

Synthesis of a partially fluorinated ZIF-8 analog for ethane/ethene separation

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Electronic supplementary information (ESI)

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1. General Remarks

The formation of ZnO is mainly due to the alkaline medium formed by the decomposition of DMF under relatively high temperature (Eq. (1)). Dimethylamine, one of the decomposed products, can be considered as an effective ligand for Zn^{2+} (Eq. (2)). At the temperature, the $[Zn(CH_3)_2NH]^{2+}$ complex equilibrium is perturbed and dimethylamine undergoes basic hydrolysis (Eq. (3)) similar as the procedure of buffer effect. Thus, when their ionic product (IP) exceeds the $Zn(OH)_2$ solubility product constant (K_{ps}) the precipitation of ZnO nuclei becomes activated, due to the presence of free Zn^{2+} and OH^- ions (Eq. (4)).¹ Moreover, the PXRD pattern of resulted product confirms that the material is consisted of ZnO with nanostructure (Figure S6).

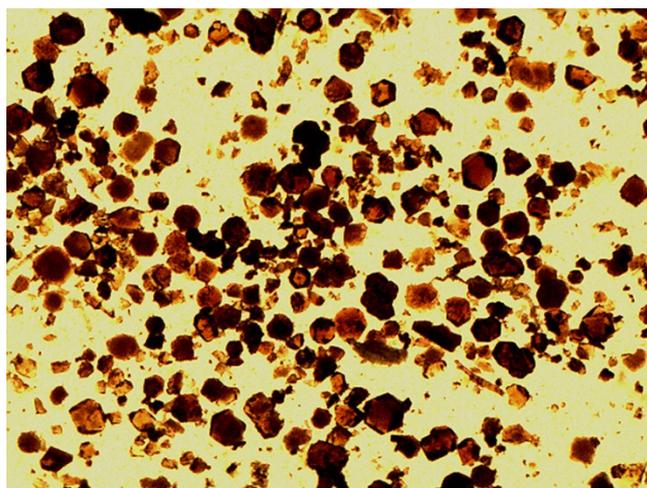
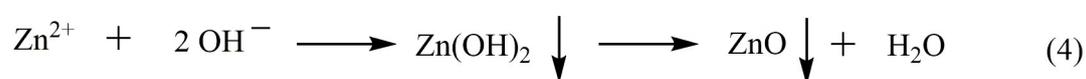
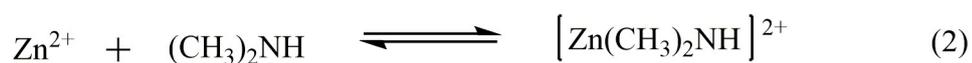


Fig. S1 Optical image of ZIF-318.

2. IR spectra

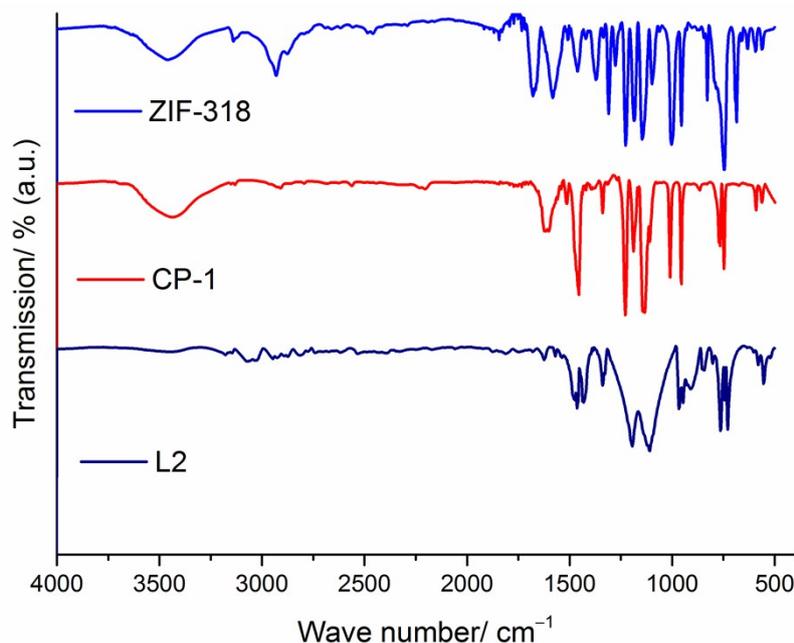


Fig. S2 IR-spectra of L2 ligand, as-synthesized CP-1 and as-synthesized ZIF-318.

3. Single Crystal X-ray Structure Determination of CP-1 and ZIF-318.

The data were corrected for absorption as well as for Lorentz and polarization effects using the program X-Area (Stoe, 2015). The structures were solved by direct methods using SHELXS-2013/2² and refined by full-matrix least squares on F^2 using the program SHELXL-2014/7.³ All non-hydrogen atoms were refined anisotropically.

In CP-1 the fluorine atoms are disordered over two sites with occupation factors of 0.63/0.37. The asymmetric unit contains a half DMF molecule giving 4 solvent molecules per unit cell, corresponding a void volume of 29.9 %⁴ All atoms of the DMF molecule lie on special positions of a mirror plane, with the exception of two hydrogen atoms of each methyl group. Additionally the carbon atoms with their hydrogen atoms are disordered over two sites (occupation factors: 0.9/0.1). The hydrogen atoms of the DMF molecule were calculated in their expected positions and refined using a riding model with C—H = 0.97 Å (CH₃) and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ or and C—H = 0.94 Å (CH) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All other hydrogen atoms were located from the difference Fourier map and free refined.

