

Electronic Supplementary Information

Preferential adsorption sites for propane/propylene separation on ZIF-8 as revealed by
solid-state NMR spectroscopy

Yuqing Xiao, Yueying Chu, Shenhui Li^{}, Jun Xu and Feng Deng^{*}*

State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, National Center for Magnetic Resonance in Wuhan, Wuhan Institute of Physics and Mathematics, Innovation Academy for Precision Measurement Science and Technology, Chinese Academy of Sciences, Wuhan 430071, P. R. China. and University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

*Corresponding author

E-mail: lishenhui@wipm.ac.cn; dengf@wipm.ac.cn

Experimental section

$^1\text{H}\rightarrow^{13}\text{C}$ CP/MAS and ^{13}C MAS NMR experiments were performed on a Bruker Avance III 400 MHz spectrometer with a 4 mm double-resonance probe under 12 kHz MAS. The $^1\text{H}\rightarrow^{13}\text{C}$ CP/MAS NMR experiment was conducted with a contact time of 2.0 ms, a recycle delay of 2 s, and a number scan of 2048. The radio-frequency field strengths are set to 50 and 38 kHz for ^1H and ^{13}C channels, respectively during $^1\text{H}\rightarrow^{13}\text{C}$ cross-polarization transfer. ^{13}C MAS NMR experiment was performed using the pulse sequence in which the signals from both direct polarization and cross polarization were simultaneously collected.

One-dimensional ^{13}C MAS NMR experiment of the glass ampoule sample was conducted on an Agilent Inova-600 MHz spectrometer with a 7.5 mm double-resonance MAS probe. The Larmor frequency is 150.8 MHz for ^{13}C nuclei. ^{13}C MAS NMR spectra were recorded with a pulse length of 8 μs , a recycle delay of 20 s, a spinning rate of 2.5 kHz and a number scan of 1596. ^{13}C NMR chemical shift was externally referenced with respect to adamantane.

Powder X-ray diffraction analysis (PXRD) of the samples were recorded with an Xpert3 powder using a Cu K α ($\lambda = 0.1543$ nm) radiation with a step of 0.02° at a resp ective voltage of 40 kV and a current of 40 mA.

Fitting of single component adsorption isotherms.

The adsorption isotherm of C_3H_8 and C_3H_6 was fitted with the Dual-site Langmuir-Freundlich isotherm model:

$$q = q_{sat,1} \frac{b_1 p^{n_1}}{1 + b_1 p^{n_1}} + q_{sat,2} \frac{b_2 p^{n_2}}{1 + b_2 p^{n_2}} \quad (\text{S1})$$

where, q is the amount of adsorbed (mmol/g), p is pressure (kPa), b is affinity parameter, and n is a constant.

Calculations of adsorption selectivity.

The selectivity of preferential adsorption of C_3H_8 (component 1) over C_3H_6 (component 2) in a gas mixtures, can be calculated as following:

$$S_{ads} = \frac{q_1/q_2}{y_1/y_2} \quad (\text{S2})$$

Where q_1 and q_2 are the component loadings of the adsorbed phase, y_1 and y_2 are the mole fraction of a pure component in the gaseous phase.

Table S1. Dual-site Langmuir–Freundlich isotherm fitting parameters.

	$q_{sat,1}$	b_1	n_1	$q_{sat,2}$	b_2	n_2	R^2
C ₃ H ₈	2.09432	0.06845	1.85094	2.63787	0.09033	0.77524	0.99991
C ₃ H ₆	3.07314	0.03277	1.59357	3.04372	0.03278	0.66931	0.99995

Table S2. The determined ratios of the loading amounts of propane and propylene on ZIF-8 at the loading pressure in range of 1.9~9.6 bar.

propane: propylene (v/v)			
sample	1.9 bar	5.8 bar	9.6 bar
ZIF-8	52:48	50:50	53:47

Table S3. The calculated binding energy ($\Delta E_{bind} = E_{ZIF-Ads} - (E_{ZIF} + E_{Ads})$) between the ZIF-8 framework and the adsorbed propylene or propane.

