**Supporting Information**

for:

Solid-state NMR insights into alcohol adsorption by metal-organic frameworks: adsorption state, selectivity, and adsorption-induced phase transitions

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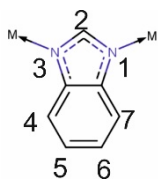
1. Synthesis and characterization

1.1 Synthesis of ZIF-8
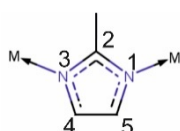
The synthesis protocol of ZIF-8 reported in the literature[1] was adapted and modified. For the synthesis of pure ZIF-8, $Zn(NO_3)\cdot 6H_2O$ (1.0 g, 3.36 mmol) and 2-methylimidazole (MIm, 6.9 g, 85 mmol) were separately dissolved in 20 ml of p.a. methanol each. Both solutions were mixed under vigorous stirring at room temperature before staying overnight without further agitation. The ZIF-8 was formed as a white precipitate, which was collected via centrifugation and washed thrice with 20 ml of MeOH. Finally, the product was dried and activated under dynamic vacuum at 150 °C overnight resulting in 300 mg of white crystalline powder (yield based on Zn = 39%). The Zn/MIm/MeOH molar ratio of the reaction mixture is 1 : 25 : 300.

1.2 Synthesis of ZIF-11

The synthesis protocol of ZIF-11 reported in the literature[2] was adopted and modified. For the synthesis of pure ZIF-11, $Zn(OAc)\cdot 2H_2O$ (1.0 g, 4.56 mmol) was dissolved in a mixture of 28 ml MeOH and 50 ml toluene. Separately, benzimidazole (BIm, 1.1 g, 9.11 mmol) was dissolved in a mixture of 28 ml MeOH and 3.3 ml 13.80 M aqueous ammonia solution. Both solutions were mixed under vigorous stirring at room temperature before staying overnight without further agitation. The work-up procedure was analogous to the ZIF-8 synthesis, except for a lower activation temperature of 100 °C. The white crystalline product amounted to 1.25 g (yield based on Zn = 90%). The molar composition of the $Zn/BIm/NH_3/MeOH/toluene$ reaction mixture was 1 : 2 : 10 : 300 : 100.

1.3 Characterization of the MOF samples

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a STOE STADI P diffractometer with Cu-K$_{\alpha1}$ radiation (λ = 1.5405 Å) and a 2D detector (Mythen, Dectris) in transmission geometry. Scanning electron microscopy (SEM) measurements were carried out on a SU8020 from Hitachi using 2 kV acceleration voltage and a working distance of 8 mm. Prior the measurements the samples were sputtered with Au to increase the conductivity. Nitrogen adsorption isotherms were measured on Quadrasorb SI.
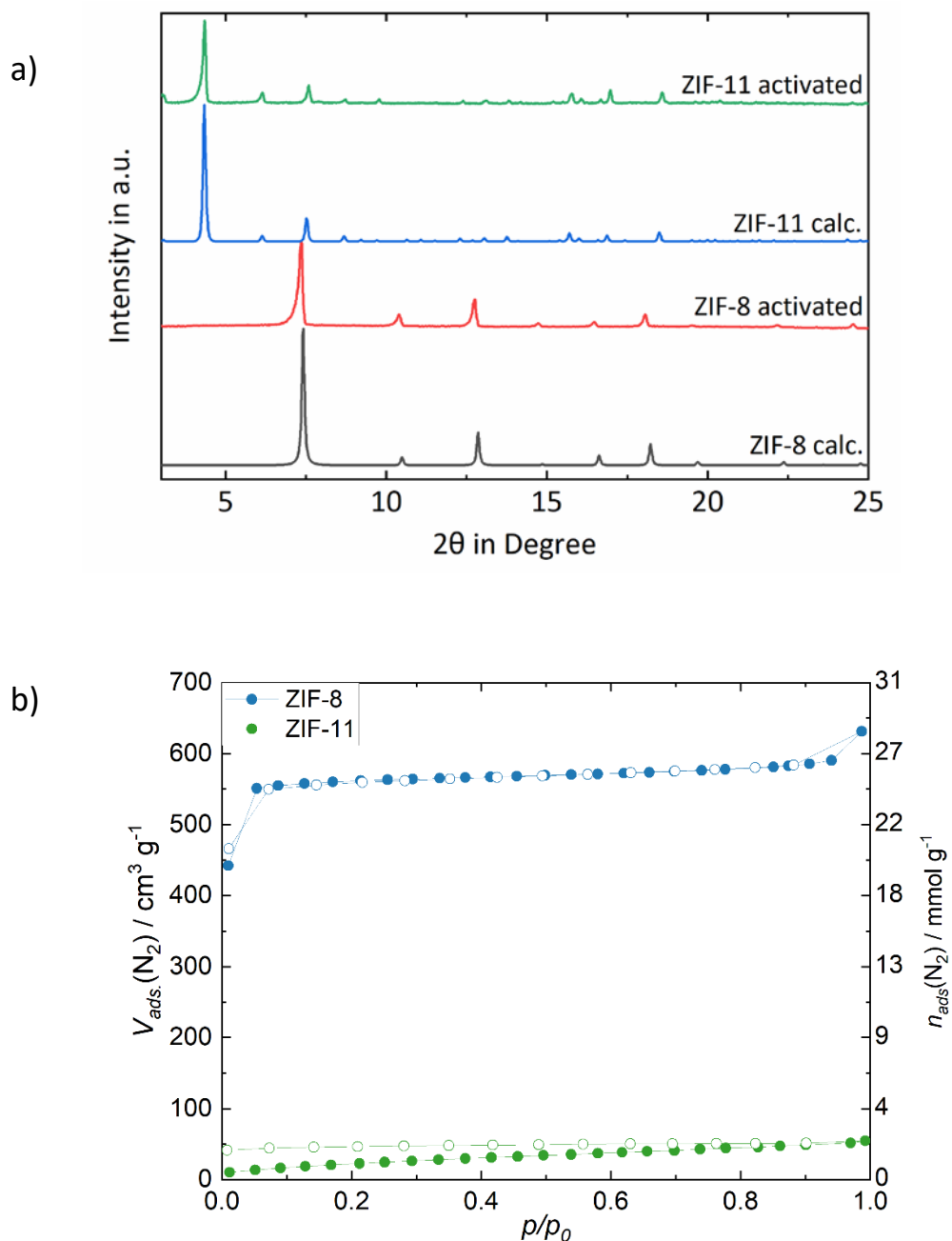