The structure of ZIF-318 could only be solved after setting of the zinc atom at a special position. No twin law was detected. The refinement with in the 2-position of the imidazole ring full occupied CF₃ group yielded too high temperature factors. It must therefore be assumed that a part of L1 linker (with CH₃) and L2 (with CF₃) partly occur as substituents. Best results (temperature factors, R values) were obtained with half occupied fluorine atoms. This means that the 2-position is occupied of 0.5/0.5 (L1/L2). The hydrogen atoms of the methyl group, consequently, also half occupied, could not be located because they are in a sense “among” the C—F bonds. The hydrogen atom of the imidazole ring was calculated and refined as riding with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The unit cell contains channels filled with disordered solvent molecules. In spite of several attempts, no chemically reasonable solution could be received for the solvent species in the channels of the crystal material. Very high displacement parameters, high estimates and partial occupancy due to the disorder make it impossible to determine accurate atomic positions for that molecules. PLATON/SQUEEZE⁴ calculated a solvent-accessible void volume of 2269 Å³ (46 % of the total cell

volume) and the corresponding number of 683 electrons in the unit cell, agreeing with about 2 molecules of dimethylformamide ($2 \times 40 \times 8 = 640$). The contribution of the disordered solvent species was subtracted from the structure factor calculations by the SQUEEZE instruction of PLATON.

CCDC 1495473 (CP-1) and CCDC 1495488 (ZIF-318) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table S1. Crystal Data, Details of Intensity Measurements, and Structure Refinement for CP-1 and ZIF-318

	CP-1	ZIF-318
Empirical formula	$C_6H_{6.5}F_3N_{2.5}O_2Zn$	$C_{18}H_{24.5}F_{4.5}N_8O_2Zn_{1.5}$
Formula weight / $g \cdot mol^{-1}$	268.01	568.51
Crystal system	orthorhombic	cubic
Space group	$P n m a$	$I -4 3 m$
Cell dimensions		
$a / \text{\AA}$	14.2627(4);	17.0786(6)
$b / \text{\AA}$	13.4623(5)	17.0786(6)
$c / \text{\AA}$	9.8745(7)	17.0786(6)
$\alpha = \beta = \gamma / ^\circ$	90	90
Volume / \AA^3	1895.99(16)	4981.5(5)
Temperature / K	293(2)	180(2)
Z	8	8
Density (calculated) / $g \cdot cm^{-3}$	1.878	1.516
Absorption coefficient / cm^{-1}	2.617	1.520
Radiation ($\lambda / \text{\AA}$)	Mo-K α (0.71073)	Mo-K α (0.71073)
2θ range / $^\circ$	5.018 – 49.992	3.372 – 49.836
Crystal shape / color	needle / colorless	prism / brown
crystal size / mm	$1.00 \times 0.42 \times 0.11$	$0.17 \times 0.16 \times 0.09$
$F(000)$	1064	2320
Index ranges	$-16 \leq h \leq 16$ $-16 \leq k \leq 15$ $-10 \leq l \leq 11$	$-20 \leq h \leq 20$ $-20 \leq k \leq 20$ $-20 \leq l \leq 20$
Reflections collected	13176	16222
Independent reflections	1742	848
Transmission min/max	0.5066 / 0.6459	0.8258 / 0.8269
Data / restraints / parameters	1742 / 0 / 188	848 / 0 / 48
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0277 / 0.0753	0.0356 / 0.0813
R_1 / wR_2 (all data)	0.0311 / 0.0775	0.0412 / 0.0838
Goodness of fit on F^2	1.043	0.953
Largest diff. peak and hole / $e \cdot \text{\AA}^{-3}$	0.468 and -0.394	0.163 and -0.233

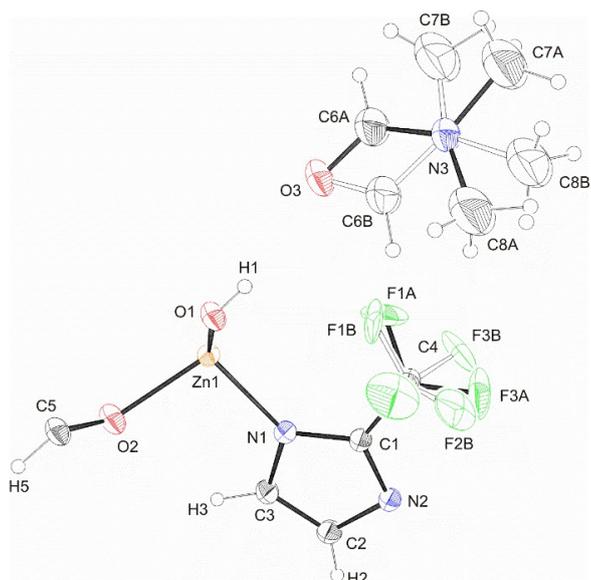


Fig. S3 ORTEP diagram of the asymmetric unit of CP-1. The fluorine atoms are disordered (disordered fluorine atoms and disordered atoms in DMF are shown without shading).

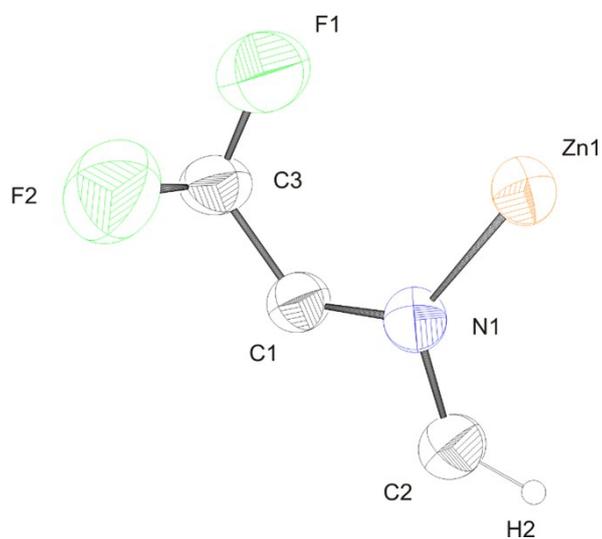


Fig. S4 ORTEP diagram of the asymmetric unit of ZIF-318.