	$\Delta E_{bind}(\text{kJ/mol})$	
	propylene	propane
1 molecule	-41.38	-42.72
2 molecules	-79.24	-88.45

Table S4. The number and the H-H average distance (in Å, in parenthesis) of strong van der Waals interactions between propane/propylene and ZIF-8. Only the H-H distance < 3 Å between adsorbed propane/propylene and ZIF-8 framework is included.

ZIF-8		
	methyl-group	CH-group
Propane (CH ₃ -group)	7 (2.60)	8 (2.79)
Propane (CH ₂ -group)	1 (2.75)	1 (2.87)
Propylene (CH ₃ -group)	2 (2.64)	3 (2.77)
Propylene (CH ₂ -group)	0	0
Propylene (CH-group)	2 (2.52)	0

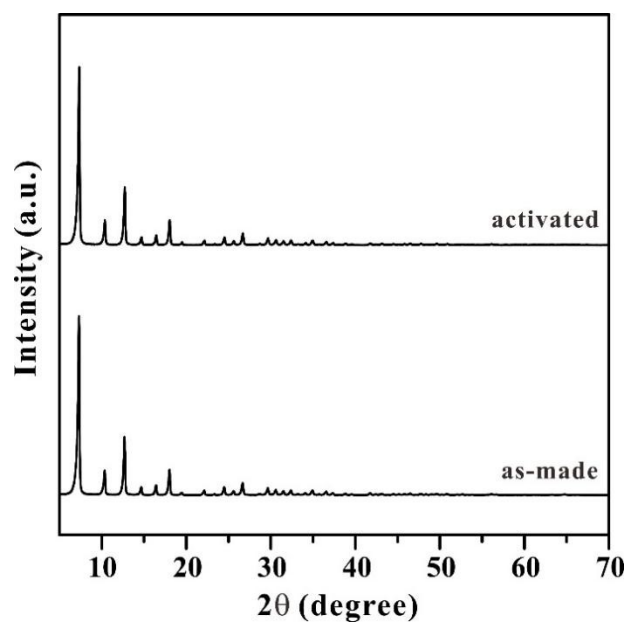


Figure S1. Powder X-ray diffraction patterns of as-made and activated ZIF-8.

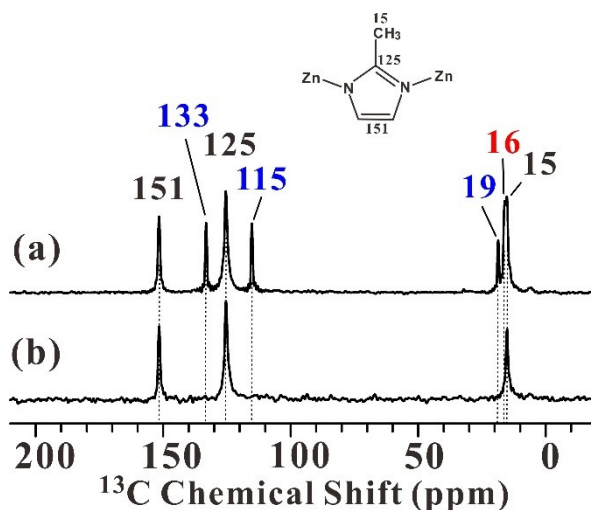


Figure S2. (a) ^{13}C MAS NMR and (b) $^1\text{H}\rightarrow^{13}\text{C}$ CP/MAS NMR spectra of ZIF-8 with co-absorbed propane and propylene mixtures at the adsorption pressure of 1.1 bar. The signal at 16 ppm is assigned to adsorbed propane and the other three additional signals at 19, 115 and 133 ppm are assigned to carbon sites in CH_3 -group, CH_2 -group and CH -group from adsorbed propylene, respectively.