Figure S1: a) Powder X-ray diffraction patterns of the activated ZIF-8 (in red) and ZIF-11 (in green) samples. Calculated PXRD patterns are depicted for comparison, b) N$_2$ physisorption isotherms at 77 K.

The porosity of ZIF-8 was estimated from the nitrogen adsorption isotherm measured at 77 K (Figure S1 b). Pore volume calculated at p/p_0 = 0.9 amounts to 0.59 cm^3/g.

The pores of ZIF-11 are not accessible for nitrogen (Figure S1 b), therefore the nitrogen adsorption could not be used for estimation of porosity in this case. The theoretical volume of ZIF-11 amounts to 0.46 cm^3/g.[4,5] This value was used to estimate the amount of alcohol solution needed to fill the pores.
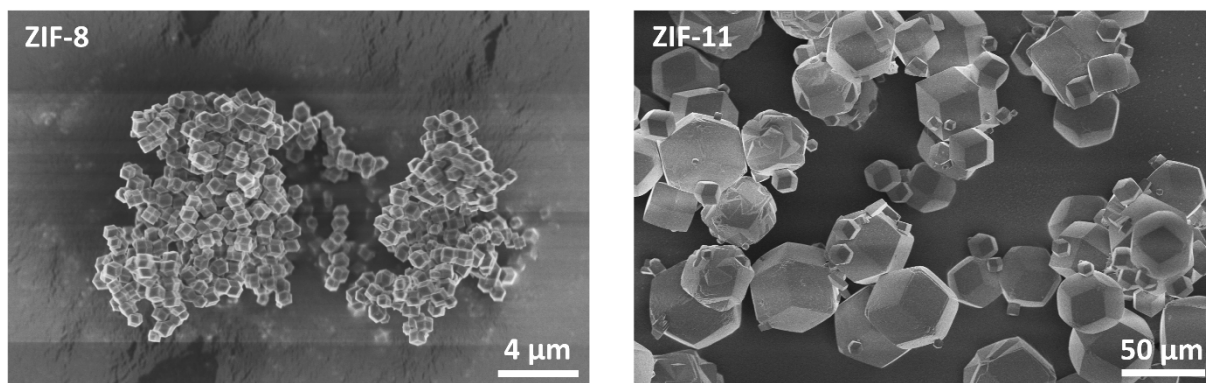

Figure S2: SEM micrographs of the activated ZIF-8 and ZIF-11 samples.

2. NMR studies of alcohol adsorption

2.1. NMR experiments

Solid-state NMR experiments were performed on ZIF-8 and ZIF-11 loaded with 1 M aqueous solutions of glycerol, ethanol, or a 1:1 mixture of both alcohols. Isotope-enriched ethanol-^{13}C-2 and glycerol-^{13}C-2 (Sigma Aldrich) were used for NMR experiments. Before the NMR experiments, ZIFs were heated in an oven at 80 °C for 1 hour.

Each sample was loaded with a certain amount of corresponding solution. To this end, 10 mg of sample were mixed with a solute volume (alcohol or alcohol mixture solution) equal to the absolute pore volume (1 V_{pore}) of the sample (for the pore volume calculation see section 1.3).

The solid-state NMR experiments (single pulse, SP; cross polarization, CP) were carried out on a 300 MHz Bruker Avance spectrometer with a commercial 2.5 mm double-resonance magic angle spinning (MAS) probe at a sample spinning rate of 15 kHz. ^{1}H decoupling (SPINAL-64) was applied except for 2D EXSY (see below) at a decoupling field strength of 45 kHz. For quantitative SP experiments, the delay between subsequent scans (180 s) was optimized by variation until the maximum signal was reached. Spectra were referenced to TMS using adamantane as a secondary reference for ^{13}C, resonating at 29.5 ppm. For CP and SP spectra, 3072 and 200 scans were acquired, respectively.

