Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information:

Diffusion as a function of guest molecule length and functionalization in flexible metal-organic frameworks

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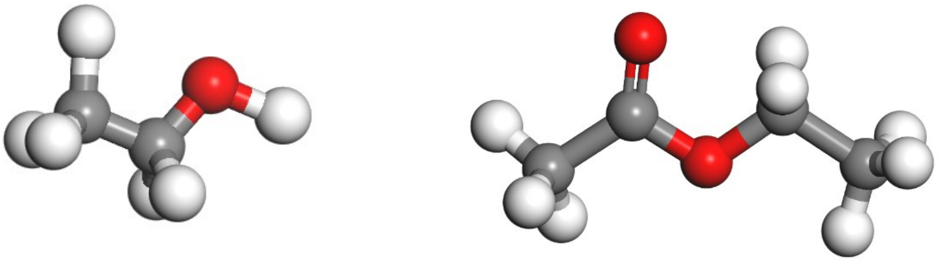
Part 1: Force field parameters



(a) (b)

Figure S1. (a) Ethanol molecule; (b) Ethyl acetate molecule.

Table S1. Bonded force parameters for flexible guest molecules in this study.

	bond potential: $E_{\mathrm{bond}} = K_b(b-b_0)^2$	
type	K_b (kcal·mol^{-1}·Å^{-2})	b_0 (Å)
C_2H_5OH: CH_3-CH_2	2000.0	1.54[a]
C_2H_5OH: CH_2-O	2000.0	1.43[a]
C_2H_5OH: O-H	2000.0	0.95[a]
$CH_3COOC_2H_5$: CH_3-C	2000.0	1.522[b],1.520[c]
$CH_3COOC_2H_5$: C=O	2000.0	1.229 [b],1.200[c]
$CH_3COOC_2H_5$: C-O	2000.0	1.430[b],1.344[c]
$CH_3COOC_2H_5$: CH_2-O	2000.0	1.430[b],1.430[c]
$CH_3COOC_2H_5$: CH_2-CH_3	2000.0	1.535[b],1.540[c]
	bending potential: $E_{\mathrm{bend}} = K_\theta(\theta-\theta_0)^2$	
type	K_θ (kcal·mol^{-1}·rad^{-2})	θ_0 (°)
C_2H_5OH: CH_3-CH_2-O	50.03[a]	109.47[a]

C_2H_5OH: CH_2-O-H	54.99[a]	180.50[a]
$CH_3COOC_2H_5$:CH_3-C=O	105.11[b],62.08[c]	120.40[b],125.00[c]
$CH_3COOC_2H_5$:CH_3-C-O	105.11[b],70.12[c]	119.20[b],110.00[c]
$CH_3COOC_2H_5$:O=C-O	105.11[b],62.08[c]	120.40[b],125.00[c]
$CH_3COOC_2H_5$:C-O-CH_2	68.534[b],62.08[c]	112.00[b],115.00[c]
$CH_3COOC_2H_5$:O-CH_2-CH_3	59.396[b],70.12[c]	109.47[b],110.00[c]

dihedral potentiala: $E_{\mathrm{proper}} = K_{\varphi}\,[1 + \cos(n\,\varphi - \varphi_0)]$

type	K_{φ} ($\mathrm{kcal \cdot mol^{-1}}$)	n	φ_0 (°)
C_2H_5OH: CH_3-CH_2-O-H	0.425[a]	3[a]	180.0[a]
$CH_3COOC_2H_5$:C-O-CH_2-CH_3	1.202[b],1.646[c]	3[b,c]	180.0[b,c]
$CH_3COOC_2H_5$:O=C-O-CH_2	5.980[b],5.384[c]	2[b,c]	180.0[b,c]
$CH_3COOC_2H_5$:C-O-CH_3-C-O-CH_2	6.119[b],6.120[c]	2[b,c]	180.0[b,c]

[a] Chen, B.; Potoff, J. J.; Siepmann, J. I., Monte Carlo Calculations for Alcohols and Their Mixtures with Alkanes. Transferable Potentials for Phase Equilibria. 5. United-Atom Description of Primary, Secondary, and Tertiary Alcohols. *J. Phys. Chem. B* **2001**, *105*, 3093-3104.