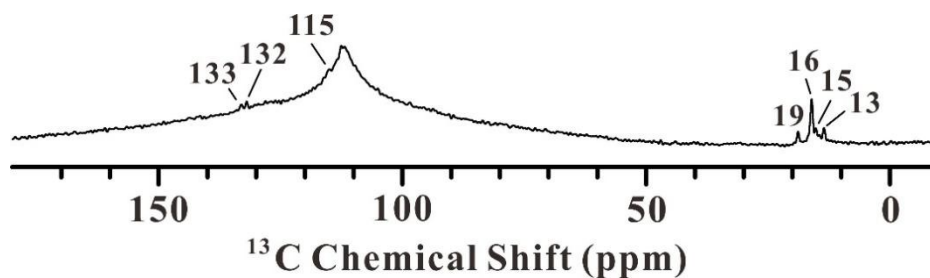


Figure S3. ^{13}C MAS NMR spectra of propane and propylene co-adsorbed on ZIF-8 at a total adsorption pressure of 9.6 bar. The signal at 13 ppm is assigned to free gaseous propane. The signals at 16 and 132 ppm are ascribed to CH_3 -group and CH -group of adsorbed propylene, respectively.

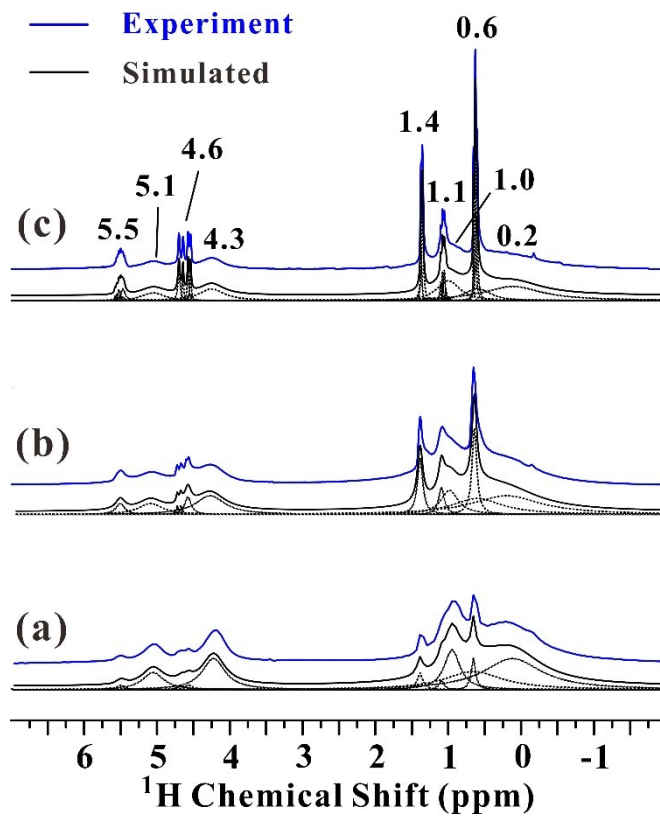


Figure S4. Deconvoluted ^1H MAS NMR spectra of propane and propylene co-adsorbed on ZIF-8 at a total adsorption pressure of (a) 1.9 bar, (b) 5.8 bar and (c) 9.6 bar.

