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Supporting Information

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Entropic Separations of Mixtures of Aromatics by Selective Face-to-Face Molecular Stacking in One-Dimensional Channels of Metal–Organic Frameworks and Zeolites

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Supporting Information to accompany:

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One-Dimensional Channels of Metal-Organic
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Single component isotherms in AFI zeolite at 433K

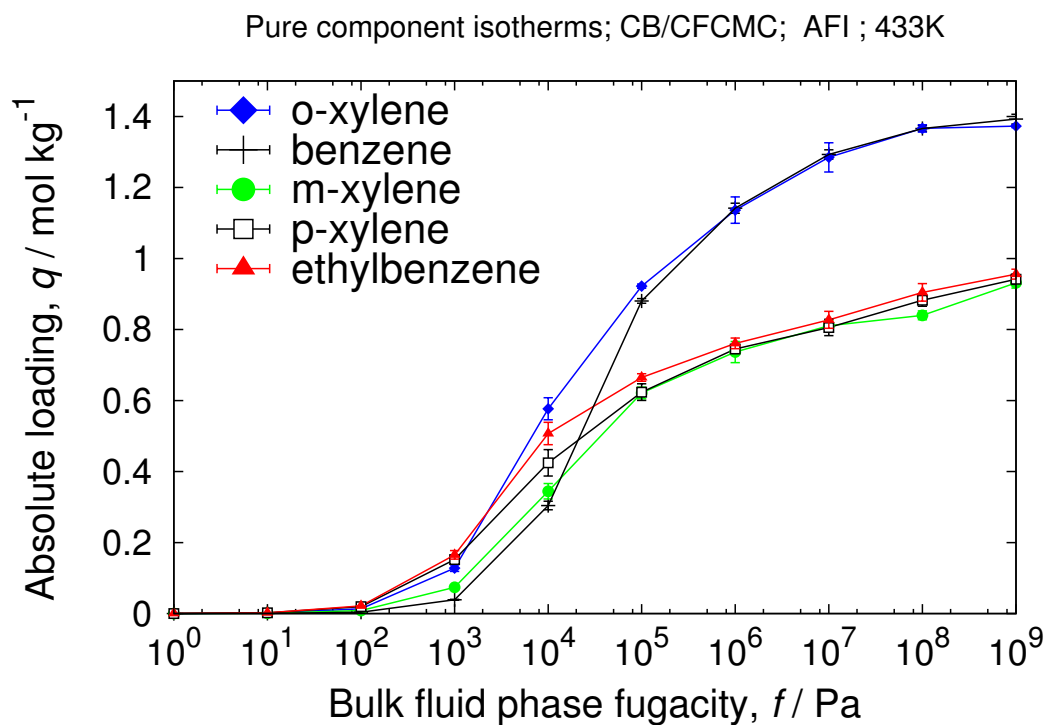


Figure S1: Single component isotherms in AFI zeolite at 433K. At saturation conditions, benzene and o-xylene can reach higher loadings because of molecular reorientation. This can be exploited as a separation mechanism in liquid conditions.

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Single component isotherms in MAZ zeolite at 433K