[b] Ferrando, N.; Lachet, V.; Boutin, A., Transferable Force Field for Carboxylate Esters: Application to Fatty Acid Methylic Ester Phase Equilibria Prediction. *J. Phys. Chem. B* **2012**, *116*, 3239-3248.

[c] Kamath, G.; Robinson, J.; Potoff, J. J., Application of Trappe-Ua Force Field for Determination of Vapor–Liquid Equilibria of Carboxylate Esters. *Fluid Phase Equilib.* **2006**, *240*, 46-55.

Table S2. Non-bonded force parameters for guest molecules in this study.

type		VDW interaction		partial charges
		ε (kcal/mol)	σ (Å)	q (e)
C_2H_5OH	CH_3-(CH_2)	0.2385 [a], 0.1946 [b]	3.607 [a], 3.750 [b]	0.0000 [a,b]
	(CH_3)-CH_2-(OH)	0.1713 [a], 0.0913 [b]	3.461 [a], 3.950 [b]	+0.2556[a], +0.2650 [b]
	(CH_2)-O-(H)	0.1688 [a], 0.1846 [b]	3.150 [a], 3.020 [b]	-0.6971 [a], -0.7000 [b]
	H-(O)	---	---	+0.4415 [a], +0.4350 [b]
$CH_3COOC_2H_5$	CH_3-(C)	0.2385[c], 0.1945[d]	3.607 [c], 3.750 [d]	-0.0890 [c], +0.0500 [d]
	(CH_3)-C-(O)	0.1229 [c], 0.0814 [d]	3.020 [c], 3.900 [d]	+0.4840 [c], +0.5500 [d]
	O=(C)	0.1916 [c], 0.1568 [d]	2.981 [c], 3.050 [d]	-0.3770 [c], -0.4500 [d]
	(C)-O-(CH_2)	0.1185 [c], 0.1092 [d]	2.991 [c], 2.800 [d]	-0.3370 [c], -0.4000 [d]
	(O)-CH_2-(CH_3)	0.1713 [c], 0.0913 [d]	3.461 [c], 3.950 [d]	+0.3190 [c],+ 0.2500 [d]
	CH_3-(CH_2)	0.2385 [c], 0.1945 [d]	3.607 [c], 3.750 [d]	0.0000 [c, d]

[a] Guevara-Carrion, G.; Nieto-Draghi, C.; Vrabec, J.; Hasse, H., Prediction of Transport Properties by Molecular Simulation: Methanol and Ethanol and Their Mixture. *J. Phys. Chem. B* **2008**, *112*, 16664-16674.

[b] Chen, B.; Potoff, J. J.; Siepmann, J. I., Monte Carlo Calculations for Alcohols and Their Mixtures with Alkanes. Transferable Potentials for Phase Equilibria. 5. United-Atom Description of Primary, Secondary, and Tertiary Alcohols. *J. Phys. Chem. B* **2001**, *105*, 3093-3104.

[c] Ferrando, N.; Lachet, V.; Boutin, A., Transferable Force Field for Carboxylate Esters: Application to Fatty Acid Methylic Ester Phase Equilibria Prediction. *J. Phys. Chem. B* **2012**, *116*, 3239-3248.

[d] Kamath, G.; Robinson, J.; Potoff, J. J., Application of Trappe-Ua Force Field for Determination of Vapor–Liquid Equilibria of Carboxylate Esters. *Fluid Phase Equilib.* **2006**, *240*, 46-55.

Part 2: Adsorption position

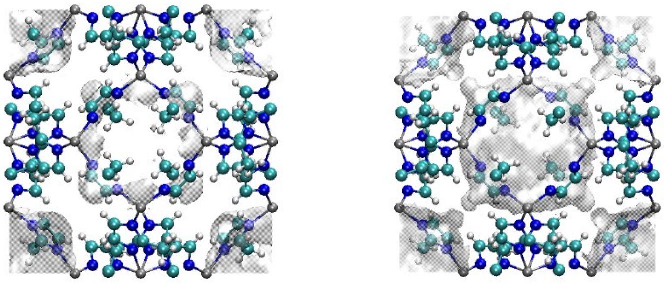

(a) (b)

Figure S2. Isoprobability contours for ethanol (C_2H_5OH) inside one unit cell of ZIF-8, xy-plane projections computed for (a) OH terminal and (b) CH_3 terminal of C_2H_5OH, with darker areas denoting higher probability.

