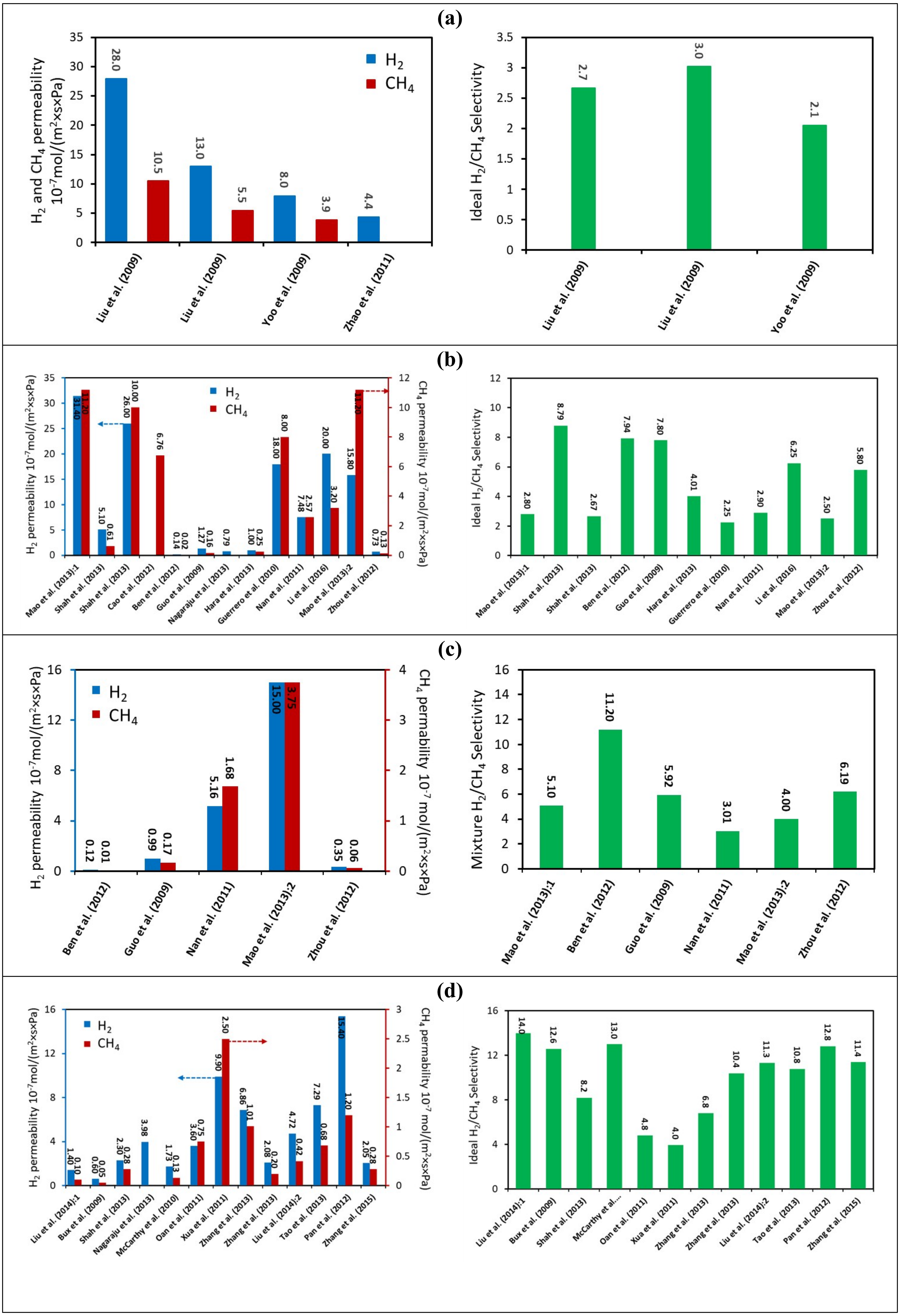
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Simulation of H_2/CH_4 Mixture Permeation through MOF Membranes Using Non-Equilibrium Molecular Dynamics

Sadiye Velioglu and Seda Keskin*

Department of Chemical and Biological Engineering, Koc University, Rumelifeneri Yolu, Sariyer, 34450, Istanbul, Turkey
*Email - skeskin@ku.edu.tr


