Electronic Supplementary Information

Biofuel Purification by Pervaporation and Vapor Permeation in Metal–Organic Frameworks: A Computational Study

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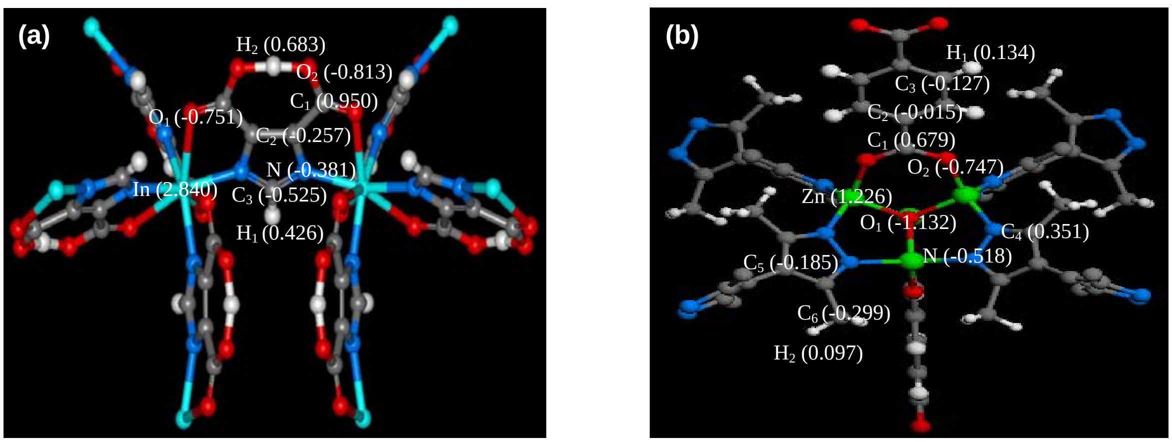

Figure S1. Atomic charges in the fragmental clusters of (a) *rho*-ZMOF and (b)$Zn_4O(bdc)(bpz)_2$. Color code: In, cyan; Zn, green; N, blue; C, grey; O, red; and H, white.

Atom	σ (Å)	ε (kJ/mol)
In	3.976	2.504
Zn	2.461	0.519
N	3.260	0.288
O	3.118	0.251
C	3.431	0.439
H	2.571	0.184
Na	15.10	2.658

Table S1. Lennard-Jones potential parameters of the framework atoms in Na-*rho*-ZMOF and $Zn_4O(bdc)(bpz)_2$.

Table S2. Potential parameters of adsorbates (water, methanol and ethanol).

Adsorbates	LJ parameters and Charges				Bond stretching	Bond bending
	Site	σ (Å)	ε/k_B (K)	q (e)		
water	O	3.151	76.47	–0.834	$r_{H\text{-}O}$ = 0.96 Å	$\theta_{\angle H\text{-}O\text{-}H}$ = 104.52°
	H	0	0	+0.417	k_b/k_B = 533020.66 K	k_θ/k_B = 34264.61 K
methanol	CH_3	3.75	98.0	+0.265	$r_{CH3\text{-}O}$ = 1.43 Å	$\theta_{\angle CH3\text{-}O\text{-}H}$ = 108.5°
	O	3.02	93.0	–0.700	$r_{O\text{-}H}$ = 0.945 Å	k_θ/k_B = 55400 K
	H	0	0	+0.435		
ethanol	CH_3	3.75	98.0	0	$r_{CH3\text{-}CH2}$ = 1.54 Å	$\theta_{\angle CH3\text{-}CH2\text{-}O}$ = 109.47°
	CH_2	3.95	46.0	+0.265	$r_{CH2\text{-}O}$ = 1.43 Å	k_θ/k_B = 50400 K
	O	3.02	93.0	–0.700	$r_{O\text{-}H}$ = 0.945 Å	$\theta_{\angle CH2\text{-}O\text{-}H}$ = 108.5°
	H	0	0	+0.435		k_θ/k_B = 55400 K

