Supplementary Information

Ethane diffusion in mixed linker zeolitic imidazolate framework-7-8 by pulsed field gradient NMR in combination with single crystal IR microscopy

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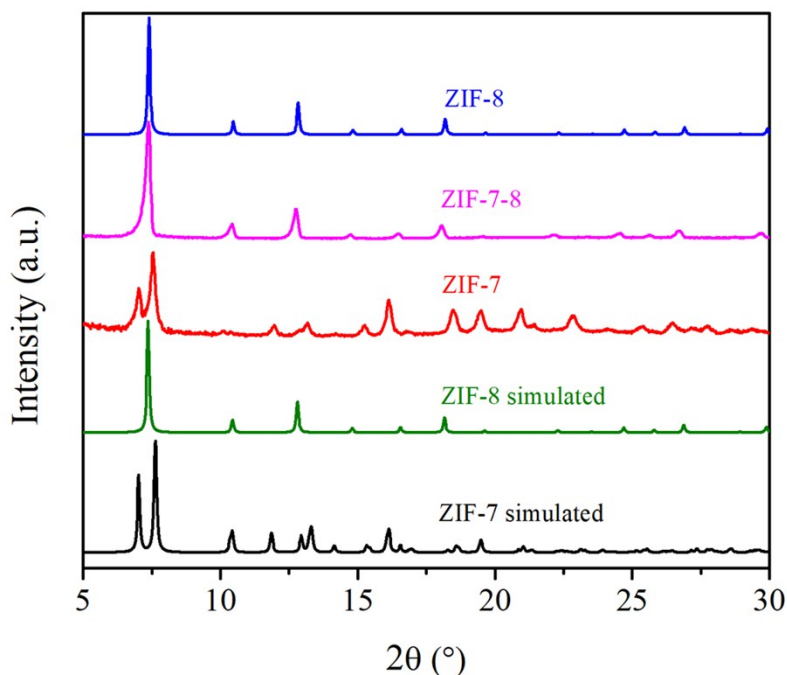[c]Texas A&M University, Artie McFerrin Dept. of Chem. Eng., College Station, TX 77843, USA

Figure S1. Powder X-ray diffraction patterns of ZIF-8, ZIF-7-8, and ZIF-7.
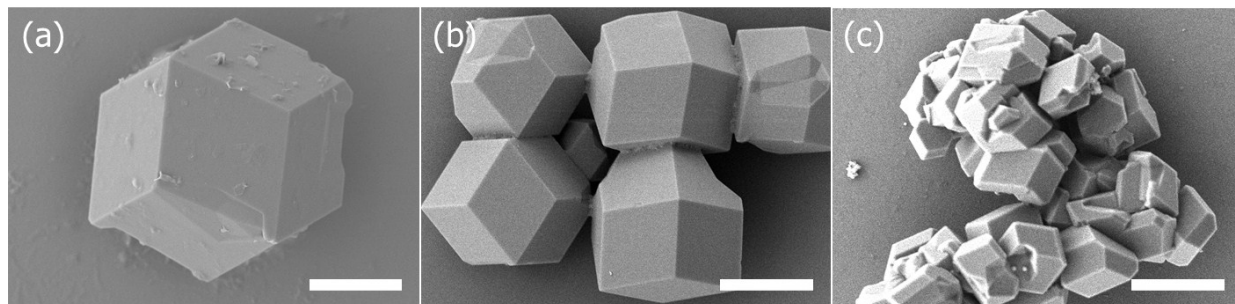
Figure S2. SEM images of (a) ZIF-8, (b) ZIF-7-8, and (c) ZIF-7 crystals. Scale bars are 10 μm.
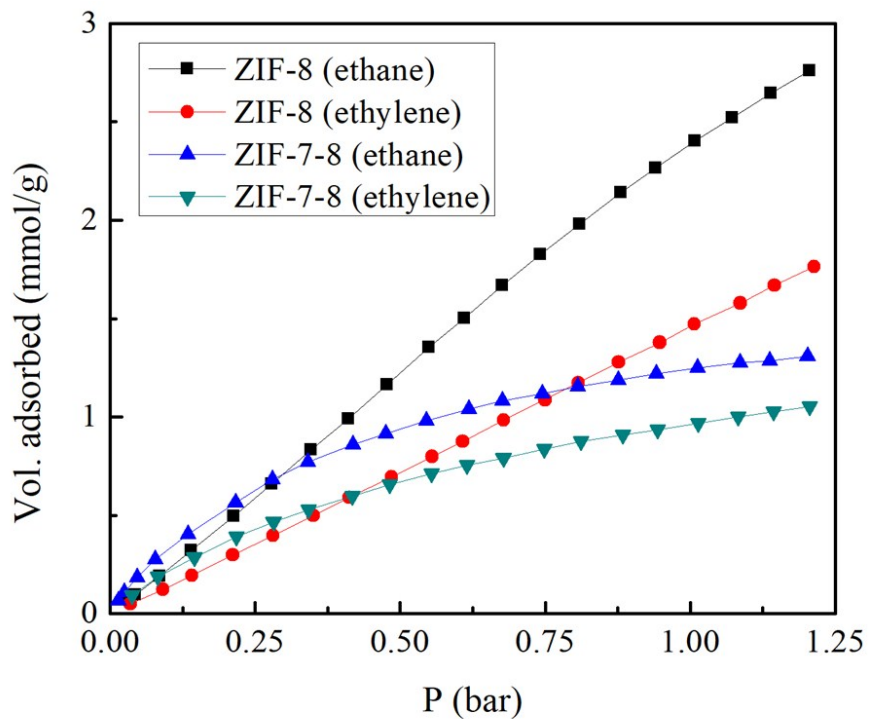