(a)
H2 and CH4 permeability 10-7mol/(m2×s×Pa)
H2
CH4
28.0
10.5
13.0
5.5
8.0
3.9
4.4
Liu et al. (2009)
Liu et al. (2009)
Yoo et al. (2009)
Zhao et al. (2011)
Ideal H2/CH4 Selectivity
2.7
3.0
2.1
Liu et al. (2009)
Liu et al. (2009)
Yoo et al. (2009)
(b)
H2 permeability 10-7mol/(m2×s×Pa)
CH4 permeability 10-7mol/(m2×s×Pa)
H2
CH4
31.40
11.20
5.10
0.61
26.00
10.00
6.76
0.02
0.14
1.27
0.16
0.79
1.00
0.25
18.00
8.00
7.48
2.57
20.00
3.20
15.80
11.20
0.73
0.13
Mao et al. (2013);1
Shah et al. (2013)
Shah et al. (2013)
Cao et al. (2012)
Ben et al. (2012)
Guo et al. (2009)
Nagaraju et al. (2013)
Hara et al. (2013)
Guerrero et al. (2010)
Nan et al. (2011)
Li et al. (2016)
Mao et al. (2013);2
Zhou et al. (2012)
Ideal H2/CH4 Selectivity
2.80
8.79
2.67
7.94
7.80
4.01
2.25
2.90
6.25
2.50
5.80
Mao et al. (2013);1
Shah et al. (2013)
Shah et al. (2013)
Ben et al. (2012)
Guo et al. (2009)
Hara et al. (2013)
Guerrero et al. (2010)
Nan et al. (2011)
Li et al. (2016)
Mao et al. (2013);2
Zhou et al. (2012)
(c)
H2 permeability 10-7mol/(m2×s×Pa)
CH4 permeability 10-7 mol/(m2×s×Pa)
H2
CH4
0.12
0.01
0.99
0.17
5.16
1.68
15.00
3.75
0.35
0.06
Ben et al. (2012)
Guo et al. (2009)
Nan et al. (2011)
Mao et al. (2013);2
Zhou et al. (2012)
Mixture H2/CH4 Selectivity
5.10
11.20
5.92
3.01
4.00
6.19
Mao et al. (2013);1
Ben et al. (2012)
Guo et al. (2009)
Nan et al. (2011)
Mao et al. (2013);2
Zhou et al. (2012)
(d)
H2 permeability 10-7mol/(m2×s×Pa)
CH4 permeability 10-7 mol/(m2×s×Pa)
H2
CH4
1.40
0.10
0.60
0.05
2.30
0.28
3.98
1.73
0.13
3.60
0.75
9.90
2.50
6.86
1.01
2.08
0.20
4.72
0.42
7.29
0.68
15.40
1.20
2.05
0.28
Liu et al. (2014);1
Bux et al. (2009)
Shah et al. (2013)
Nagaraju et al. (2013)
McCarthy et al. (2010)
Oan et al. (2011)
Xua et al. (2011)
Zhang et al. (2013)
Zhang et al. (2013)
Liu et al. (2014);2
Tao et al. (2013)
Pan et al. (2012)
Zhang et al. (2015)
Ideal H2/CH4 Selectivity
14.0
12.6
8.2
13.0
4.8
4.0
6.8
10.4
11.3
10.8
12.8
11.4
Liu et al. (2014);1
Bux et al. (2009)
Shah et al. (2013)
McCarthy et al....
Oan et al. (2011)
Xua et al. (2011)
Zhang et al. (2013)
Zhang et al. (2013)
Liu et al. (2014);2
Tao et al. (2013)
Pan et al. (2012)
Zhang et al. (2015)