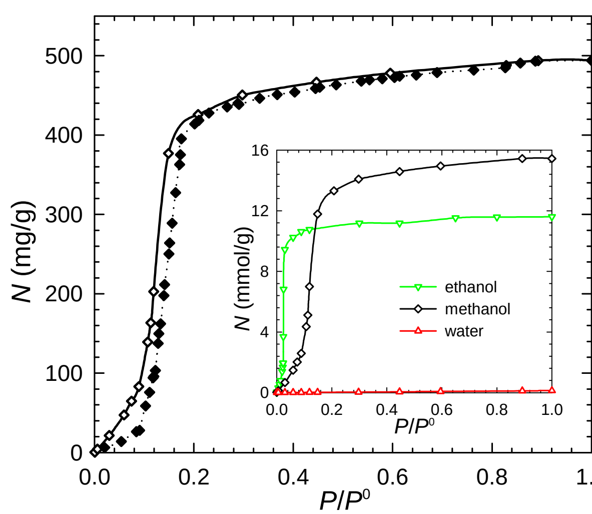

Figure S2. Adsorption isotherms of methanol in $Zn_4O(bdc)(bpz)_2$ at 298 K. The open diamonds are the simulation results of this work, and the filled diamonds are experimental data (Hou et al. *Inorg. Chem.* 2008, 47, 1346). Good agreement between the simulation and experimental results. The inset shows the isotherms of single-component ethanol, methanol and water.

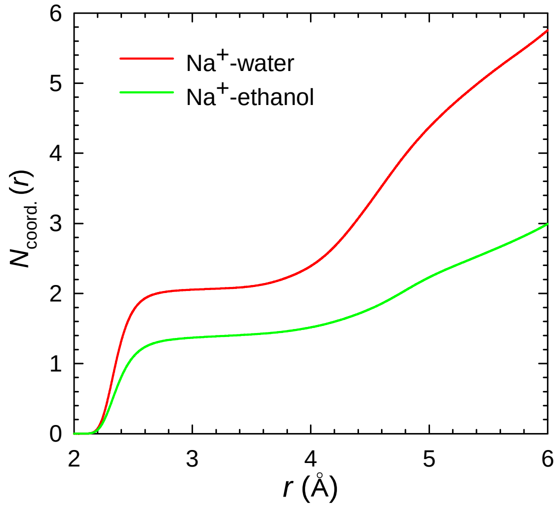

Figure S3. Coordination numbers of water and ethanol around Na^+ ions for water/ethanol mixture (10:90) at PV condition in Na-*rho*-ZMOF.

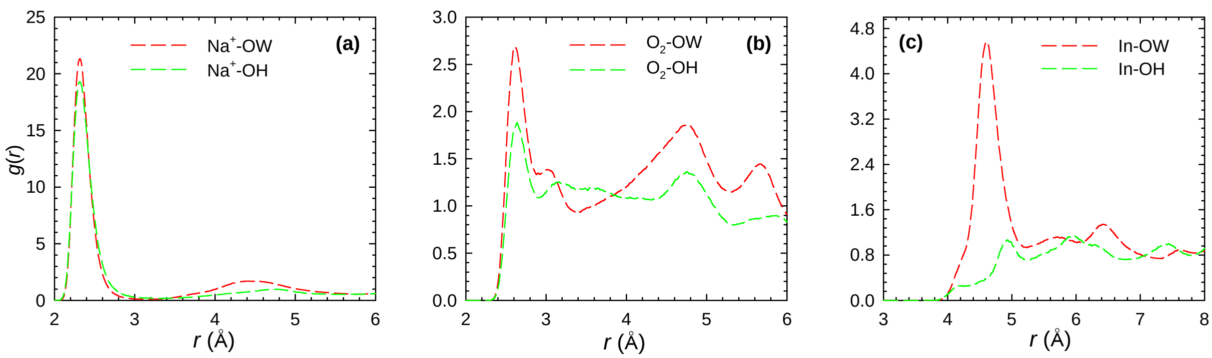

Figure S4. Radial distribution functions of (a) Na^+-OW (OH), (b) O_2-OW (OH), and (c) In-OW (OH) for water/ethanol mixture (10:90) at PV condition in Na-*rho*-ZMOF. OW and OH are the oxygen atoms in water and ethanol, respectively.