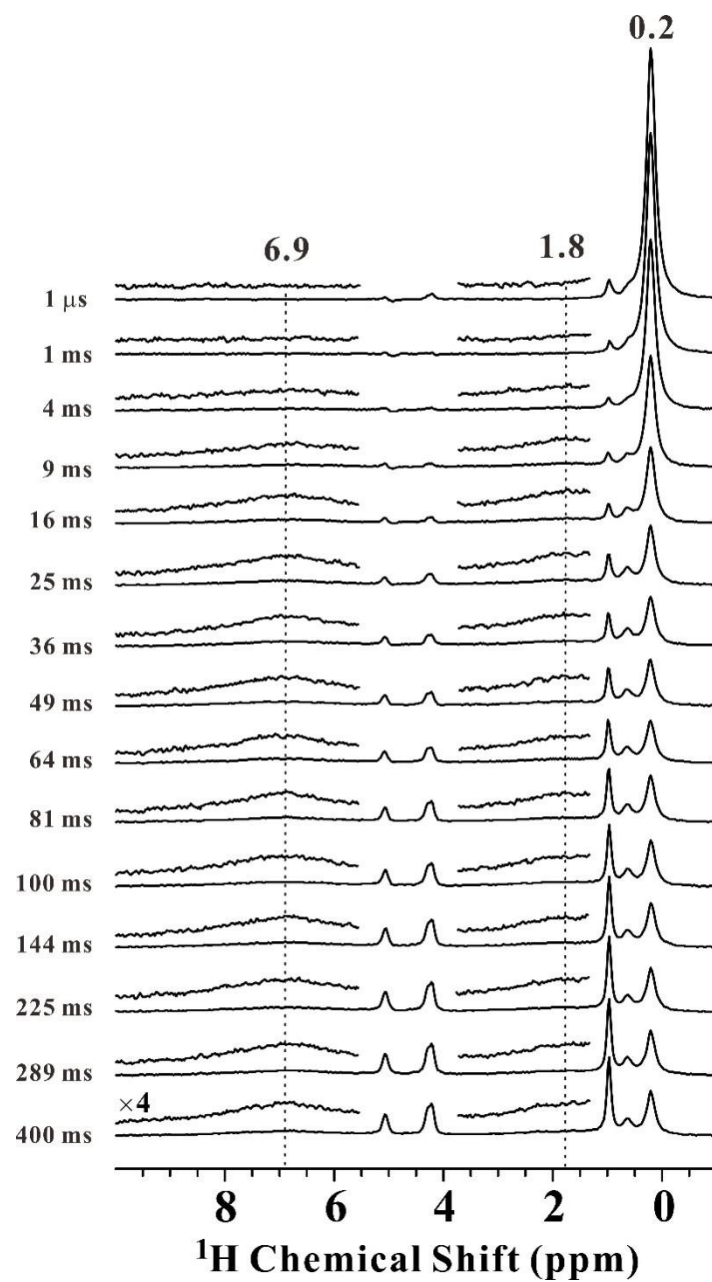


Figure S5. Extracted F_2 slices ($F_1 = 0.2$ ppm) in the 2D ^1H - ^1H T_2 -filtered spin diffusion homo-nuclear correlation NMR spectra of ZIF-8 loaded with propane/propylene mixture with spin diffusion mixing time of $1 \mu\text{s} \sim 400$ ms.