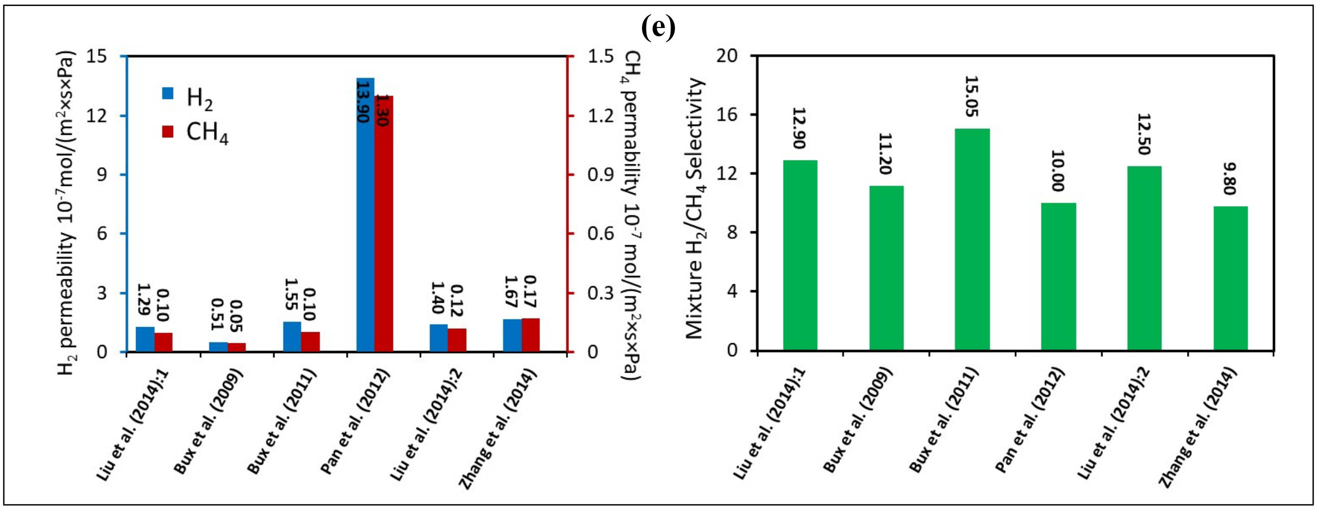


Figure S1. Experimental membrane data reported for (a) MOF-5[1-3], (b) and (c) Cu-BTC[4-15] and (d) and (e) ZIF-8[16-27]. (a), (b) and (d) represent the single-component H_2 and CH_4 permeabilities and ideal selectivities for MOF-5, Cu-BTC and ZIF-8, respectively. (c) and (e) represent the binary gas mixture (H_2/CH_4: 50/50) permeabilities and selectivities for Cu-BTC and ZIF-8, respectively.