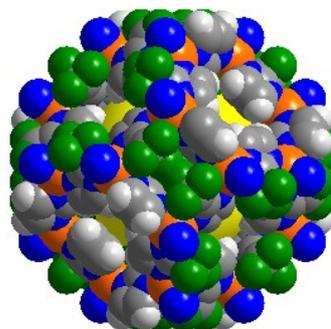


Fig. S5 Space-filling model of one *sod* cage of ZIF-318;

Table S2. Hydrogen-bonding parameters [\AA , $^\circ$] for CP-1.

	D–H	H \cdots A	D \cdots A	D–H \cdots A
C2–H2 \cdots O3 ^I	0.96(3)	2.44(3)	3.396(3)	175(2)
C3–H3 \cdots F3A ^{II}	0.94(3)	2.56(3)	3.095(5)	116(2)
O1–H1 \cdots O3	0.73(5)	2.18(5)	2.903(4)	166(5)
C7B–H7F \cdots N2 ^{III}	0.97	2.74	3.46(6)	131.8

Symmetry operators:

^I $-x+1/2, -x, z+1/2$ ^{II} $x-1/2, y, -z+2/3$ ^{III} $-x+1, y+1/2, -z+1$

4. Powder X-ray-diffraction

The diffractometer was equipped with a copper tube, a scintillation counter, automatic incident- and diffracted-beam soller slits and a graphite secondary monochromator. The generator was set to 40 kV and 40 mA. All measurements were performed with sample rotation. Data were collected digitally from 3° to 70° 2θ using a step size of 0.02° 2θ and a count time of 4 seconds per step. The simulated powder pattern for the materials were calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4.2 program provided by the Cambridge Crystallographic Data Centre.

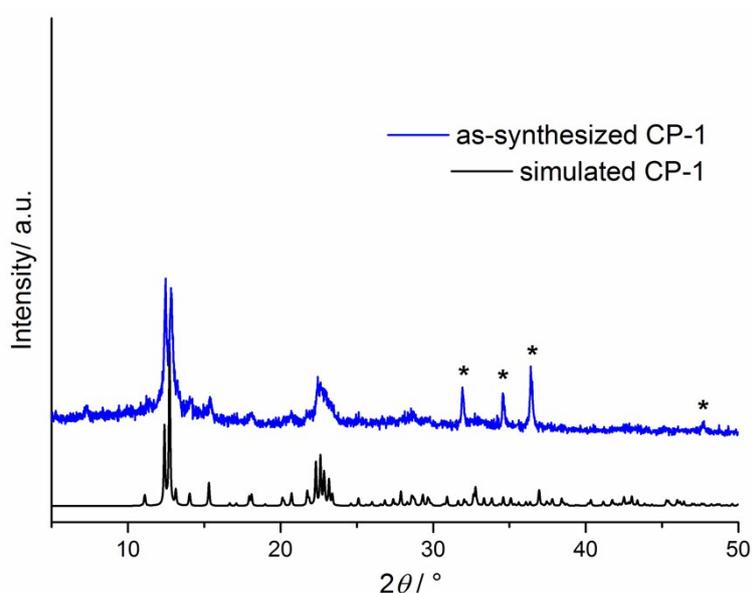


Fig. S6 PXRD pattern of CP-1. Difference in the relative intensities is because of the simulated pattern does not account for the disordered solvent molecules in the pores. The insert star marks (*) are assigned to diffraction peaks of ZnO phase.¹

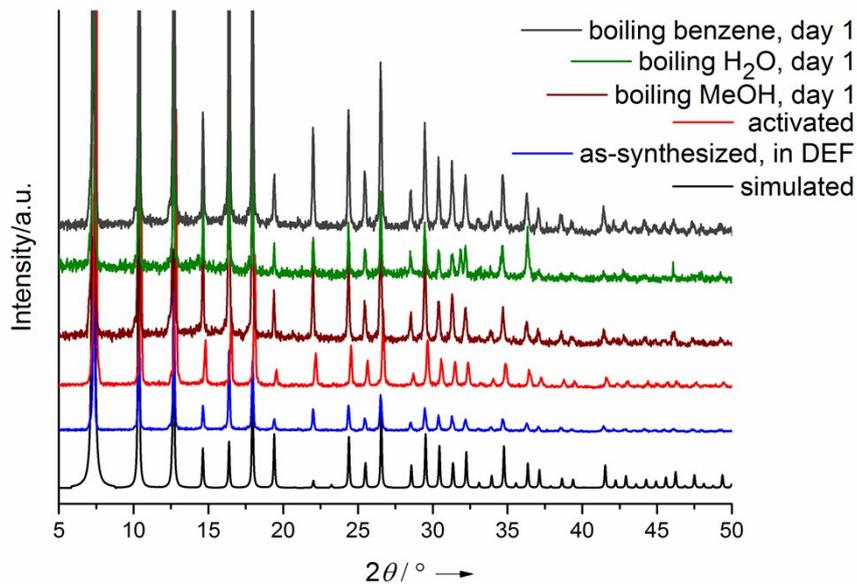


Fig. S7 PXRD patterns of activated ZIF-318 and the chemical stability tests in various solvents.