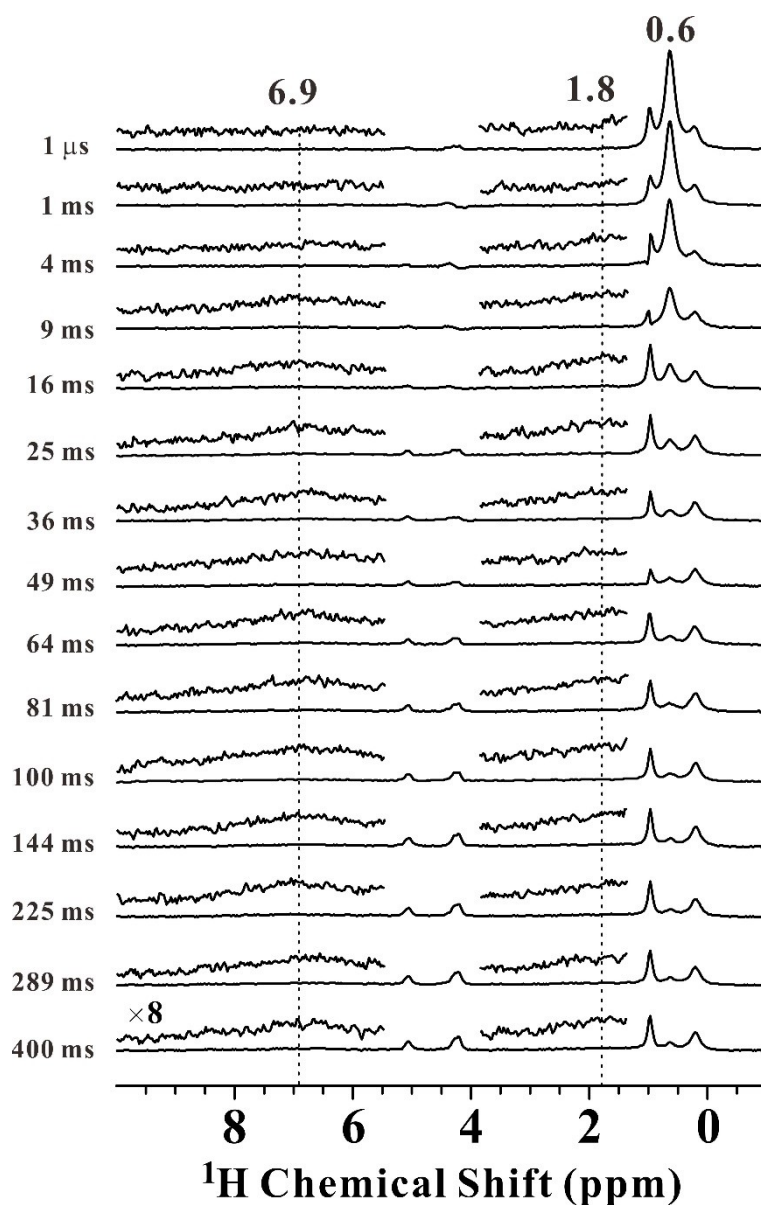


Figure S6. Extracted F_2 slices ($F_1 = 0.6$ ppm) in the 2D ^1H - ^1H T_2 -filtered spin diffusion homo-nuclear correlation NMR spectra of ZIF-8 loaded with propane/propylene mixture with spin diffusion mixing time of $1\ \mu\text{s} \sim 400\ \text{ms}$.