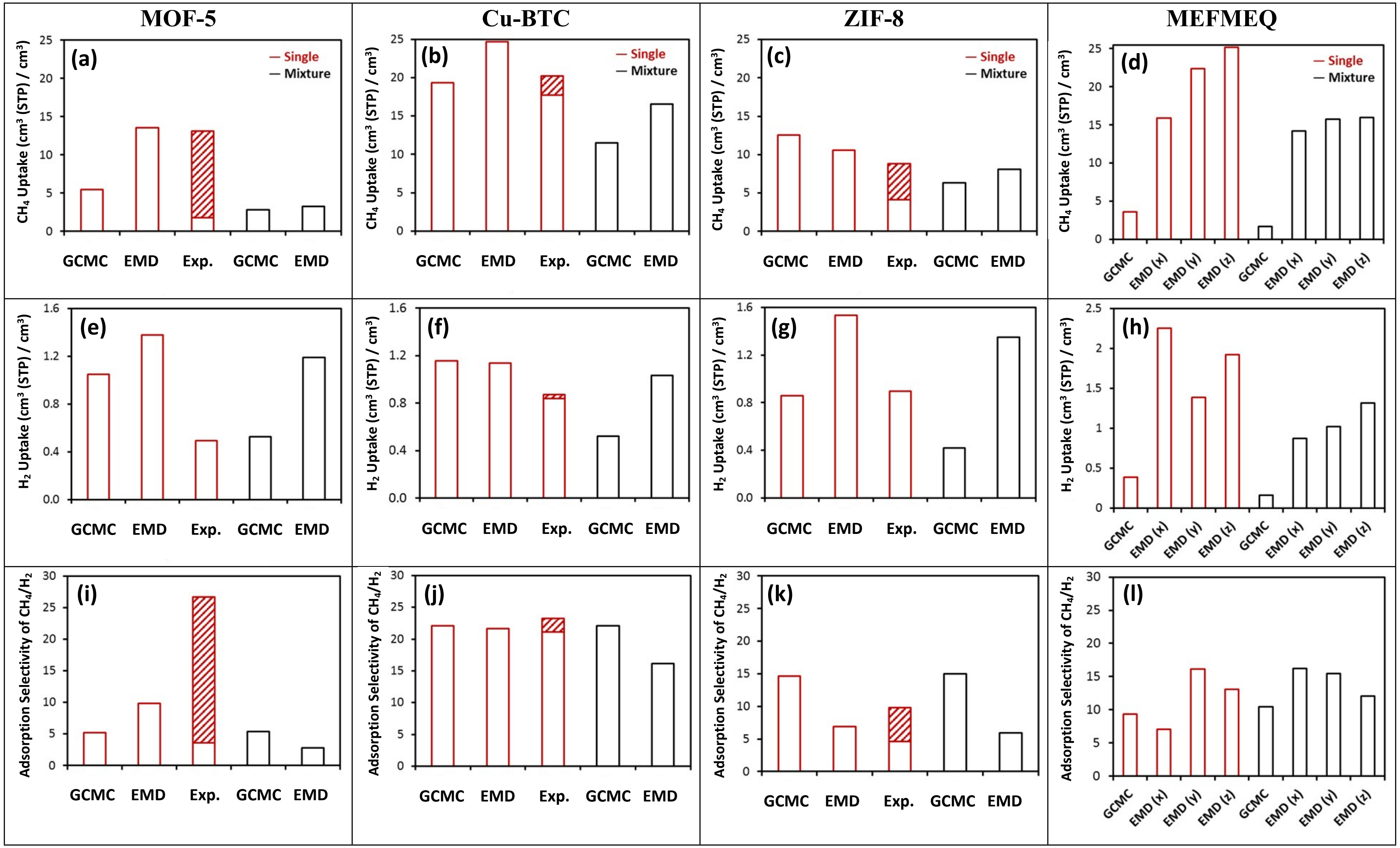


Figure S2. (a) – (d) CH_4, (e) – (h) H_2 adsorption properties, (i) – (l) H_2/CH_4 adsorption selectivities of MOF-5, Cu-BTC, ZIF-8, and MEFMEQ. Single-component and binary gas mixture properties are shown with red and black columns. EMD simulations for the adsorption calculations were performed without any external force in this study. The filled part with a pattern in the experimental data represents the variations by showing the minimum and maximum values corresponding to its bottom and top borders. Adsorption mechanism is investigated at each surface of MEFMEQ due to its asymmetry. Experimental gas uptakes (referred as Exp.) available in the literature are given in Table S1.

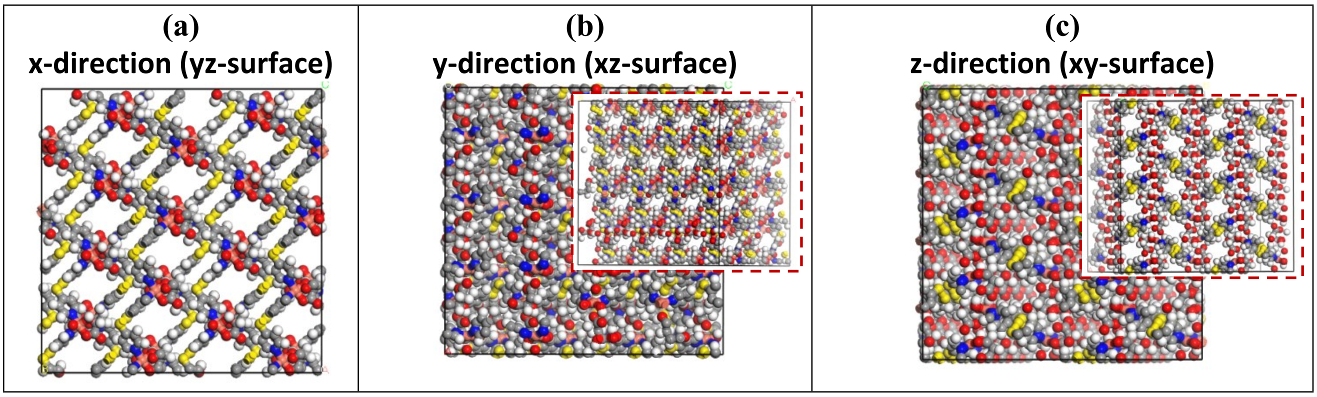


Figure S3. Unit cell view of MEFMEQ from (a) x, (b) y and (c) z direction. The inset snapshots are given for the clarification of the available paths for gas transport.