Alcohol uptake measurements from alcohol mixtures were carried out by quantitative liquid-state ^{13}C NMR experiments at a 300 MHz Bruker Avance spectrometer with a commercial 5 mm high-resolution probe. Direct ^{13}C SP excitation was applied without [1]H-decoupling to avoid unwanted NOE effects. For quantitative SP experiments, the delay between subsequent scans (40 s) was optimized by variation until the maximum signal was reached. Prior to the NMR experiments, defined amounts (as given in Table S1) of activated MOF were placed into vials. A volume of 0.5 ml from the 0.25:0.25 glycerol:ethanol solution (0.5 M total alcohol concentration) was added and the samples were equilibrated under shaking for 24 h (if not stated else). Afterwards, 0.3 ml of pure supernatant was extracted using a syringe with filter mesh. ^{13}C NMR spectra of these samples were measured and quantitatively compared with the corresponding spectra of the initial mixture solution.
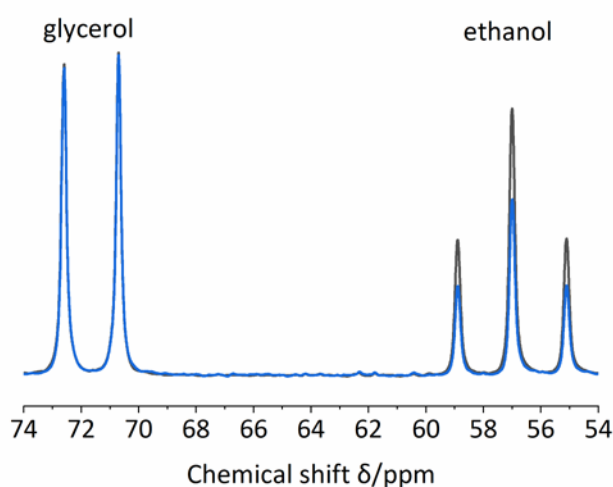

Figure S3: Quantitative liquid-state ^{13}C NMR spectra of supernatant solutions before and after contact with ZIF-11. Black: Before contact with ZIF-11. Blue: After contact with ZIF-11.

2.2 Liquid-state alcohol uptake measurements

Table S1: Quantitative alcohol uptake data derived from liquid-state ^{13}C NMR data (cf. Figure S3) for ZIF 8 and ZIF-11 after contact with 0.5 ml of a 1:1 glycerol:ethanol solution (0.5 M total alcohol concentration, 0.25 M concentration for each individual alcohol).

Sample	Amount	Glycerol uptake / µmol/g	Ethanol uptake / µmol/g
ZIF-8 (24 h equilibrated)	83 mg	60	151
ZIF-8 (48 h equilibrated)	50 mg	300	500
ZIF-11 (24 h equilibrated)	50 mg	100	975

2.3 Solid-state ^{13}C NMR studies of alcohols adsorbed in ZIF-11

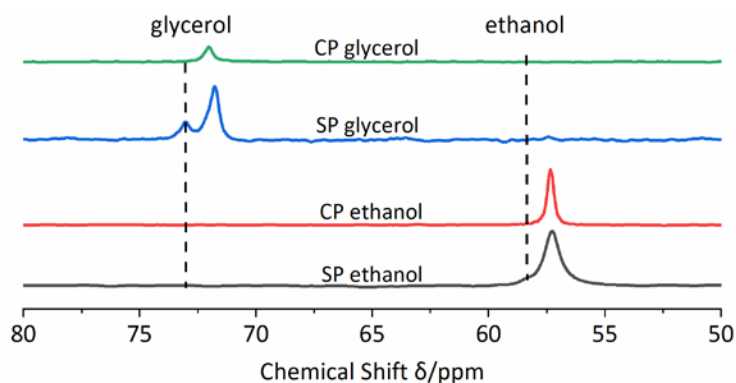Figure S4: ^{13}C SP and CP MAS NMR spectra of ZIF-11 loaded with a 1 M aqueous solution (1 V_{Pore}) of ethanol and glycerol (CP MAS NMR spectra measured at 6 ms contact time). The vertical dashed lines indicate the respective bulk chemical shifts.

Figure S4 shows the ^{13}C SP and CP MAS NMR spectra of ZIF-11 freshly loaded with 1 M alcohol solutions (1 V_{Pore}). For adsorbed ethanol, a chemical shift of 57.2 ppm is found. This is almost 1 ppm lower than the value of 58.3 ppm measured for 1M ethanol solution (bulk). This negative shift is explained by the influence of the ring current effect of aromatic groups in the ZIF-11 linkers. Remarkably, however, glycerol gives rise to two signals at chemical shifts of 71.8 ppm and 73.2 ppm in the SP spectrum immediately after sample preparation and transfer into the spectrometer whereas the CP spectrum exhibits only the signal at 71.8 ppm.