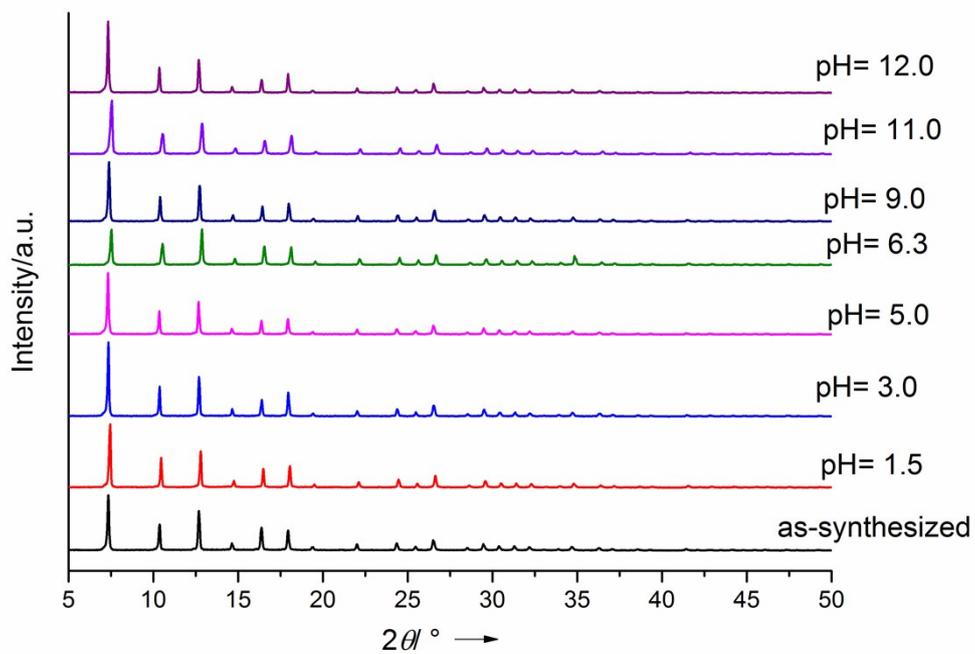


Fig. S8 PXRD patterns of ZIF-318 at various pH range.

5. Thermogravimetric analysis

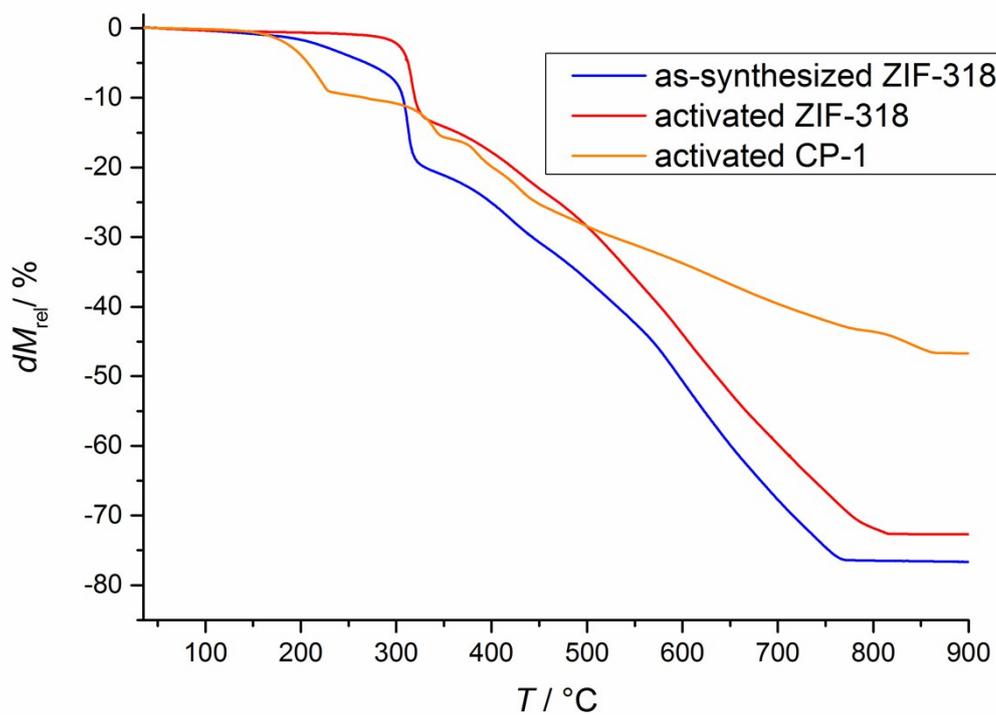


Fig. S9 TGA curves for CP-1 and ZIF-318.

6. SEM – Scanning Electron Microscopy and EDX - Energy-dispersive X-ray spectroscopy

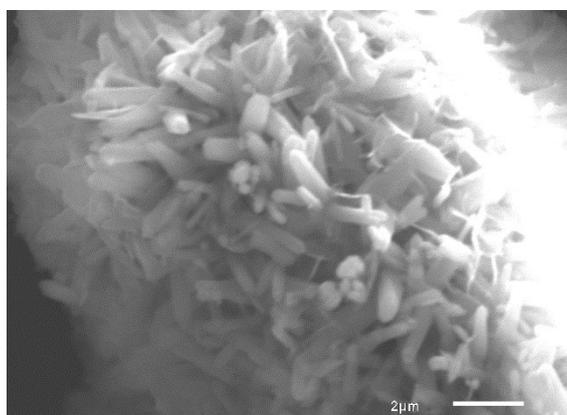
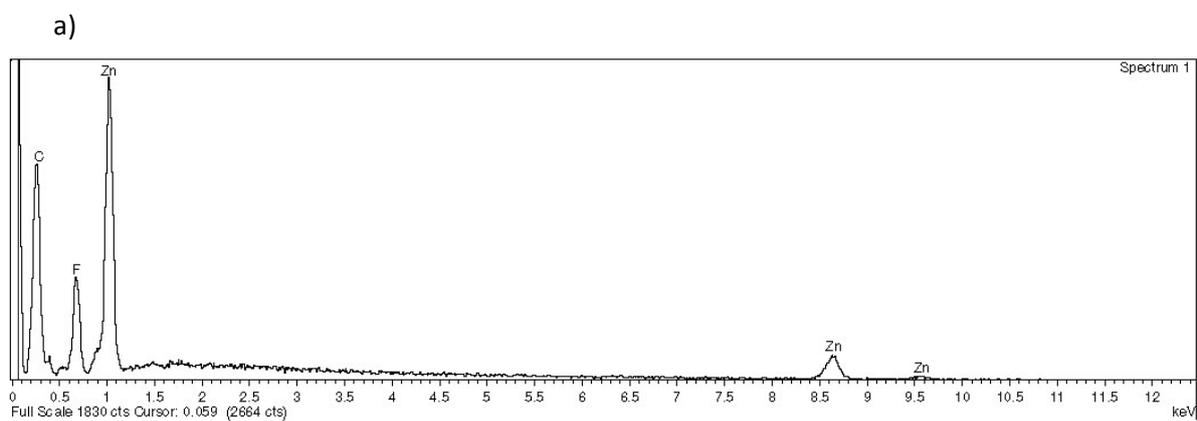