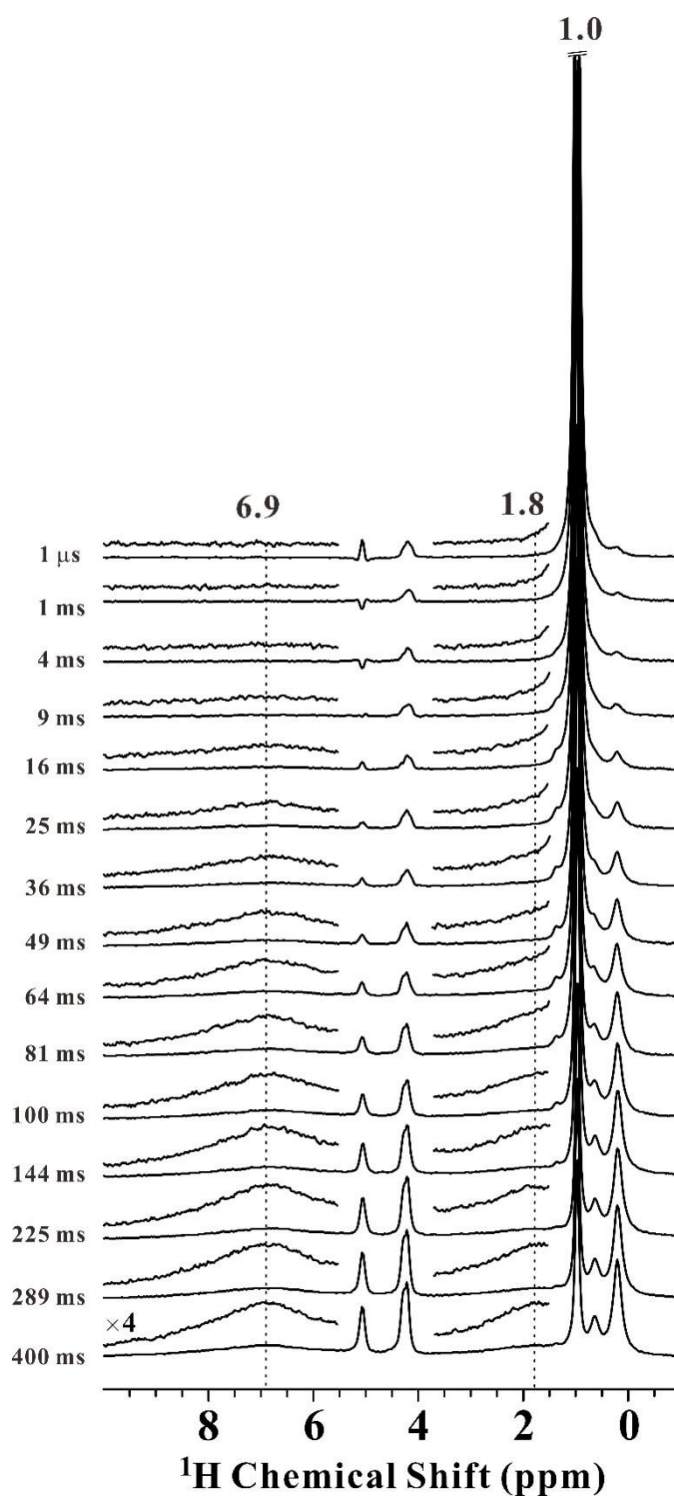


Figure S7. Extracted F_2 slices ($F_1 = 1.0$ ppm) in the 2D ^1H - ^1H T_2 -filtered spin diffusion homo-nuclear correlation NMR spectra of ZIF-8 loaded with propane/propylene mixture with spin diffusion mixing time of $1 \mu\text{s} \sim 400$ ms.