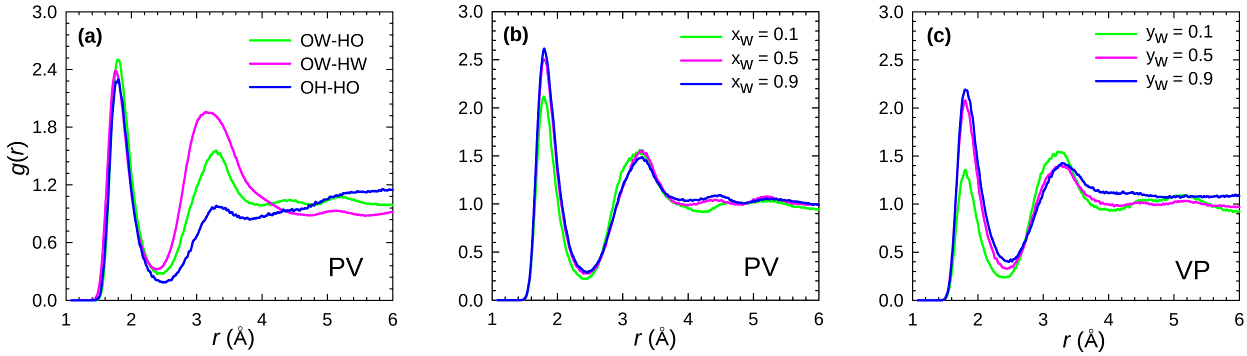

Figure S5. Radial distribution functions of (a) O_{water}-$H_{ethanol}$, O_{water}-H_{water} and $O_{ethanol}$-$H_{ethanol}$ for water/ethanol equimolar mixture at PV condition. (b) O_{water}-$H_{ethanol}$ at PV condition and (c) O_{water}-$H_{ethanol}$ at VP condition with various feed compositions in Na-*rho*-ZMOF.

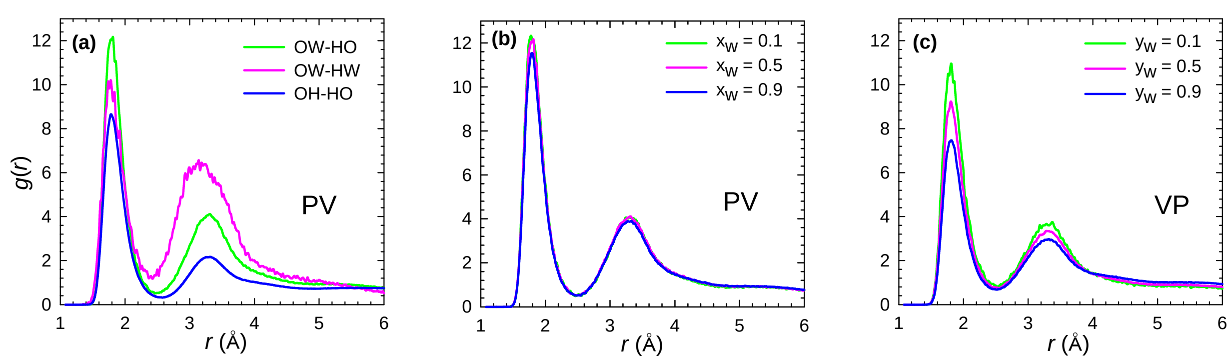

Figure S6. Radial distribution functions of (a) O_{water}-$H_{ethanol}$, O_{water}-H_{water} and $O_{ethanol}$-$H_{ethanol}$ for water/ethanol equimolar mixture at PV condition. (b) O_{water}-$H_{ethanol}$ at PV condition and (c) O_{water}-$H_{ethanol}$ at VP condition with various feed compositions in $Zn_4O(bdc)(bpz)_2$.