Fig. S10 Scanning electron micrograph (SEM) for CP-1.



b)

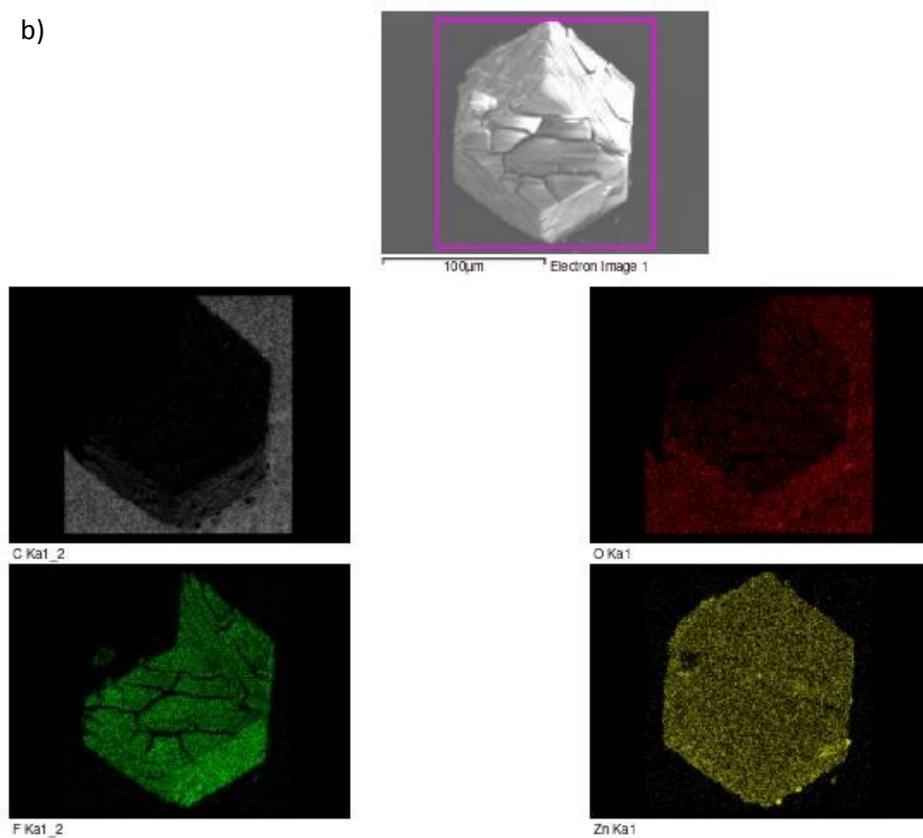


Fig. S11 a) EDX-spectrum and b) elemental mapping of ZIF-318.

7. Contact-angle measurement

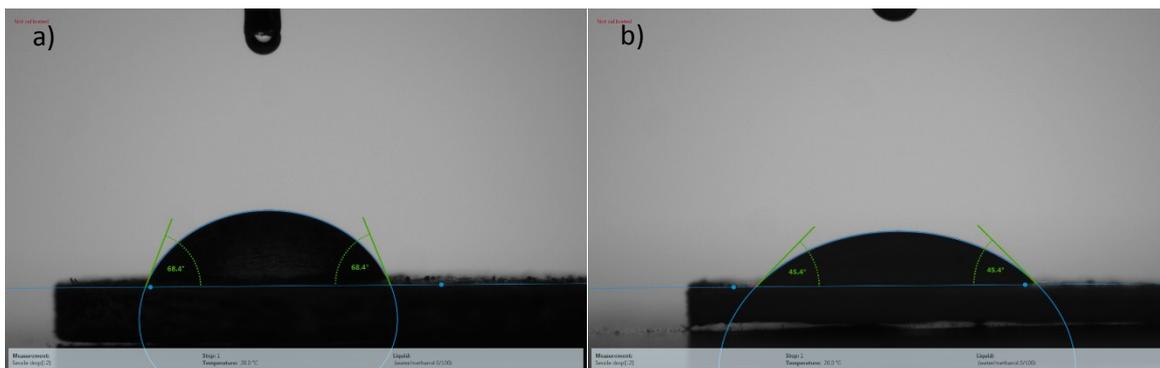
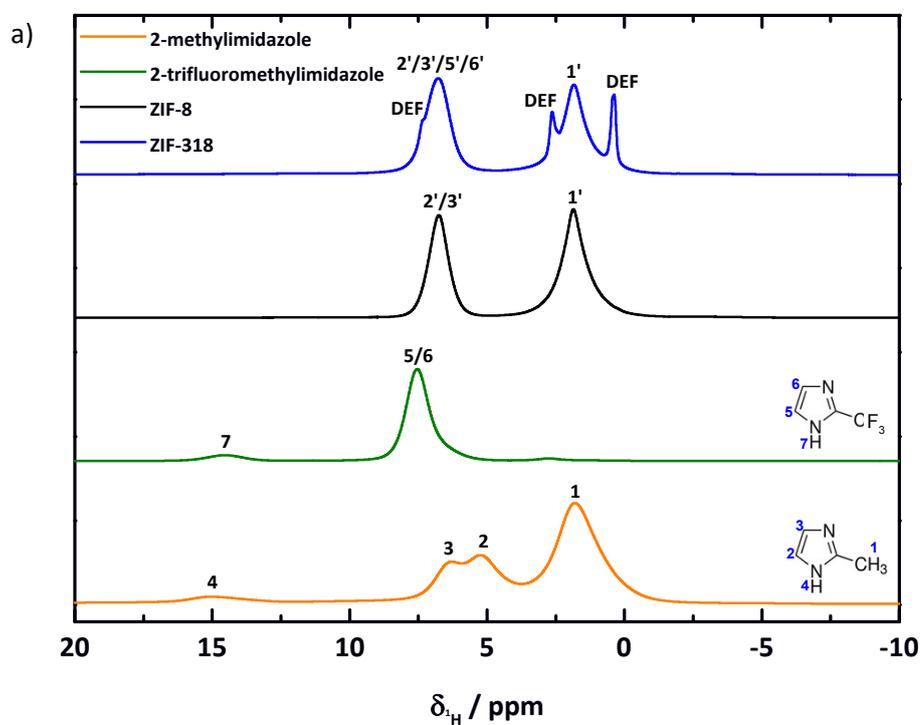