Figure S3. Adsorption Isotherms for ethylene and ethane in ZIF-8 and ZIF-7-8 at 296 K.

Table S1. Ethane loading pressures, ethane self-diffusion coefficients, root mean squared displacements of ethane* (RMSD), T_1 and T_2 ^{13}C NMR relaxation times for ethane in ZIF-8 on a 14 T spectrometer.

Material	Pressure (bar)	D ($\times 10^{-11}$ m^2/s)	RMSD* (μm)	T_1 (s)	T_2 (ms)
ZIF-8	7.9 ± 0.8	2.0 ± 0.3	4.2 ± 0.4	2.0 ± 0.2	11 ± 1
ZIF-8	2.7 ± 0.3	1.7 ± 0.3	4.0 ± 0.4	2.1 ± 0.2	22 ± 2
ZIF-8	0.89 ± 0.09	1.7 ± 0.3	4.0 ± 0.4	1.1 ± 0.1	19 ± 2
ZIF-8	0.34 ± 0.03	1.8 ± 0.3	4.1 ± 0.4	0.94 ± 0.09	25 ± 3

*RMSD reported for measurements at the highest reported diffusion time (Δ) of 160 ms.

Table S2. Ethane loading pressures, ethane self-diffusion coefficients, root mean squared displacements of ethane* (RMSD), T_1 and T_2 ^{13}C NMR relaxation times for ethane in ZIF-7-8 on a 14 T spectrometer.

Material	Pressure (bar)	D_{eff} ($\times 10^{-12}$ m^2/s)	RMSD* (µm)	T_1 (s)	T_2 (ms)
ZIF-7-8	7.9 ± 0.8	6.4 ± 1.0	1.8 ± 0.2	2.7 ± 0.3	26 ± 3
ZIF-7-8	2.7 ± 0.3	5.1 ± 0.8	1.5 ± 0.2	3.0 ± 0.3	29 ± 3
ZIF-7-8	0.78 ± 0.08	3.6 ± 0.5	1.3 ± 0.1	2.2 ± 0.2	25 ± 3
ZIF-7-8	0.28 ± 0.03	3.6 ± 0.5	1.3 ± 0.1	2.0 ± 0.2	24 ± 2

*RMSD reported for measurements at the highest reported diffusion time (Δ) of 160 ms.