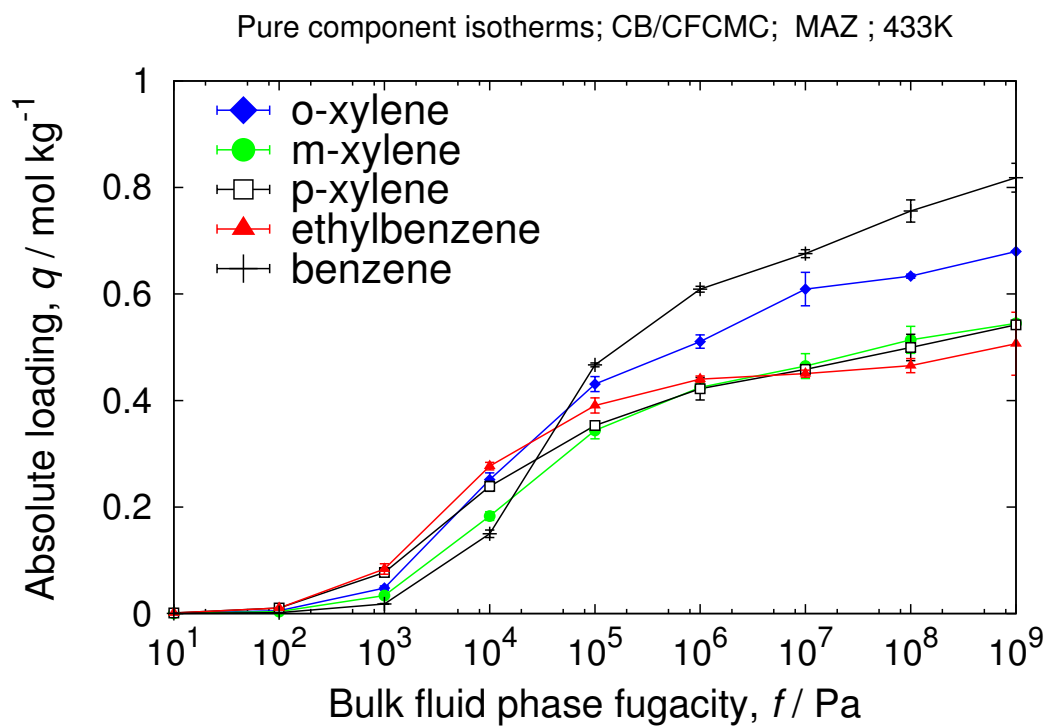


Figure S2: Single component isotherms in MAZ zeolite at 433K. The smaller channel of MAZ compared to AFI allows for a better reorientation of benzene.

3

Heat of adsorption in AFI and MAZ zeolite

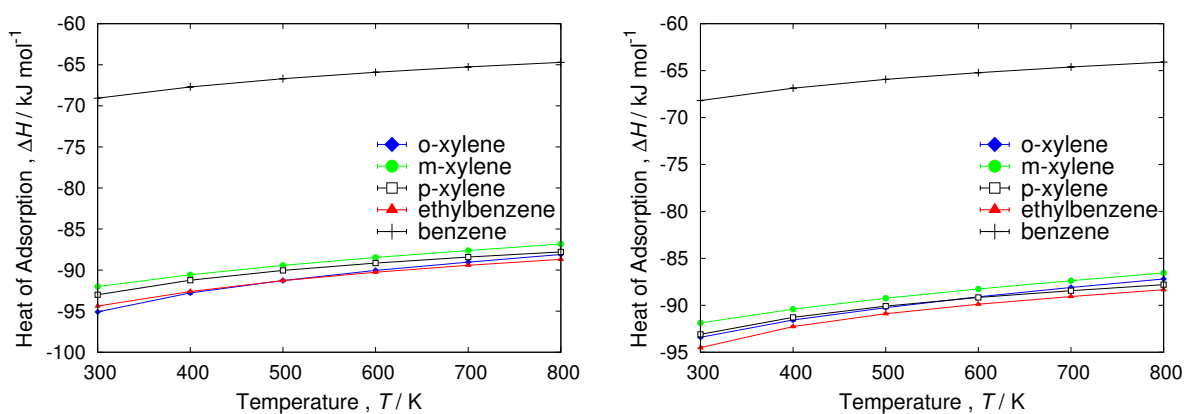


Figure S3: Infinite dilution heat of adsorption of benzene, *o*-, *m*-, *p*-xylene and ethylbenzene in AFI (left) and MAZ (right) zeolites at different temperatures. For AFI zeolite, our results agree qualitatively with the experimental results of Chiang et al. [1]. In the Henry regime, benzene is the least strongly adsorbed species in both zeolites.

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Langmuir-Freundlich parameters for pure component aromatics at 433K in AFI

	site A			site B		
	$q_{i,A,sat}$ [molec. uc ⁻¹]	$b_{i,A}$ [Pa ^{-$\nu_{i,A}$]}	$\nu_{i,A}$ [-]	$q_{i,B,sat}$ [molec. uc ⁻¹]	$b_{i,B}$ [Pa ^{-$\nu_{i,B}$]}	$\nu_{i,B}$ [-]
o-xylene	0.402	7.63×10^{-7}	1	0.957	1.5×10^{-4}	1
m-xylene	0.208	1.26×10^{-7}	1	0.6935	0.6935×10^{-4}	1
p-xylene	0.277	5×10^{-7}	1	0.624	0.624×10^{-4}	1
ethylbenzene	0.208	3.18×10^{-7}	1	0.6935	0.6935×10^{-4}	1
benzene	0.2635	1.94×10^{-7}	1	1.123	1.123×10^{-5}	1
toluene	0.444	4.15×10^{-7}	1	0.929	0.929×10^{-5}	1

Table S1: Dual-site Langmuir-Freundlich parameters for pure component xylene isomers at 433 K in AFI. The saturation capacities are expressed in molecules per unit cell; these numbers need to be multiplied by the conversion factor of 1.082 to get mol kg⁻¹.

$$q_i = q_{i,A,sat} \frac{b_{i,A} f_i^{\nu_{i,A}}}{1 + b_{i,A} f_i^{\nu_{i,A}}} + q_{i,B,sat} \frac{b_{i,B} f_i^{\nu_{i,B}}}{1 + b_{i,B} f_i^{\nu_{i,B}}} \quad (4.1)$$