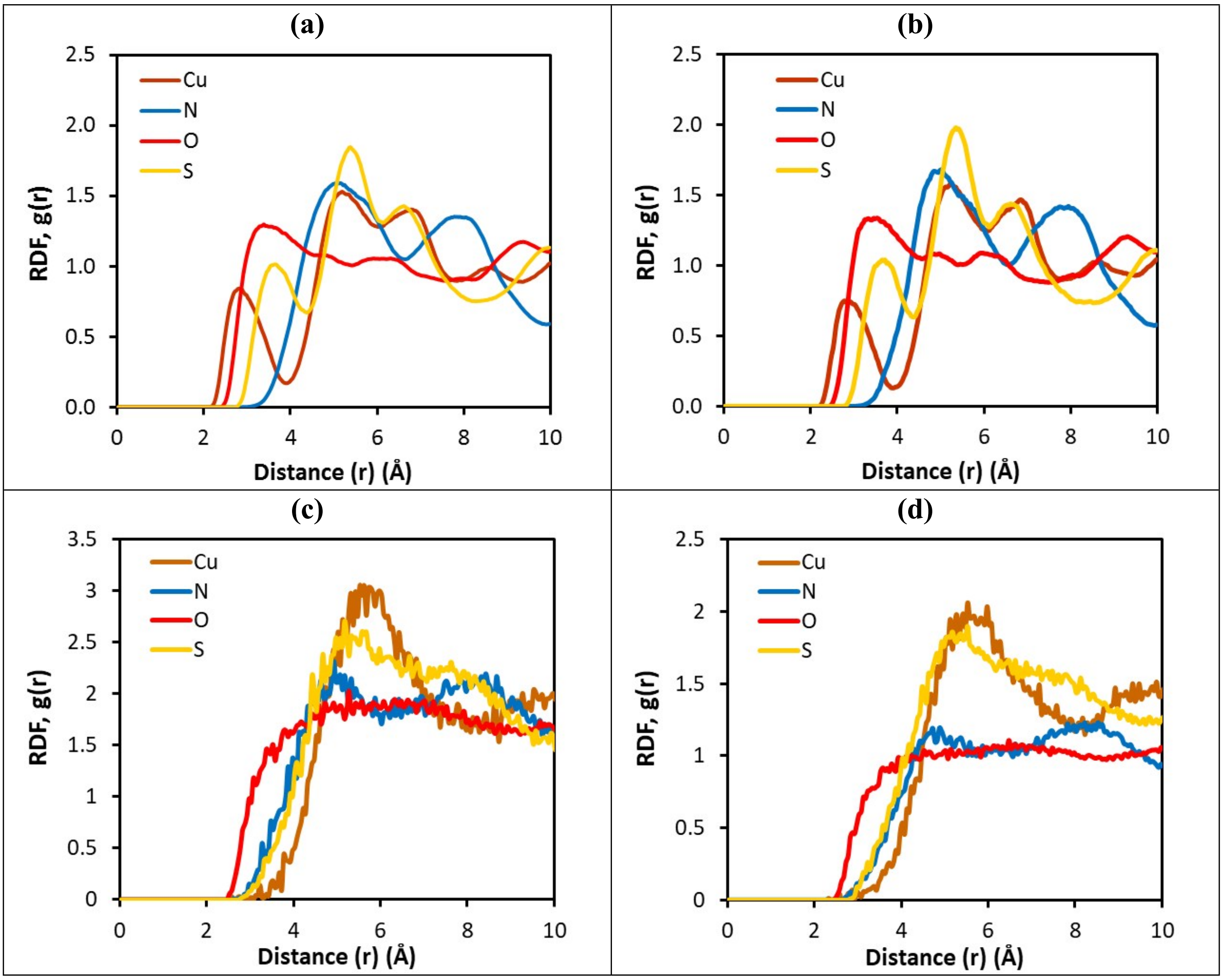


Figure S4. Radial distribution functions (RDF) between the adsorbate, H_2 and four different atom types (namely, Cu, N, O, and S) existing in the framework of MEFMEQ defined by (a) single-component EMD simulations, (b) mixture EMD simulations, (c) single-component NEMD simulations, and (d) mixture NEMD simulations. H_2 population around Cu, N, O, and S atoms is represented by brown, blue, red and yellow colors.