Fig. S12 Contact angle for a) activated ZIF-318 and b) activated ZIF-8.

8. Solid-state ^1H and ^{13}C NMR of activated ZIF-318



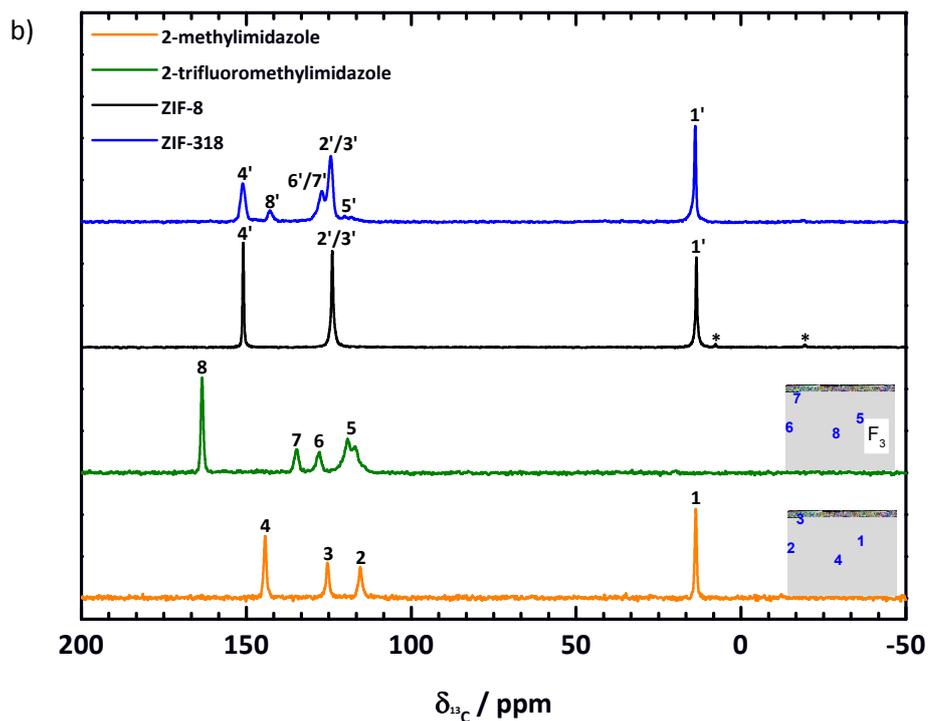
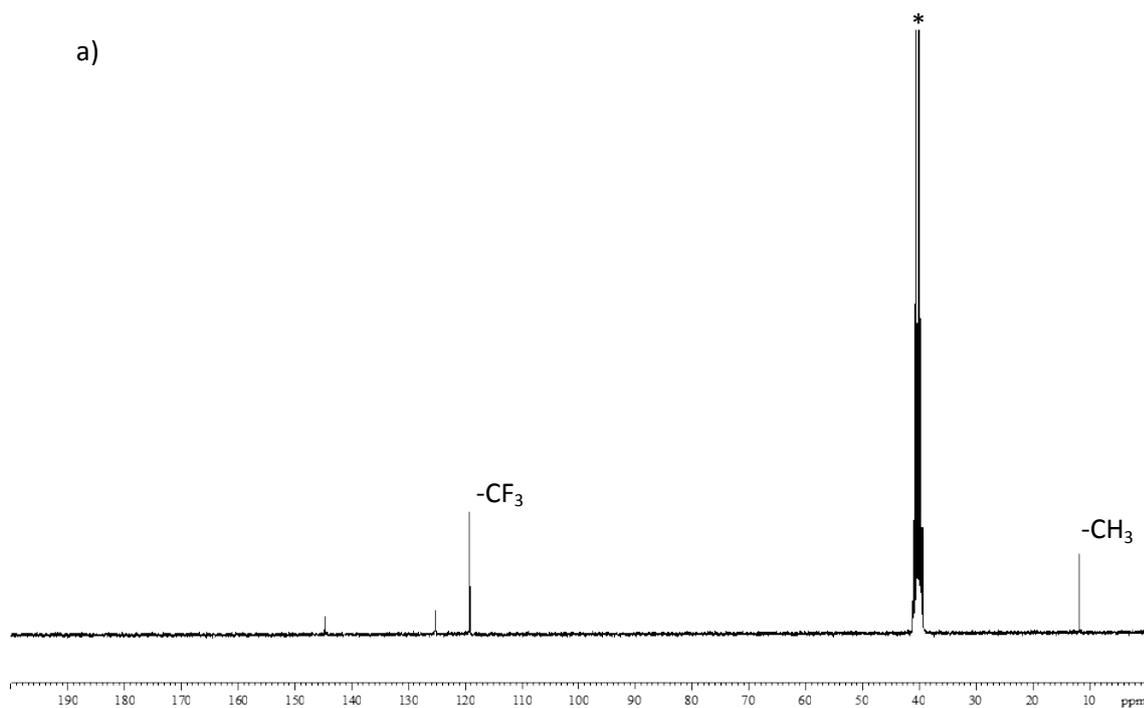


Fig. S13 a) ^1H MAS NMR spectra and b) ^1H - and ^{13}C CPMAS NMR spectra of activated ZIF-318, ZIF-8 and the linkers 2-methylimidazole and 2-trifluoromethylimidazole. Numbers without apostrophe represent the pure linkers. Numbers marked with an apostrophe denote the synthesized ZIF-318 and ZIF-8. Asterisks designate spinning sidebands.