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$\text{Fe}_2(\text{BDP})_3$ variant

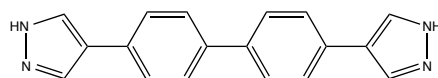
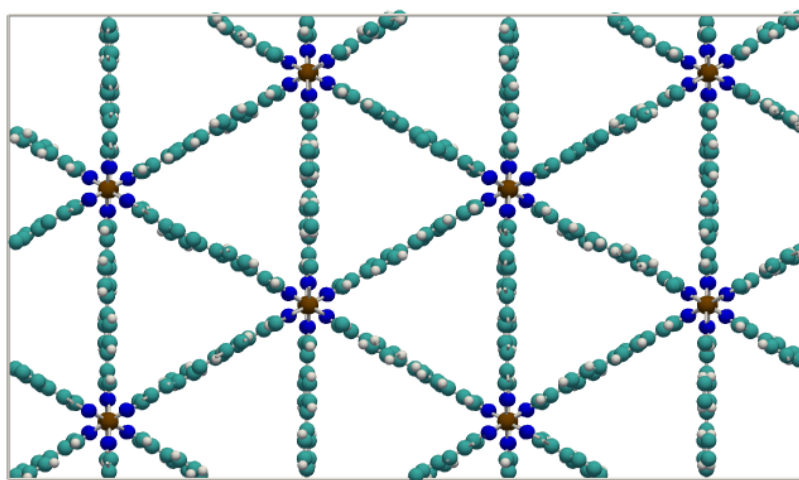


Figure S4: $\text{Fe}_2(\text{BDP})_3$ variant with a 4,4'-bis(1H-pyrazol-4-yl)biphenyl instead of a BDP linker. The topology of the metal organic framework is the same as the $\text{Fe}_2(\text{BDP})_3$, triangular 1D channels running in the z-direction, but the size of the channels is larger due to the extra aromatic molecule in the linker. Color code: organic linker (cyan), iron (brown), nitrogen (blue).

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Single component isotherms of trichlorobenzene isomers

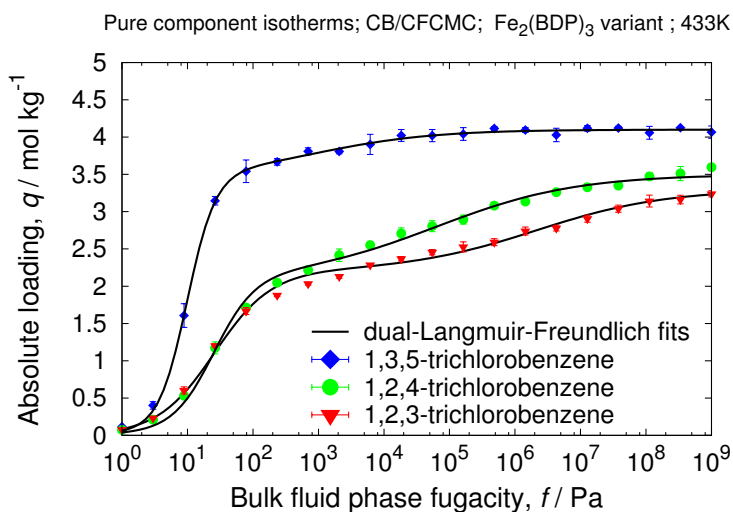


Figure S5: Single component isotherms of 1,3,5-/1,2,4- and 1,2,3-trichlorobenzene in Fe₂(BDP)₃ variant at 433K. The 1,3,5-trichlorobenzene is the only isomer that can reorient within the metal-organic framework channels, which permits a higher saturation capacity.

	site A			site B		
	$q_{i,A,sat}$ [mol. kg ⁻¹]	$b_{i,A}$ [Pa ^{-$\nu_{i,A}$}]	$\nu_{i,A}$ [-]	$q_{i,B,sat}$ [mol. kg ⁻¹]	$b_{i,B}$ [Pa ^{-$\nu_{i,B}$}]	$\nu_{i,B}$ [-]
1,3,5	3.45	1.03×10^{-2}	2	0.65	4.3×10^{-2}	0.47
1,2,4	1.4	1.07×10^{-2}	0.41	2.1	2.1×10^{-2}	1.38
1,2,3	1.1	1.64×10^{-3}	0.44	2.2	2.2×10^{-2}	1

Table S1: Dual-site Langmuir-Freundlich parameters for pure component trichlorobenzene isomers at 433 K in Fe₂(BDP)₃ variant. The saturation capacities are expressed in mol kg⁻¹

Bibliography

- [1] A.S.T. Chiang, C.K. Lee, and Chang Z. H. *Zeolites*, 11:380, 1991.