2.4 Cross-polarization (CP) build-up curves for adsorbed alcohols in ZIF-11

The normalized CP build-up curves for the different alcohols and the 1:1 mixture reveals a similar behaviour for the adsorbed alcohols as already observed in ZIF-8 (see Figure 2, main manuscript). The highest slope is again observed for ethanol and indicates stronger immobilization than found for glycerol. Note, that there might also be an intrinsic difference in cross polarization for the two different alcohols. However, the ^{13}C-labels in both molecules actually exhibit directly bound ^{1}H nuclei and other closely neighbored ^{1}H. The observed huge differences in CP buildup must thus be attributed mainly to the degree of immobilization – not structural differences. Adsorbed glycerol in the mixture with ethanol is even more mobile than glycerol adsorbed from aqueous solution without ethanol.
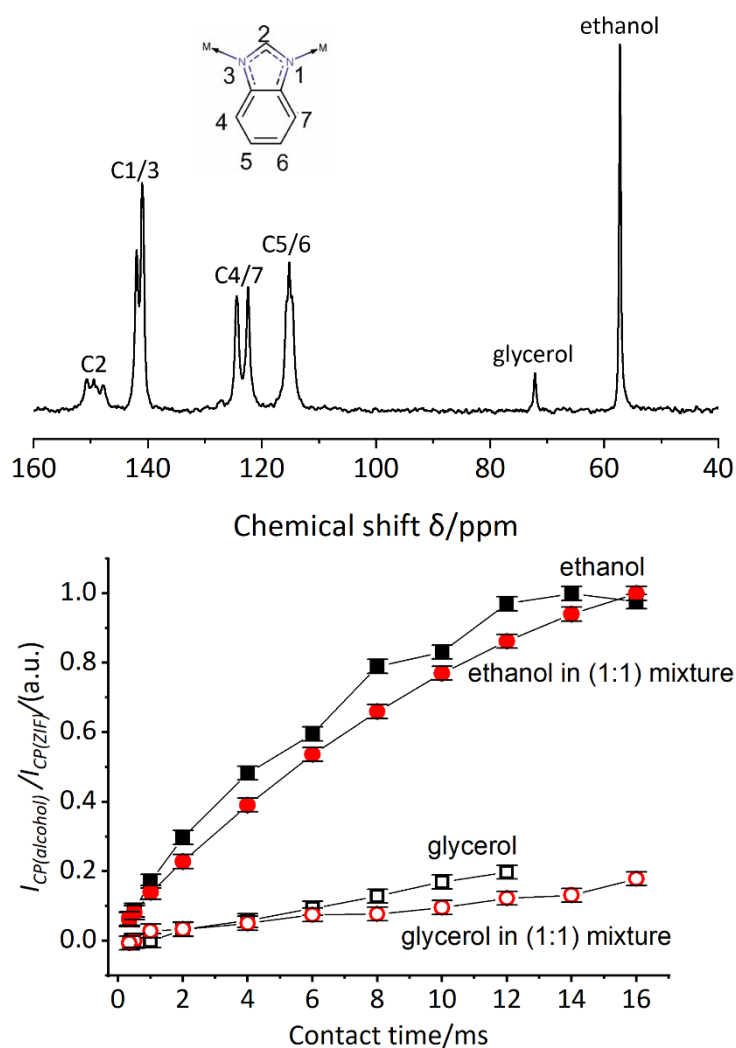

Figure S5: Top: ^{13}C CP MAS NMR spectrum of ZIF-11 loaded with 1M solution (1 V_{pore}) of 1:1 glycerol:ethanol mixture measured at 10 ms contact time. The linker structure of ZIF-11 and signal assignment[3] are provided. Bottom: CP build-up curves for ZIF-11 loaded with 1M solutions (1 V_{pore}) of ethanol, glycerol, or the 1:1 mixture of both alcohols. For comparison, the intensity measured for the respective alcohol is normalized to the intensity of the C-5/6 CP signal in ZIF-11 measured at 2 ms contact time.

2.5 2D EXSY experiments for 1M glycerol solution in ZIF-11

Figure S6 displays two-dimensional exchange (2D EXSY) spectra of glycerol solution loaded to ZIF-11. Note that these spectra were acquired without ^{1}H decoupling. In these spectra, the ^{13}C signals split into doublets due to the heteronuclear J coupling with directly bound ^{1}H nuclei. In principle, two different types of cross peaks can then be distinguished due to the presence of two different exchange phenomena: Cross peaks due to ^{1}H spin diffusion, i.e., spin exchange (marked with blue dots) and cross peaks due to molecular exchange (positions marked with open red dots). However, there are no cross peaks indicative for exchange of the molecules (red dots) between the two observed signals for both mixing times, 5 ms and 50 ms. Only proton spin exchange occurs (blue dots). The absence of molecular exchange even at 50 ms shows that the molecules cannot exchange between the two different states. This is in line with the discussed phase transition.
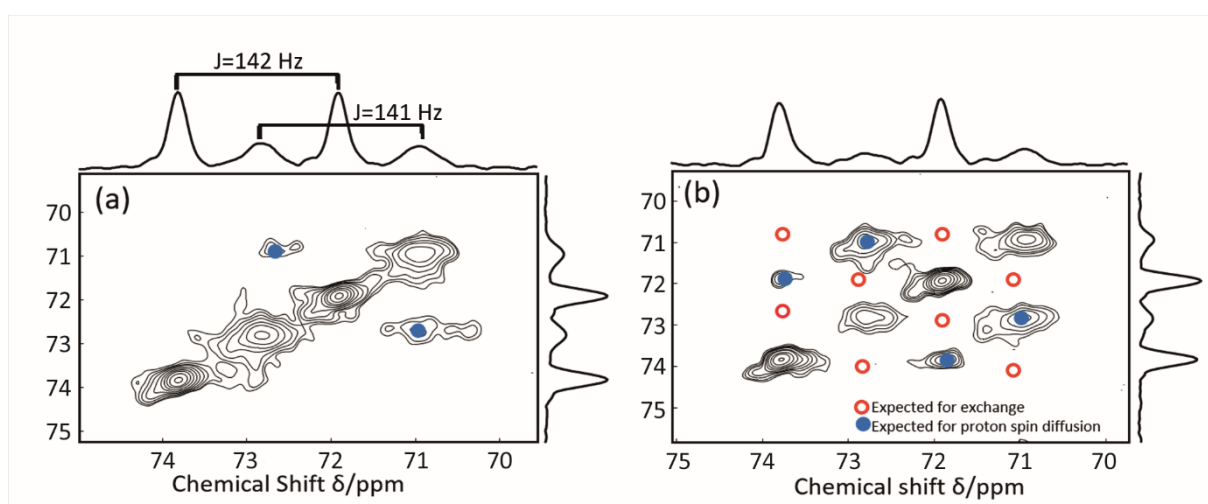

