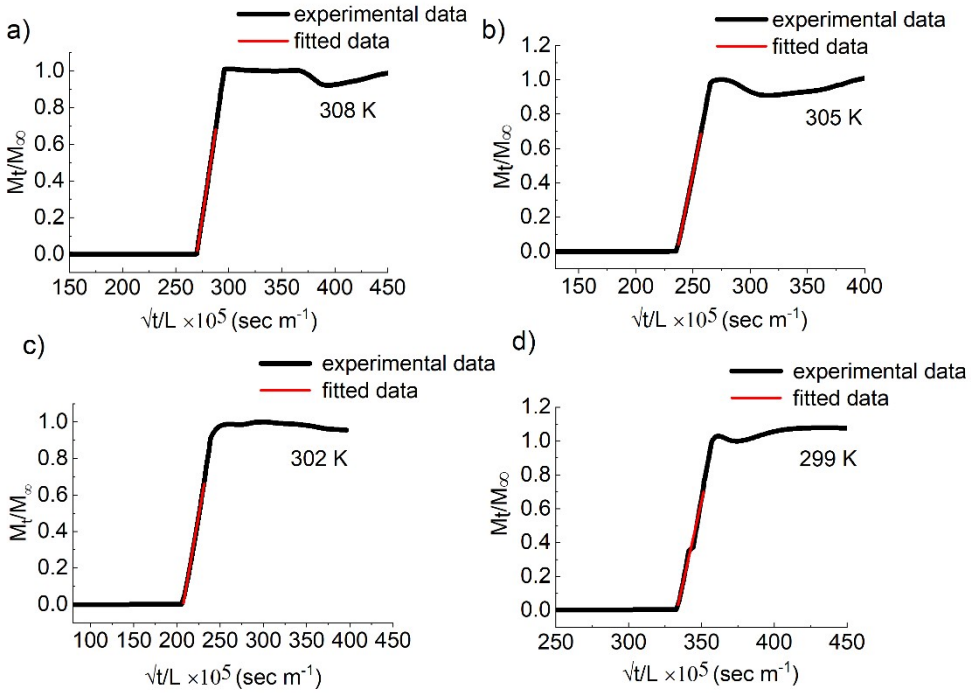

Fig. S5 Methanol uptake profiles at different temperature for ZIF-$8_{\text{mixed-oriented}}$.

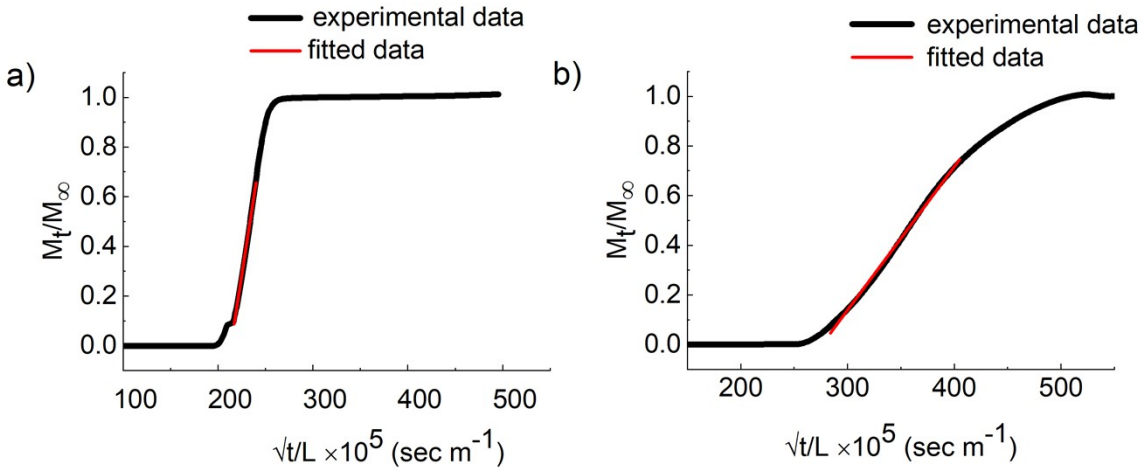

Fig. S6 Mass uptake profiles for (a) 1-propanol and (b) 2-propanol for ZIF-$8_{Oriented}$.

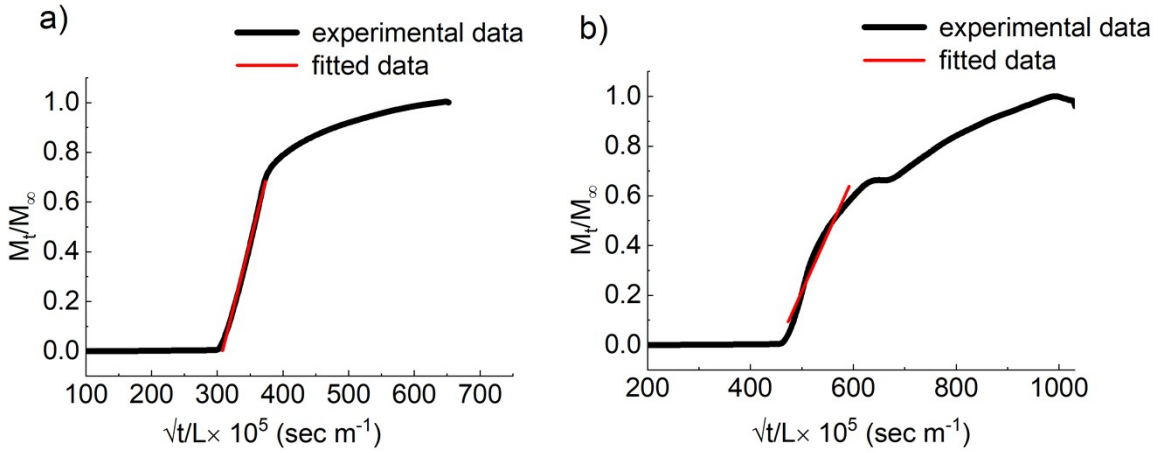

Fig. S7 Mass uptake profiles for (a) 1-propanol and (b) 2-propanol for ZIF-$8_{Mixed\text{-}Oriented}$.

References

1. G. Lu and J. T. Hupp, *Journal of the American Chemical Society*, 2010, **132**, 7832-7833.
2. S. Friebe, B. Geppert, F. Steinbach and J. Caro, *ACS Applied Materials & Interfaces*, 2017, **9**, 12878-12885.
3. K. I. Hadjiivanov, D. A. Panayotov, M. Y. Mihaylov, E. Z. Ivanova, K. K. Chakarova, S. M. Andonova and N. L. Drenchev, *Chemical Reviews*, 2021, **121**, 1286-1424.