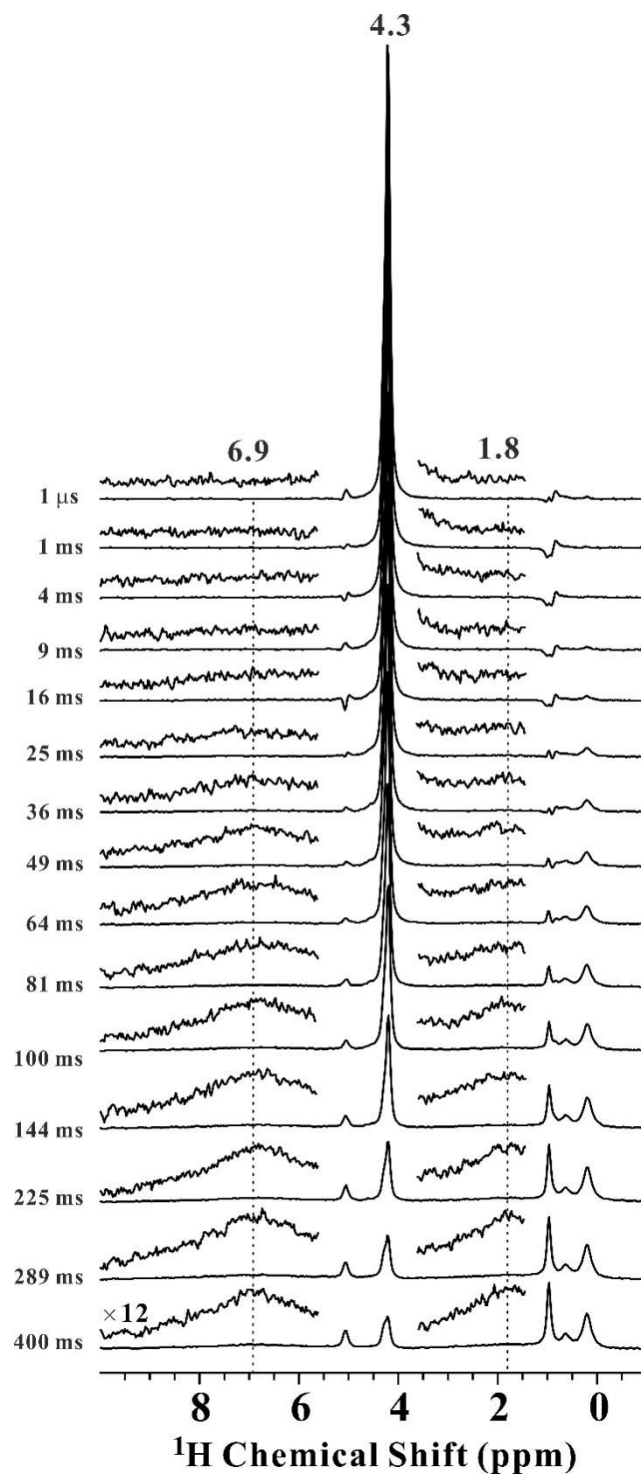


Figure S8. Extracted F_2 slices ($F_1 = 4.3$ ppm) in the 2D ^1H - ^1H T_2 -filtered spin diffusion homo-nuclear correlation NMR spectra of ZIF-8 loaded with propane/propylene mixture with spin diffusion mixing time of $1 \mu\text{s} \sim 400$ ms.