Figure S6: Two-dimensional exchange spectroscopy (2D EXSY) experiment of ZIF-11 loaded with a 1 M solution (1 V_{Pore}) of isotope-labelled glycerol-^{13}C-2. (a) 5 ms mixing time. (b) 50 ms mixing time. Note that the spectra were measured without ^{1}H decoupling. i.e., the ^{13}C signals split into doublets with a J-coupling constant of about 140 Hz as indicated.

The 1D projection (Figure S7) indicates a time-dependence of the two signals which is further described in section 2.6.
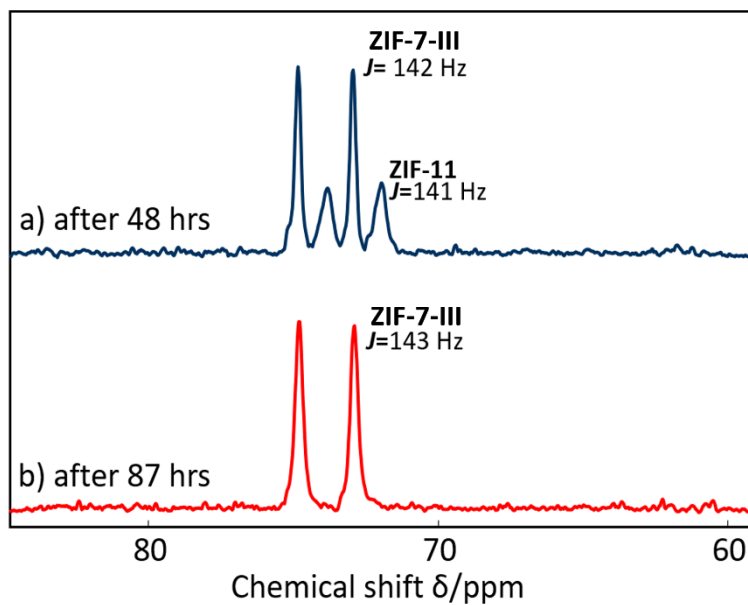

Figure S7: 1D projection of the 2D EXSY experiment of ZIF-11 loaded with a 1 M solution of glycerol-^{13}C-2 (1 V_{Pore}). a) after 48 hrs. b) after 87 hrs. Note that the spectra were measured without ^{1}H decoupling. i.e., the ^{13}C signals split into doublets with ca. 140 Hz J-coupling constant as indicated.

2.6 Time-dependent single pulse NMR experiments for 1 M ethanol and glycerol in ZIF-11

These figures show the time-dependence of the signals of ethanol and glycerol solutions loaded to ZIF-11. When alcohols solutions are loaded to ZIF-11, the phase transition of ZIF-11 to ZIF-7-III occurs over time and the signal for adsorbed alcohols in the pores decreases at the expanse of the increasing signals for desorbed alcohols. The "desorbed" signal of both alcohols remains at the chemical shift of bulk alcohols.
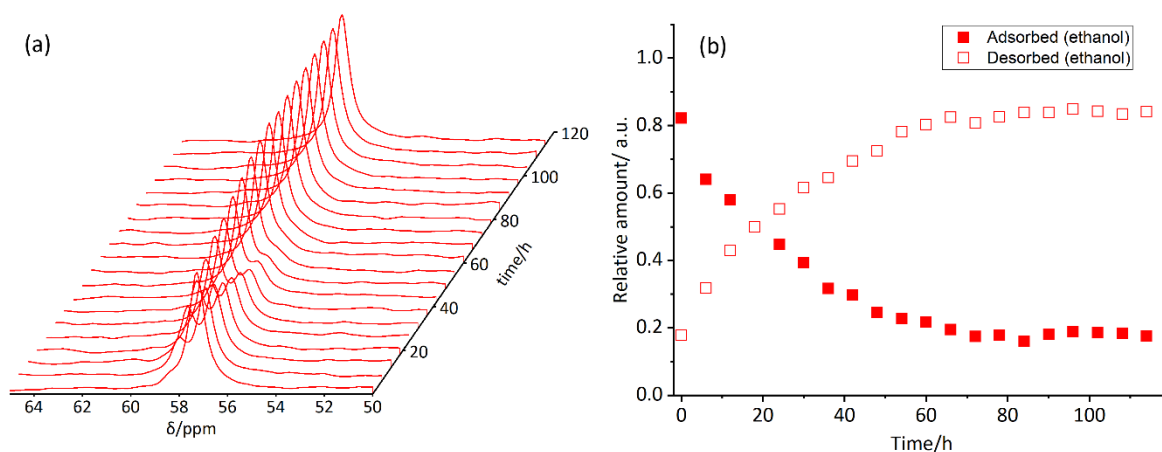