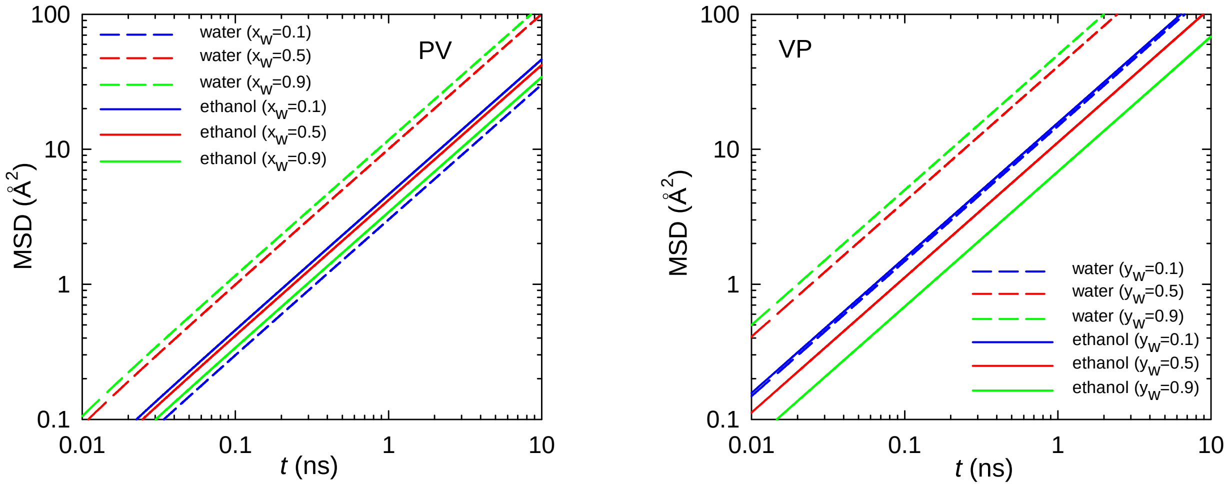

Figure S7. Mean-squared displacements for water/ethanol mixtures in Na-*rho*-ZMOF with various feed compositions.

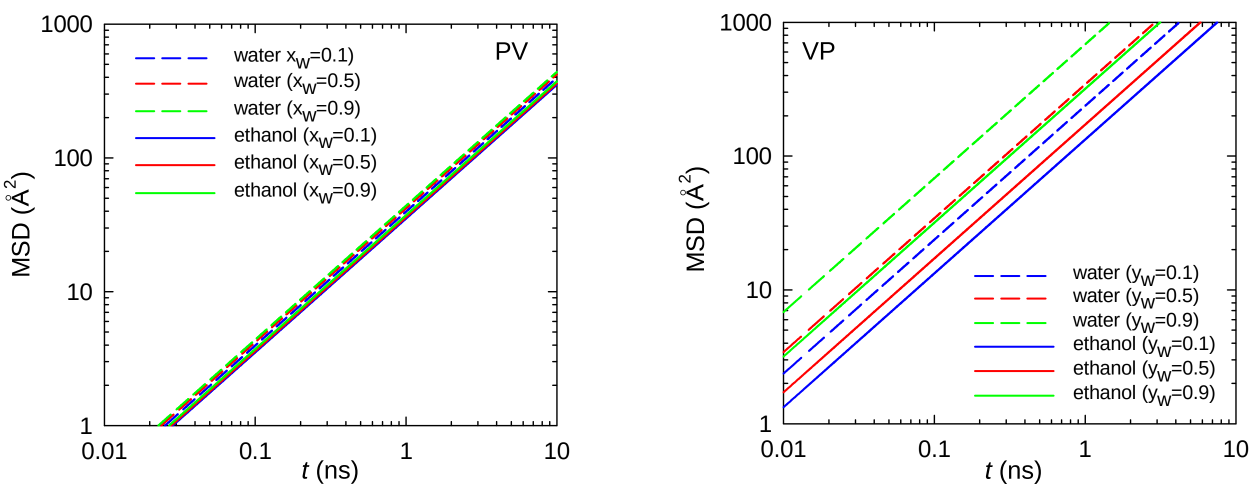

Figure S8. Mean-squared displacements for ethanol/water mixtures in $Zn_4O(bdc)(bpz)_2$ with various feed compositions.