Liquid-phase ^{13}C NMR spectroscopy of activated ZIF-318

Resonances for NMR spectra are reported relative to Me_4Si ($\delta = 0.0$ ppm) and calibrated based on the solvent signal for ^{13}C and ^{19}F . Liquid-phase NMR spectroscopy of activated ZIF-318 sample (28 mg) was digested in 0.5 mL $[\text{D}_6]$ DMSO and 0.05 mL DCI (20%)/ D_2O .



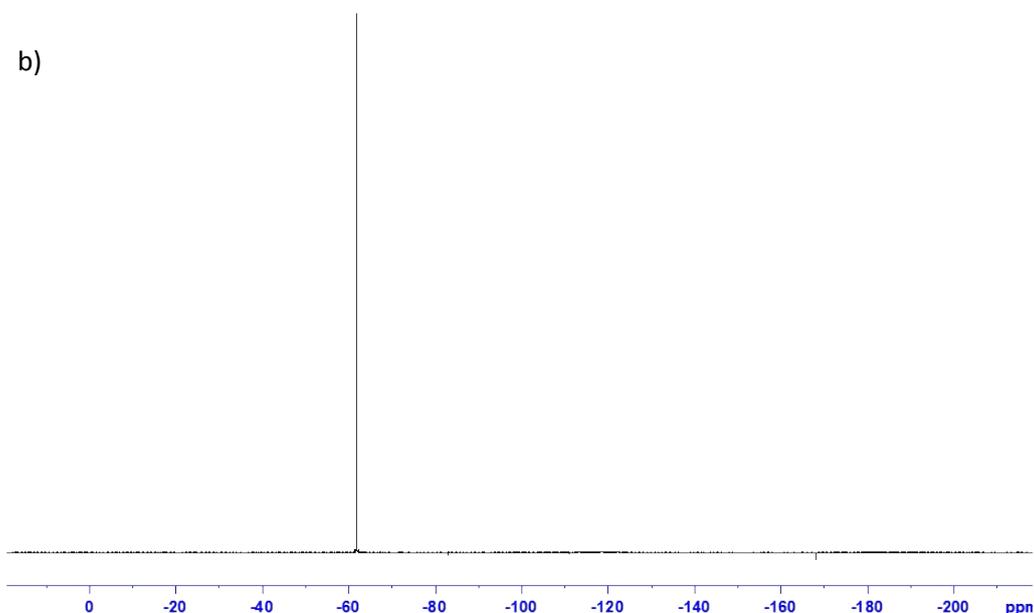


Fig. S14 a) ^{13}C -, and b) ^{19}F -NMR spectra of a digested activated sample ZIF-318 in 0.05 mL DCI (20%)/ D_2O and 0.5 mL $[\text{D}_6]$ DMSO. Solvent signals ($[\text{D}_6]$ DMSO) are marked with an asterisk. Digested sample of ZIF-318 in DMSO-d_6 and $\text{DCI/D}_2\text{O}$, there is no coordination to zinc.

9. Liquid-phase ESI-MS for ZIF-318

The ESI-MS spectra were recorded using a Micromass Q-TOFmicro mass spectrometer. As synthesized ZIF-318 sample (0.4 mg) was digested in 0.2 mL 0.01 N HCl.

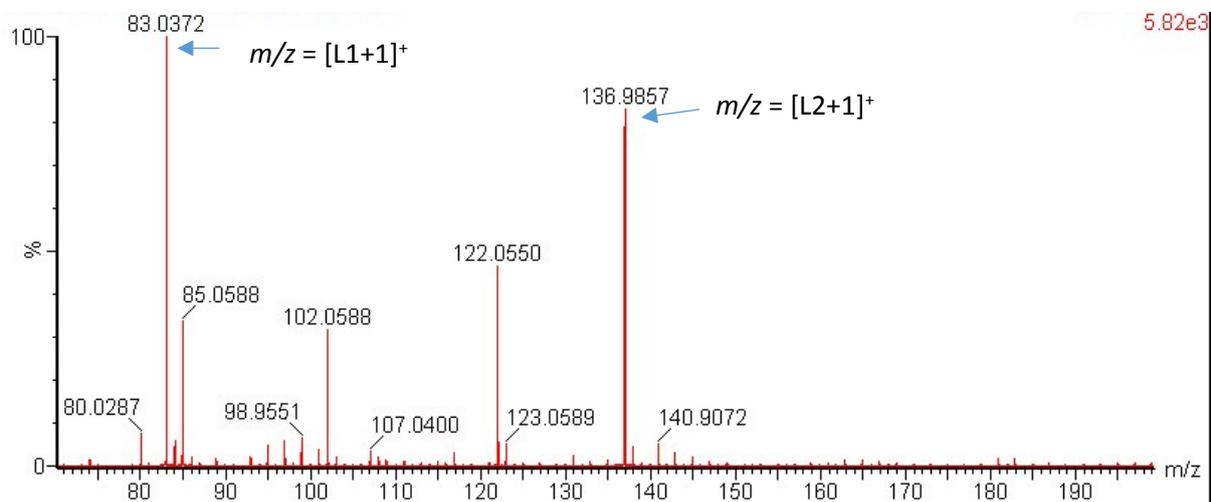


Fig. S15 Mass spectrum of a digested sample of as-synthesized ZIF-318.