Figure S8: (a): Time-dependence of the ^{13}C SP NMR spectrum of ZIF-11 loaded with a 1 M solution (1 V_{Pore}) of ethanol over 120 hours after sample preparation. (b): Time-dependence of the signal intensities for the signals.
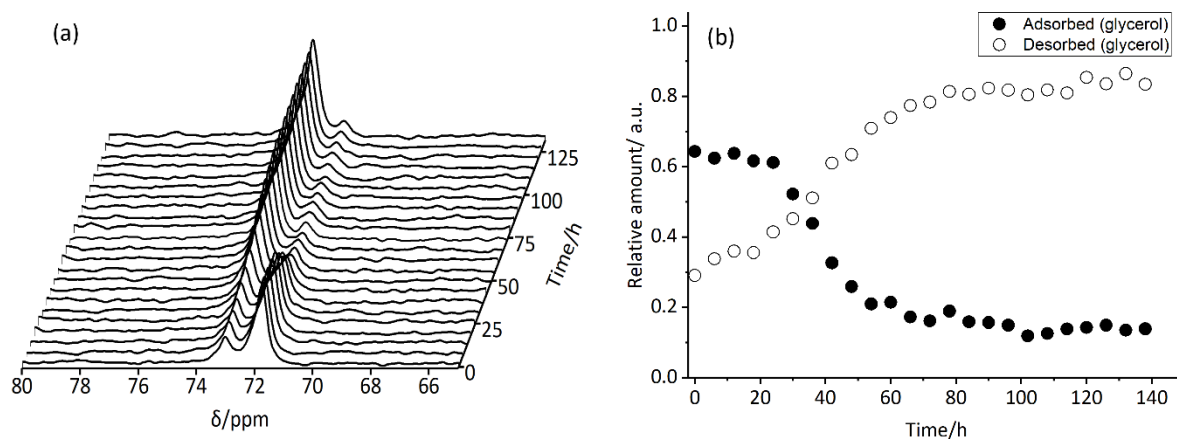

Figure S9: (a) Time-dependence of the ^{13}C SP NMR spectrum of ZIF-11 loaded with a 1 M solution (1 V_{Pore}) of glycerol over 120 hours after sample preparation. (b) Time-dependence of the glycerol signals.

2.7 Determination of NMR signal intensities for alcohols in the 1:1 glycerol:ethanol mixture

Figure S10 demonstrates the time-dependence of ^{13}C SP MAS NMR signal intensities of adsorbed and desorbed alcohols for the (1:1) glycerol:ethanol mixture loaded to ZIF-11. It shows that 90 % ethanol is adsorbed in ZIF-11 while just less than 60 % of glycerol is adsorbed in ZIF-11 after sample preparation and the initial NMR measurement. At increasing time, the intensity of both signals due to adsorbed alcohols decreases significantly. The intensity of the signal due to desorbed glycerol increases steeply from the beginning of the experiments. In contrast, ethanol desorption is retarded compared to glycerol. The intensity of the signal of desorbed ethanol reaches a maximum after 100 hours meaning that the phase transition of ZIF-11 to ZIF-7III has further proceeded. A certain amount of ethanol (ca. 20 %) remains inside the material even after 140 hours in contrast to glycerol.
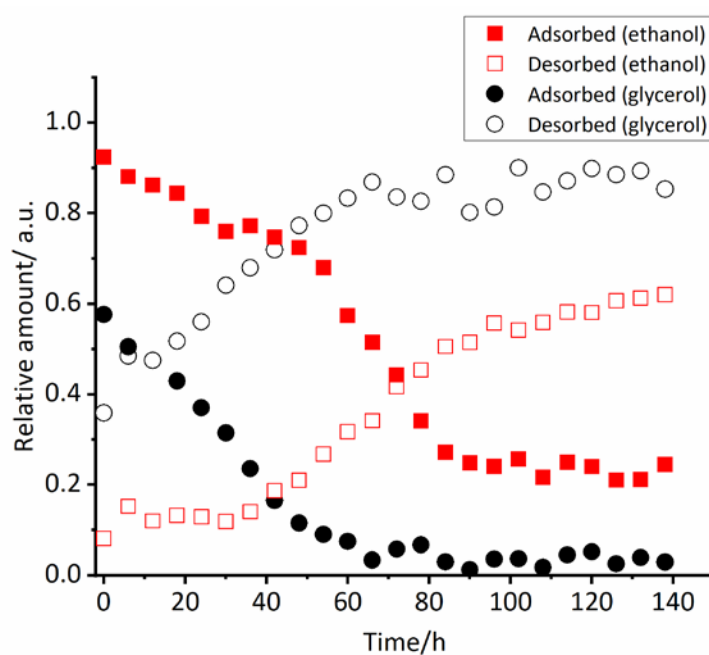

Figure S10: Time-dependence of ^{13}C SP MAS NMR signals for ZIF-11 loaded with the 1:1 mixture of both alcohols over 140 hours after sample preparation.