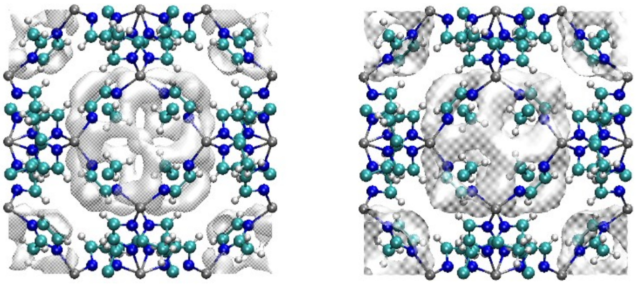

(a) (b)

Figure S3. Isoprobability contours for Ethyl acetate ($CH_3COOC_2H_5$) inside one unit cell of ZIF-8, xy-plane projections computed for (a) CH_3(–CO) terminal and (b) CH_3 (–CH_2) terminal of $CH_3COOC_2H_5$, with darker areas denoting higher probability.

Part 3: residence time of guests in ZIF-8 cage

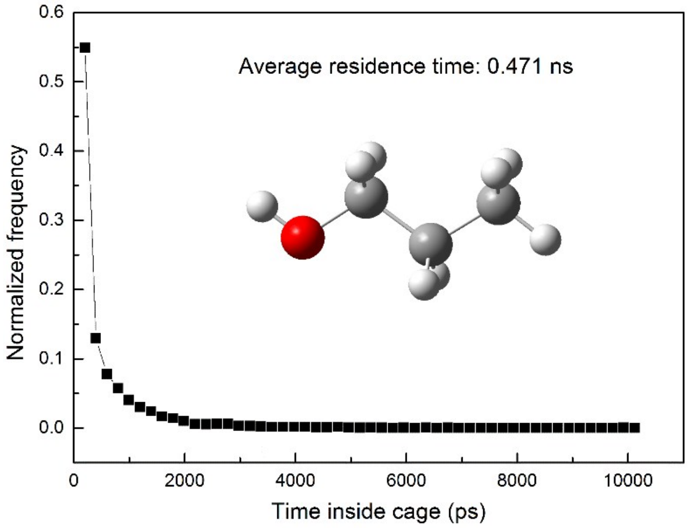


Figure S4. Residence time of propanol inside ZIF-8 cage.

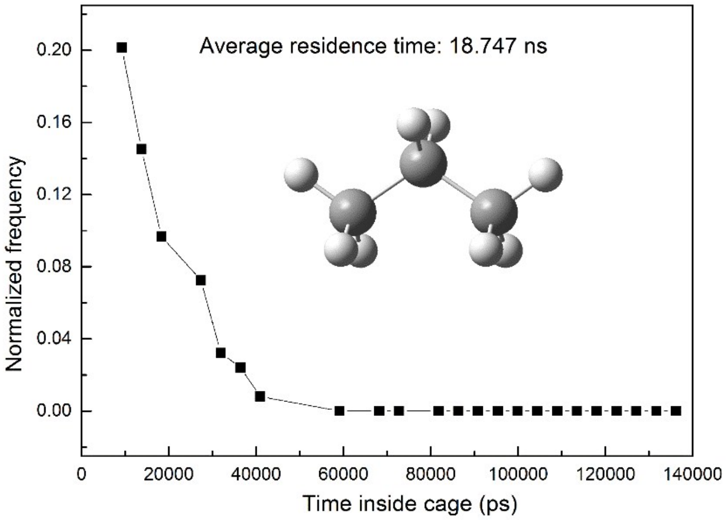


Figure S5. Residence time of propane inside ZIF-8 cage.