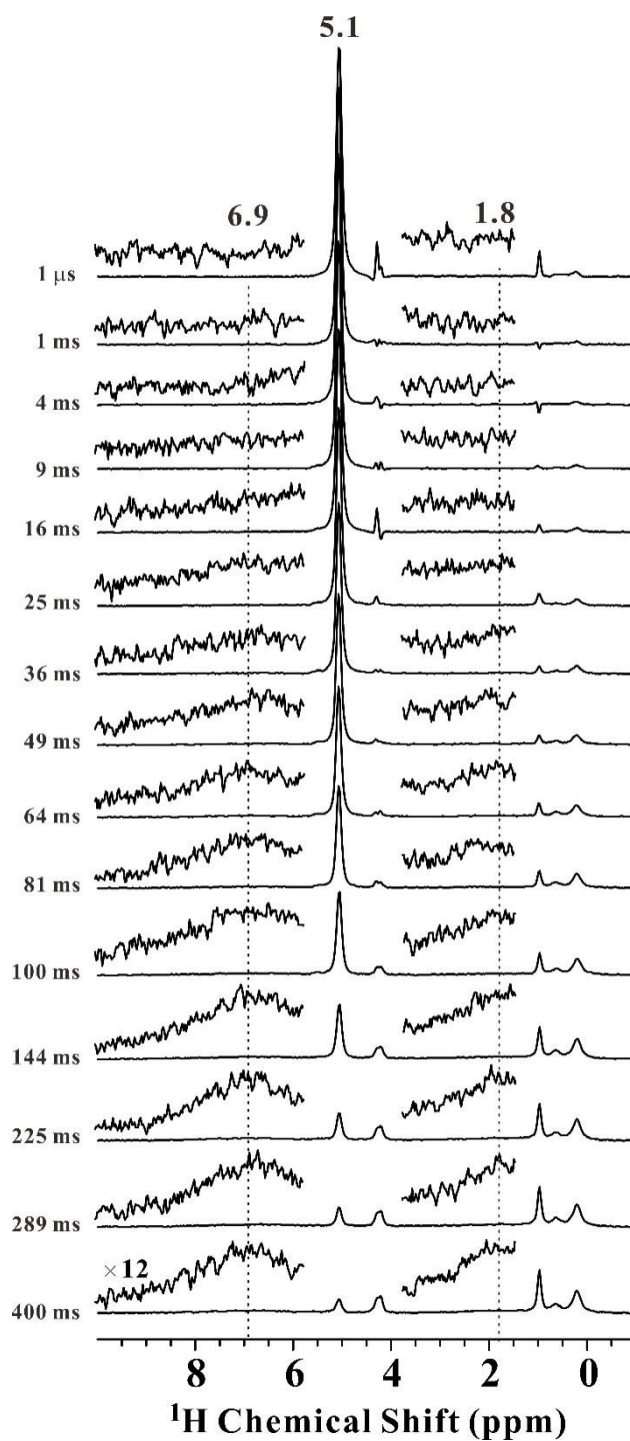


Figure S9. Extracted F_2 slices ($F_1 = 5.1$ ppm) in the 2D ^1H - ^1H T_2 -filtered spin diffusion homo-nuclear correlation NMR spectra of ZIF-8 loaded with propane/propylene mixture with spin diffusion mixing time of 1 μs ~ 400 ms.

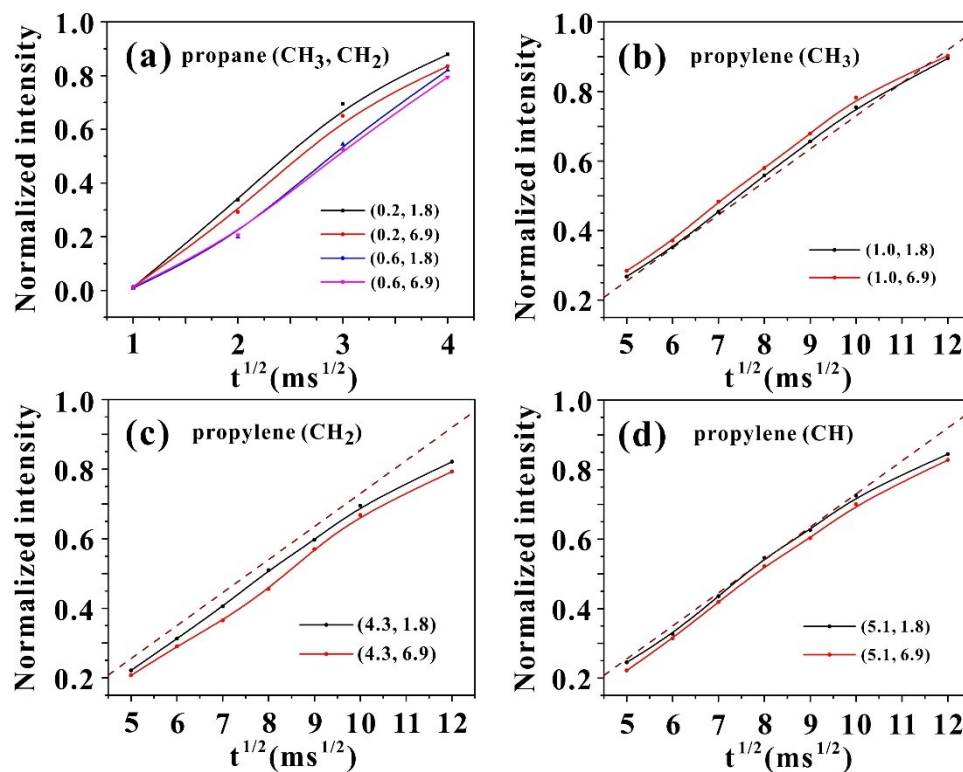


Figure S10. Enlargement of the spin diffusion buildup curves for the designated polarization transfer pathway from propane CH_3 and CH_2 -group (a), and propylene CH_3 -group (b), CH_2 -group (c), CH -group (d) to ZIF-8. The spin diffusion buildup curves are extracted from the normalized correlation peaks intensity in the 2D ^1H - ^1H T_2 -filtered spin diffusion HOMCOR MAS NMR experiments as a function of square root of spin diffusion mixing time in range of 1~16 ms (a) and 25~144 ms (b-d).