Gas Sorption Measurement

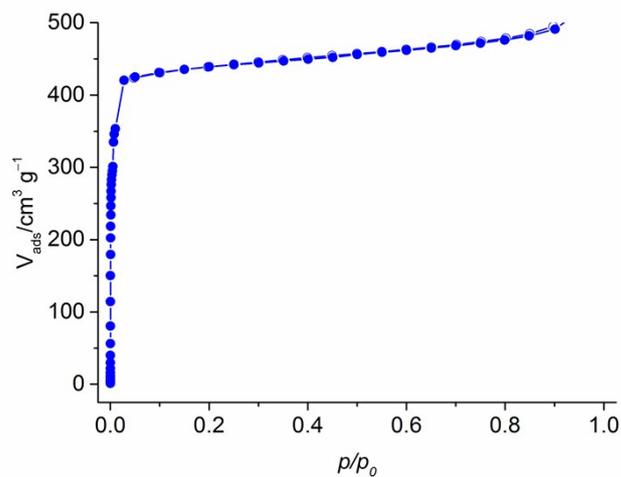


Fig. S16 N₂ sorption isotherm at 77 K of ZIF-8 (adsorption and desorption branches are indicated with closed and open symbols, respectively).

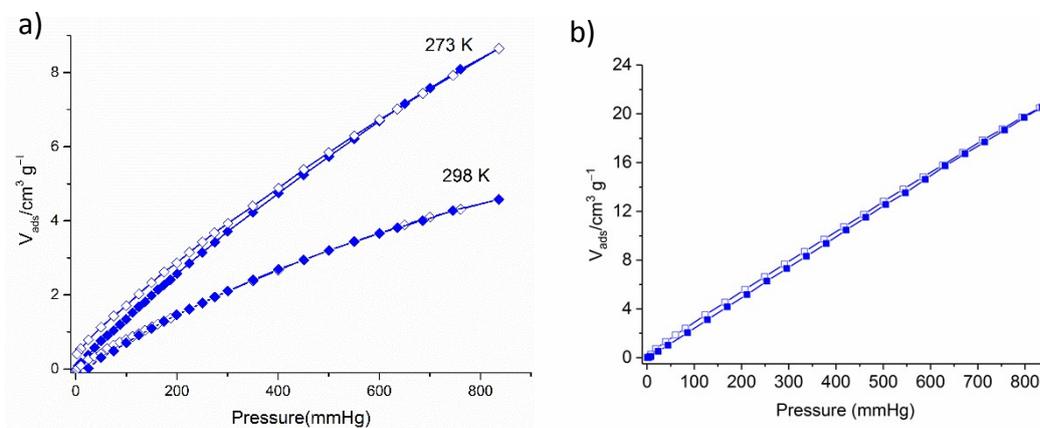


Fig. S17 CH₄ sorption isotherms of a) ZIF-318 and b) ZIF-8 (adsorption and desorption branches are indicated with closed and open symbols, respectively).

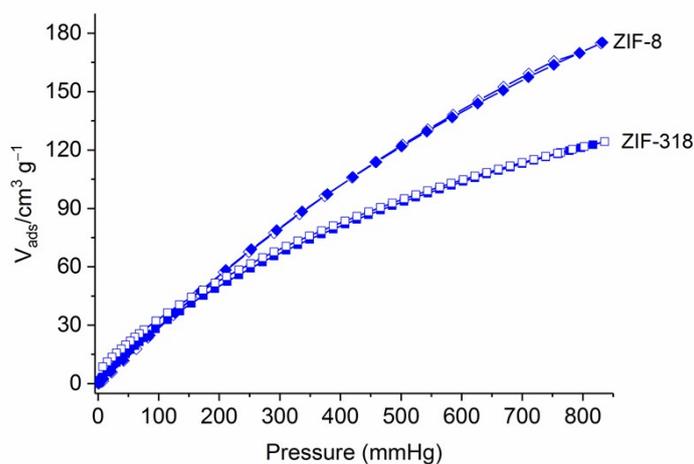


Fig. S18 H₂ sorption isotherms at 77 K up to 1 bar of ZIF-318 and ZIF-8 (adsorption and desorption branches are indicated with closed and open symbols, respectively).

Heat of adsorption

From two adsorption isotherms acquired at different temperatures T_1 and T_2 , the differential heat of adsorption $\Delta H_{ads,diff}$ can be calculated for any amount of adsorbed substance after determining the required relative pressures p_1 and p_2 . A modified form of the Clausius-Clapeyron equation is used (eq. (1))⁵ $\Delta H_{ads,diff}$ was calculated over the whole adsorption range from the 273 K and 298 K isotherms for CO₂.

$$\Delta H_{ads,diff} = -R \ln \left(\frac{p_2}{p_1} \right) \frac{T_1 T_2}{T_2 - T_1} \quad (1)$$

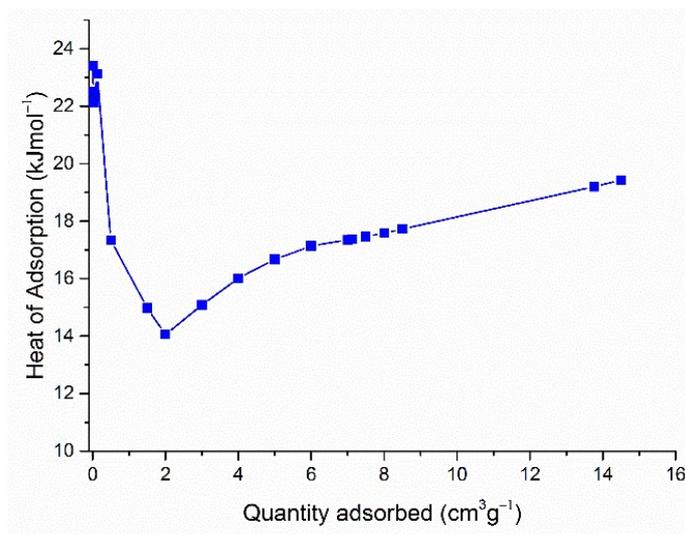


Fig. S19 Isothermic heats of CO₂ adsorption as a function of the adsorbent loading for ZIF-318.

11. References

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