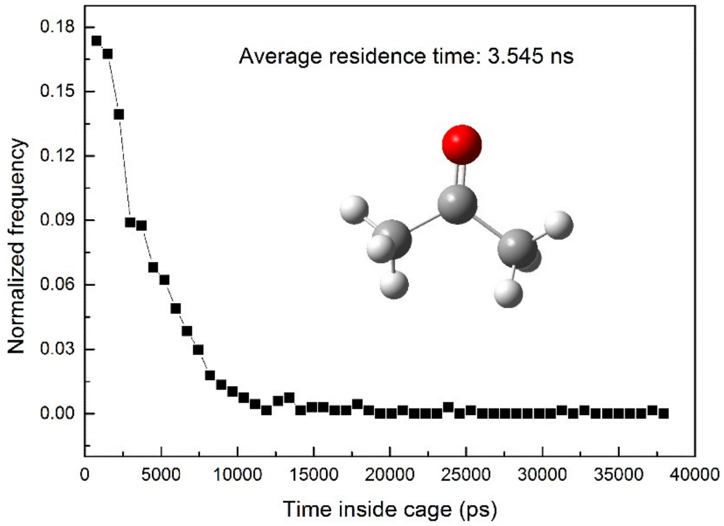


Figure S6. Residence time of acetone inside ZIF-8 cage.

Part 4: Preferential path for the guest passing through ZIF-8 gate

In order to find the most preferential path for the guest passing through ZIF-8 gate, we used the strategy of potential energy scan (PES), as shown in Figure S7. A hydrogen atom in the corner was created and it is frozen in calculation. And the distance, between the predefined hydrogen atom and one terminal atom of guest molecule (Figure S7), was used to define the position of guest. With the decreasing of the distance, the guest molecule approaches and passes through the ZIF-8 gate. For every position of guest molecule, we fixed the distance and performed a geometry optimization calculation. Then, the most probable orientation of guest and the preferential configuration of the gate were obtained. It should be noted that the added hydrogen atom with small mass and electrical neutrality is not strong enough to negatively impact on the searching for the preferential path for guest. After the geometry position was obtained, we deleted the hydrogen atom on corner and performed a single point energy calculation. The largest energy value is the energy barrier for the guest passing through gate.

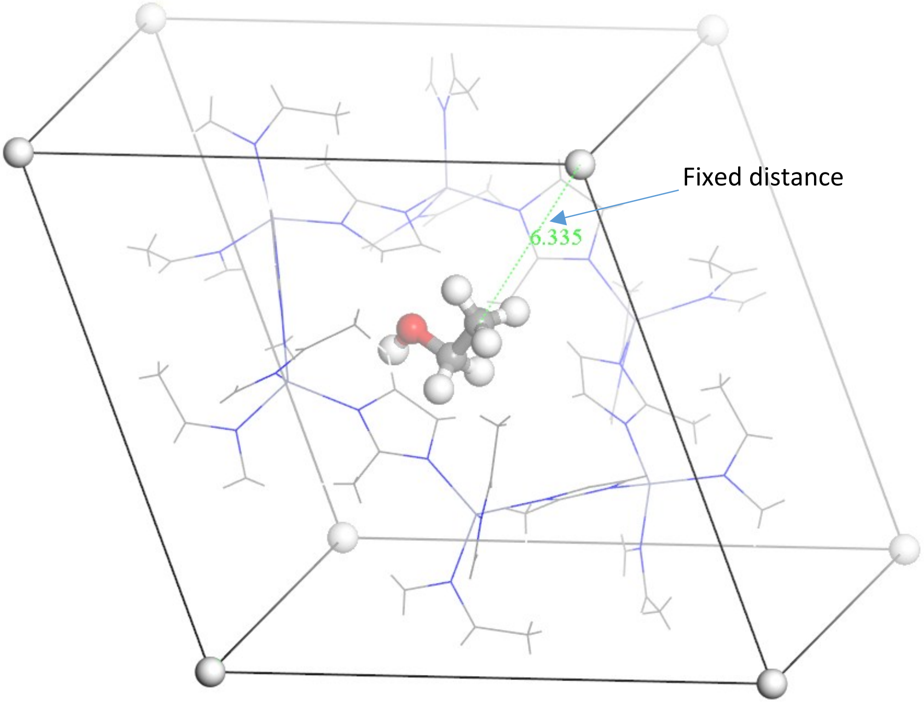


Figure S7. Calculation model to search for the potential energy barrier.