3. MOF characterization after NMR experiments and stability tests
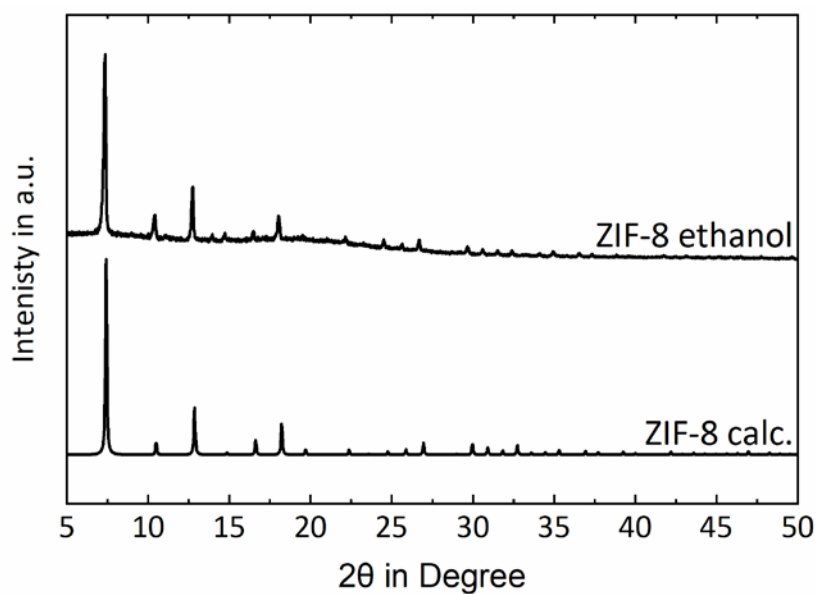
3.1 MOF characterization after NMR experiments

Figure S11: PXRD pattern of ZIF-8 loaded with 1 M aqueous solution of ethanol after the NMR experiments. The calculated PXRD pattern is shown for comparison and reveals that no phase change occurs during the NMR measurements.
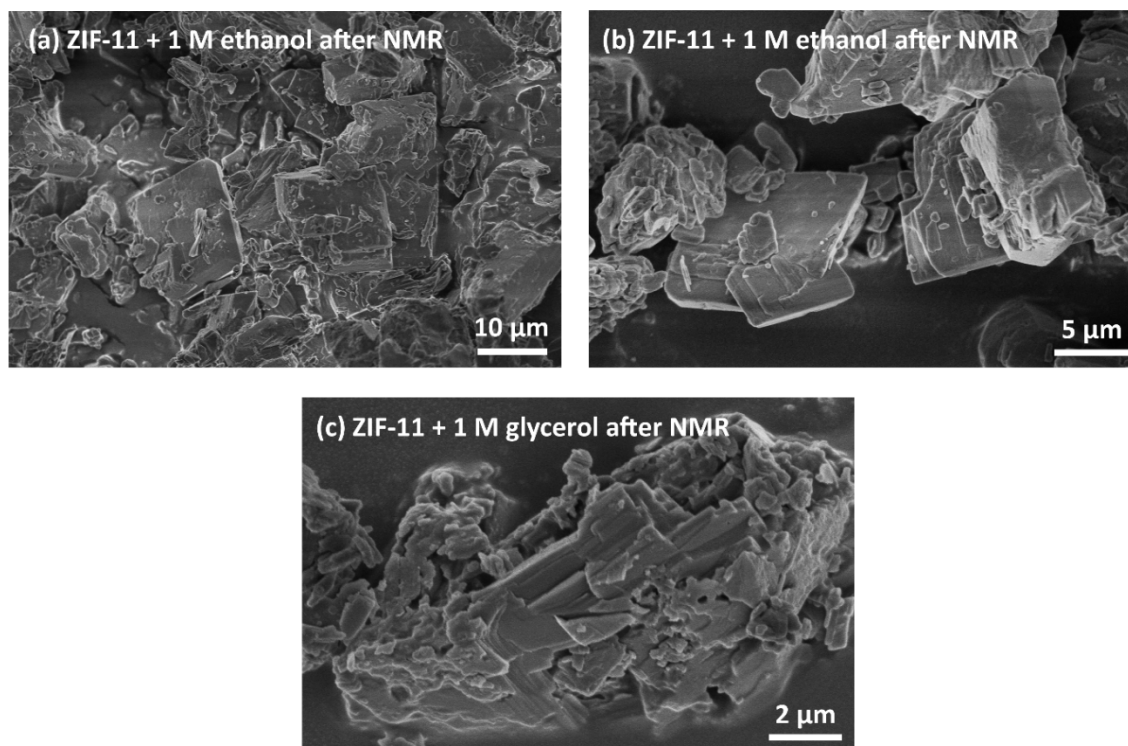

Figure S12: SEM micrographs of the ZIF-11 sample after conducted NMR measurements in 1 M alcohol solutions.

Obvious morphology changes were observed for the ZIF-11 samples after conducting the NMR measurements. The dodecahedron-like crystals observed in the pristine sample transform to an assembly of prismatic platelets, characteristic of the monoclinic space group.

3.2 ZIF-11 stability in pure water, pure ethanol, and in alcohol solutions

To examine the stability of desolvated ZIF-11, a sample amount of 2 mg is dispersed in 30 µl of the respective solution or pure liquid inside a Polypropylene vessel. The vessels were sealed at ambient conditions and stored either on the bench (ca. 22 °C) or in an oven at 80 °C, respectively. The PXRD patterns were collected for the air-dried solids.