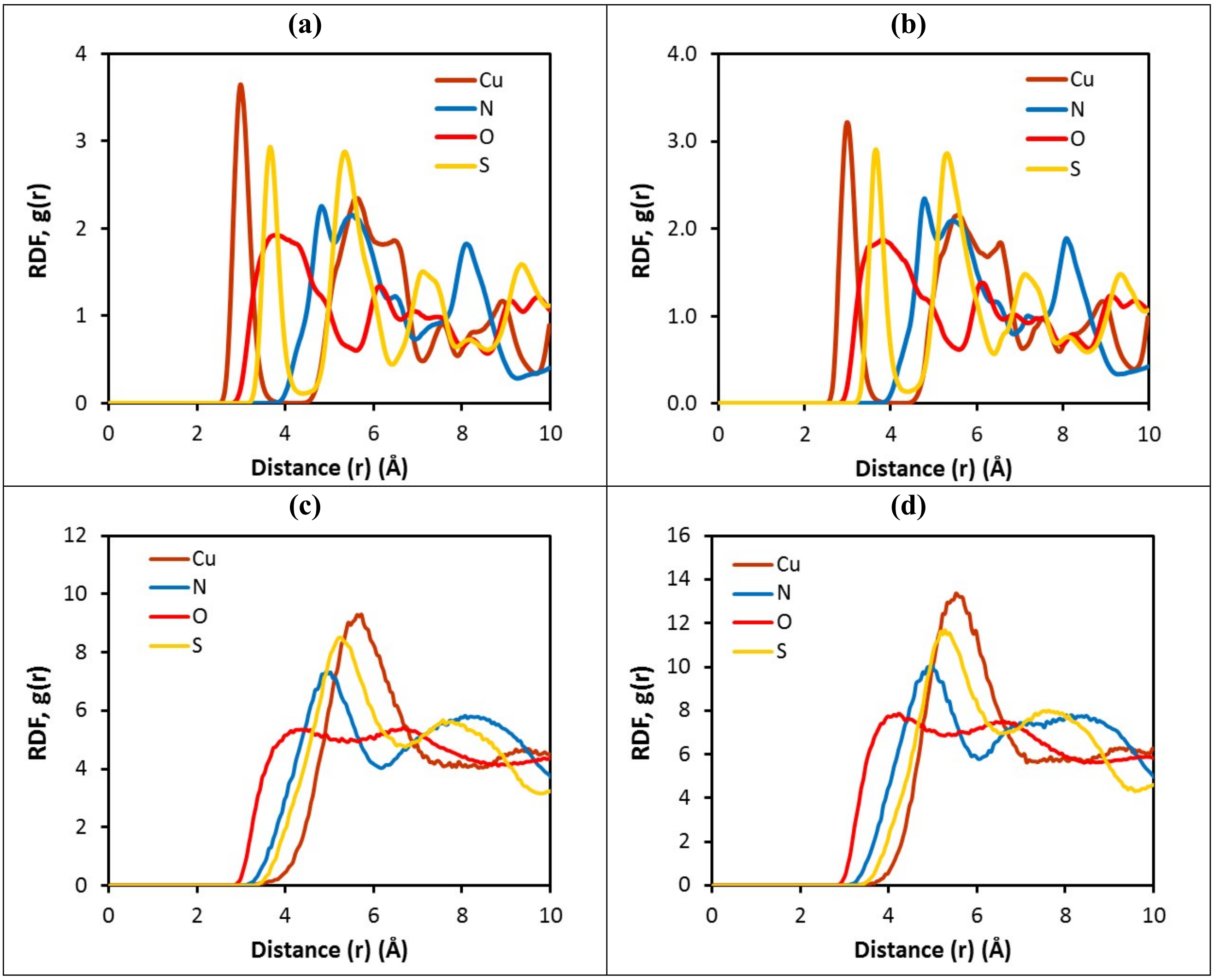


Figure S5. Radial distribution functions (RDF) between the adsorbate, CH_4 and four different atom types (namely, Cu, N, O, and S) existing in the framework of MEFMEQ defined by (a) single-component EMD simulations, (b) mixture EMD simulations, (c) single-component NEMD simulations, and (d) mixture NEMD simulations. H_2 population around Cu, N, O, and S atoms is represented by brown, blue, red and yellow colors.

Table S1. CH_4 and H_2 adsorption performances of MOF-5, Cu-BTC and ZIF-8 reported by experiments.

	CH_4 uptake (cm^3 STP/cm^3)		H_2 uptake (cm^3 STP/cm^3)	
MOF-5				
	1.78	@ 1 bar, 298 K[28]	0.492	@ 1 bar, 300 K[29]
	3.27	@ 1 bar, 298 K[30]		
	8.91	@ 1 bar, 298 K[31]		
	11.40	@ 1 bar, 298 K[32]		
	13.14	@ 1 bar, 298 K[33]		
Cu-BTC				
	17.71	@ 1 bar, 298 K[30]	0.84	@ 1 bar, 300 K[29]
	18.46	@ 1 bar, 303 K[34]	0.87	@ 1 bar, 298 K[35]
	19.10	@ 1 bar, 295 K[36]		
	20.20	@ 1 bar, 300 K[37]		
ZIF-8				
	4.15	@ 1 bar, 300 K[38]	0.898	@ 1 bar, 300 K[38]
	5.55	@ 1 bar, 298 K[39]		
	8.82	@ 1 bar, 298 K[40]		

References:

1. Liu, Y.; Ng, Z.; Khan, E. A.; Jeong, H.-K.; Ching, C.-b.; Lai, Z., Synthesis of continuous MOF-5 membranes on porous α-alumina substrates. *Microporous and Mesoporous Materials* **2009,** *118* (1), 296-301.
2. Yoo, Y.; Lai, Z.; Jeong, H.-K., Fabrication of MOF-5 membranes using microwave-induced rapid seeding and solvothermal secondary growth. *Microporous and mesoporous materials* **2009,** *123* (1-3), 100-106.
3. Zhao, Z.; Ma, X.; Li, Z.; Lin, Y., Synthesis, characterization and gas transport properties of MOF-5 membranes. *Journal of membrane science* **2011,** *382* (1-2), 82-90.
4. Cao, F.; Zhang, C.; Xiao, Y.; Huang, H.; Zhang, W.; Liu, D.; Zhong, C.; Yang, Q.; Yang, Z.; Lu, X., Helium recovery by a Cu-BTC metal–organic-framework membrane. *Industrial & Engineering Chemistry Research* **2012,** *51* (34), 11274-11278.
5. Nagaraju, D.; Bhagat, D. G.; Banerjee, R.; Kharul, U. K., In situ growth of metal-organic frameworks on a porous ultrafiltration membrane for gas separation. *Journal of Materials Chemistry A* **2013,** *1* (31), 8828-8835.
6. Guerrero, V. V.; Yoo, Y.; McCarthy, M. C.; Jeong, H.-K., HKUST-1 membranes on porous supports using secondary growth. *Journal of Materials Chemistry* **2010,** *20* (19), 3938-3943.
7. Li, W.; Zhang, Y.; Zhang, C.; Meng, Q.; Xu, Z.; Su, P.; Li, Q.; Shen, C.; Fan, Z.; Qin, L., Transformation of metal-organic frameworks for molecular sieving membranes. *Nature communications* **2016,** *7*, 11315.
8. Hara, N.; Yoshimune, M.; Negishi, H.; Haraya, K.; Hara, S.; Yamaguchi, T., Metal–organic framework membranes with layered structure prepared within the porous support. *RSC Advances* **2013,** *3* (34), 14233-14236.
9. Nan, J.; Dong, X.; Wang, W.; Jin, W.; Xu, N., Step-by-step seeding procedure for preparing HKUST-1 membrane on porous α-alumina support. *Langmuir* **2011,** *27* (8), 4309-4312.
10. Shah, M. N.; Gonzalez, M. A.; McCarthy, M. C.; Jeong, H.-K., An unconventional rapid synthesis of high performance metal–organic framework membranes. *Langmuir* **2013,** *29* (25), 7896-7902.
11. Guo, H.; Zhu, G.; Hewitt, I. J.; Qiu, S., "Twin copper source" growth of metal−organic framework membrane: $Cu_3(BTC)_2$ with high permeability and selectivity for recycling H_2. *Journal of the American Chemical Society* **2009,** *131* (5), 1646-1647.