Table S3. Band intensities related to ZIF-7 (bIm) and ZIF-8 (mIm) obtained by averaging the IR signals at 3115 and 3060 cm^{-1} and 4100, 2700 and 2475 cm^{-1}, respectively. Assuming an averaged mIm content of 87%, the variation of the bIm-fraction among the crystals is estimated. Maximum and minimum fraction ratios are shown highlighted in orange and blue, respectively.

crystal number	Relative ZIF-7 band intensity	Relative ZIF-8 band intensity	ZIF-7/ZIF-8 ratio (relative signals)	ZIF-7 (bIm) fraction (%)	ZIF-8 (mIm) fraction (%)
1	0.0964	0.1415	0.68	12*	88*
2	0.1025	0.1508	0.68	12	88
3	0.3072	0.5337	0.58	11	89
4	0.0329	0.0301	1.09	18	82
5	0.0333	0.0340	0.98	17	83
6	0.0382	0.0451	0.85	15	85
7	0.0169	0.0238	0.71	13	87
8	0.0319	0.0380	0.84	15	85
9	0.0268	0.0478	0.56	10	90
10	0.1415	0.2018	0.70	13	87
11	0.2734	0.4048	0.68	12	88
12	0.0423	0.0545	0.78	14	86
13	0.0884	0.0959	0.92	16	84
14	0.0887	0.0839	1.06	18	82
15	0.1529	0.2536	0.60	11	89
16	0.1631	0.2803	0.58	11	89
17	0.0865	0.1439	0.60	11	89
18	0.0395	0.0673	0.59	11	89
19	0.0600	0.0747	0.80	14	86
20	0.0206	0.0433	0.48	9	91
21	0.1571	0.2513	0.63	11	89
			average:	13	87

*all normalized mIm and bIm fractions displayed in these columns have an uncertainty of ± 10%
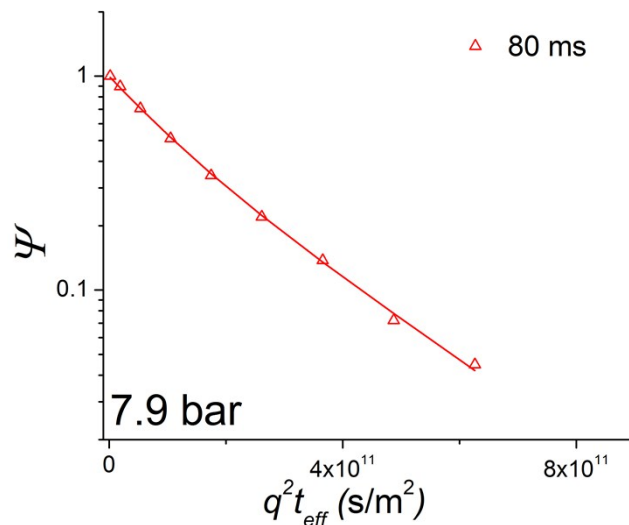
Figure S4. An example of ^{13}C PFG NMR attenuation curve measured for high loading pressure (7.9 ± 0.8 bar) of ethane in ZIF-7-8 at 296 K on the 14 T spectrometer. The solid red line represents a biexponential fit using Eq. S1 to the data.

$$\Psi = p_1 \exp(-q^2 D_1 t_{eff}) + p_2 \exp(-q^2 D_2 t_{eff}) \qquad \text{Eq. S1}$$

Equation S1 represents a biexponential PFG NMR attenuation function that would apply given two molecular ensembles with different diffusivities in a measured sample. p_1 and p_2 represent the fractions of the diffusion ensembles. D_1 and D_2 are the corresponding diffusivities of the ensembles. Table S4 shows the best fit values obtained by fitting the curve in Fig. S4 using Eq. S1.

Table S4. Results of a biexponential fit (Eq. S1) for ethane in ZIF-7-8 at 7.9 bar

Diffusion Time	p_1	D_1 ($\times 10^{-12}$ m²/s)	p_2	D_2 ($\times 10^{-12}$ m²/s)
80 ms	0.39	11	0.61	4.3