The phase transition in pure water takes place on a time scale of several days. Note, however, that the phase transition was not complete even after 5 days (see Figure S13). Pure ethanol is not able to initiate the phase transition at room temperature indicating that the presence of water is essential for this phase transition.
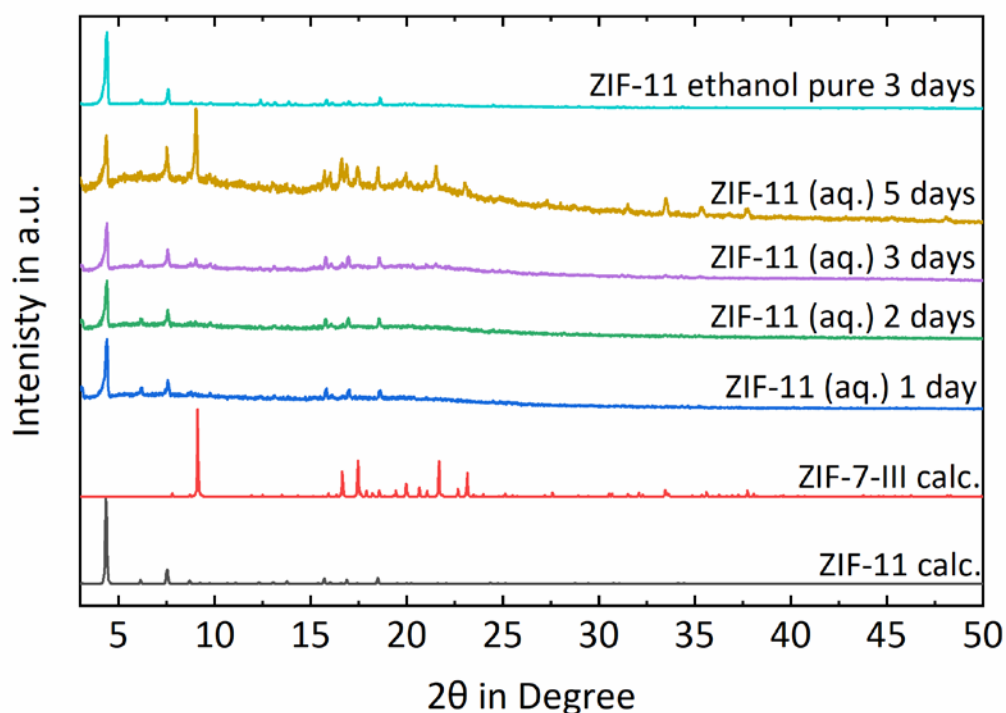

Figure S13: PXRD patterns of activated ZIF-11 samples stored in pure de-ionized water or pure ethanol, respectively. For comparison, the calculated PXRD patterns for ZIF-11 and ZIF-7-III are shown.

Further experiments (see below) demonstrate a temperature-dependence and an influence of the alcohol on the transition kinetics from ZIF-11 to ZIF-7-III. The presence of glycerol in water as well as higher temperatures clearly facilitate the phase transition (see Figure S14).
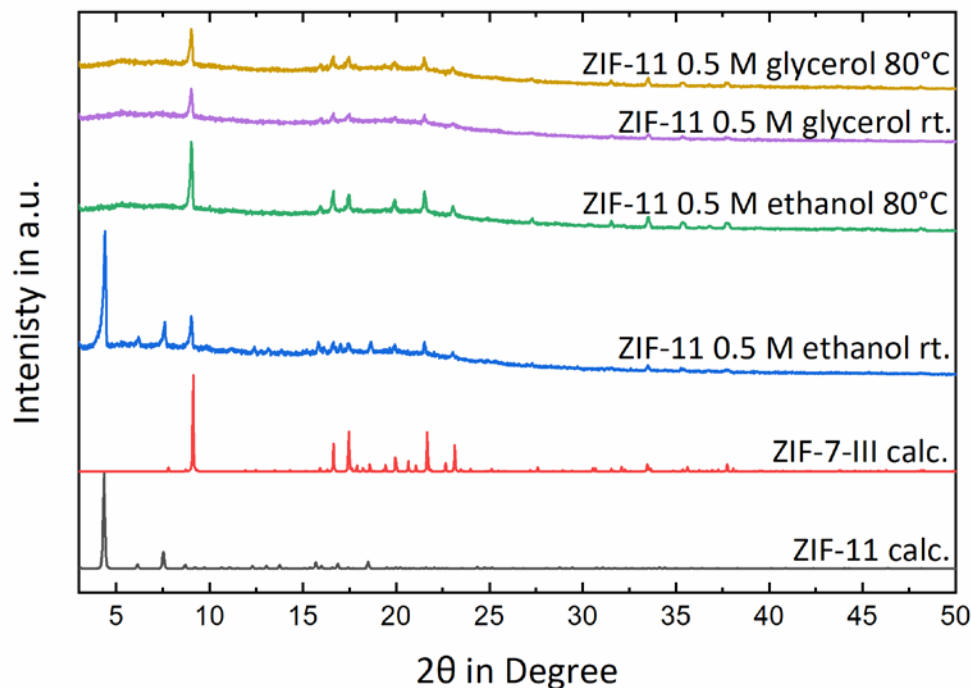

Figure S14: PXRD pattern of activated ZIF-11 samples stored in the respective solutions for 3 days at room temperature (rt.) or 80 °C, respectively. For comparison, the calculated PXRD patterns for ZIF-11 and ZIF-7-III are shown.

References

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