12. Mao, Y.; Cao, W.; Li, J.; Liu, Y.; Ying, Y.; Sun, L.; Peng, X., Enhanced gas separation through well-intergrown MOF membranes: seed morphology and crystal growth effects. *Journal of Materials Chemistry A* **2013,** *1* (38), 11711-11716.
13. Mao, Y.; Huang, H.; Cao, W.; Li, J.; Sun, L.; Jin, X.; Peng, X., Room temperature synthesis of free-standing HKUST-1 membranes from copper hydroxide nanostrands for gas separation. *Chemical Communications* **2013,** *49* (50), 5666-5668.
14. Ben, T.; Lu, C.; Pei, C.; Xu, S.; Qiu, S., Polymer-Supported and Free-Standing Metal–Organic Framework Membrane. *Chemistry–A European Journal* **2012,** *18* (33), 10250-10253.
15. Zhou, S.; Zou, X.; Sun, F.; Zhang, F.; Fan, S.; Zhao, H.; Schiestel, T.; Zhu, G., Challenging fabrication of hollow ceramic fiber supported $Cu_3(BTC)_2$ membrane for hydrogen separation. *Journal of Materials Chemistry* **2012,** *22* (20), 10322-10328.
16. Zhang, X.; Liu, Y.; Kong, L.; Liu, H.; Qiu, J.; Han, W.; Weng, L.-T.; Yeung, K. L.; Zhu, W., A simple and scalable method for preparing low-defect ZIF-8 tubular membranes. *Journal of Materials Chemistry A* **2013,** *1* (36), 10635-10638.
17. Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. R., Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. *Journal of the American Chemical Society* **2009,** *131* (44), 16000-16001.
18. Liu, Y.; Wang, N.; Diestel, L.; Steinbach, F.; Caro, J., MOF membrane synthesis in the confined space of a vertically aligned LDH network. *Chemical communications* **2014,** *50* (32), 4225-4227.
19. Bux, H.; Feldhoff, A.; Cravillon, J.; Wiebcke, M.; Li, Y.-S.; Caro, J., Oriented zeolitic imidazolate framework-8 membrane with sharp H_2/C_3H_8 molecular sieve separation. *Chemistry of Materials* **2011,** *23* (8), 2262-2269.
20. Liu, D.; Ma, X.; Xi, H.; Lin, Y., Gas transport properties and propylene/propane separation characteristics of ZIF-8 membranes. *Journal of Membrane Science* **2014,** *451*, 85-93.
21. Tao, K.; Cao, L.; Lin, Y.; Kong, C.; Chen, L., A hollow ceramic fiber supported ZIF-8 membrane with enhanced gas separation performance prepared by hot dip-coating seeding. *Journal of Materials Chemistry A* **2013,** *1* (42), 13046-13049.
22. Pan, Y.; Wang, B.; Lai, Z., Synthesis of ceramic hollow fiber supported zeolitic imidazolate framework-8 (ZIF-8) membranes with high hydrogen permeability. *Journal of membrane science* **2012,** *421*, 292-298.
23. Xu, G.; Yao, J.; Wang, K.; He, L.; Webley, P. A.; Chen, C.-S.; Wang, H., Preparation of ZIF-8 membranes supported on ceramic hollow fibers from a concentrated synthesis gel. *Journal of membrane science* **2011,** *385*, 187-193.
24. McCarthy, M. C.; Varela-Guerrero, V.; Barnett, G. V.; Jeong, H.-K., Synthesis of zeolitic imidazolate framework films and membranes with controlled microstructures. *Langmuir* **2010,** *26* (18), 14636-14641.
25. Pan, Y.; Lai, Z., Sharp separation of C_2/C_3 hydrocarbon mixtures by zeolitic imidazolate framework-8 (ZIF-8) membranes synthesized in aqueous solutions. *Chemical Communications* **2011,** *47* (37), 10275-10277.
26. Shah, M.; Kwon, H. T.; Tran, V.; Sachdeva, S.; Jeong, H.-K., One step in situ synthesis of supported zeolitic imidazolate framework ZIF-8 membranes: Role of sodium formate. *Microporous and Mesoporous Materials* **2013,** *165*, 63-69.
27. Liu, Y.; Wang, N.; Pan, J. H.; Steinbach, F.; Caro, J. R., In situ synthesis of MOF membranes on ZnAl-CO_3 LDH buffer layer-modified substrates. *Journal of the American Chemical Society* **2014,** *136* (41), 14353-14356.
28. Saha, D.; Bao, Z.; Jia, F.; Deng, S., Adsorption of CO_2, CH_4, N_2O, and N_2 on MOF-5, MOF-177, and zeolite 5A. *Environmental science & technology* **2010,** *44* (5), 1820-1826.
29. Panella, B.; Hirscher, M.; Pütter, H.; Müller, U., Hydrogen adsorption in metal–organic frameworks: Cu-MOFs and Zn-MOFs compared. *Advanced Functional Materials* **2006,** *16* (4), 520-524.
30. Mason, J. A.; Veenstra, M.; Long, J. R., Evaluating metal–organic frameworks for natural gas storage. *Chemical Science* **2014,** *5* (1), 32-51.
31. Düren, T.; Sarkisov, L.; Yaghi, O. M.; Snurr, R. Q., Design of new materials for methane storage. *Langmuir* **2004,** *20* (7), 2683-2689.

32. Kondo, M.; Yoshitomi, T.; Matsuzaka, H.; Kitagawa, S.; Seki, K., Three-Dimensional Framework with Channeling Cavities for Small Molecules: $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot xH_2O\}_n$ (M=Co, Ni, Zn). *Angewandte Chemie International Edition in English* **1997,** *36* (16), 1725-1727.
33. Pillai, R. S.; Pinto, M. L.; Pires, J.; Jorge, M.; Gomes, J. R., Understanding gas adsorption selectivity in IRMOF-8 using molecular simulation. *ACS applied materials & interfaces* **2015,** *7* (1), 624-637.
34. Hamon, L.; Jolimaître, E.; Pirngruber, G. D., CO_2 and CH_4 separation by adsorption using Cu-BTC metal−organic framework. *Industrial & Engineering Chemistry Research* **2010,** *49* (16), 7497-7503.
35. Li, Y.; Yang, R. T., Hydrogen storage in metal-organic and covalent-organic frameworks by spillover. *AIChE Journal* **2008,** *54* (1), 269-279.
36. Chowdhury, P.; Mekala, S.; Dreisbach, F.; Gumma, S., Adsorption of CO, CO_2 and CH_4 on Cu-BTC and MIL-101 metal organic frameworks: Effect of open metal sites and adsorbate polarity. *Microporous and Mesoporous Materials* **2012,** *152*, 246-252.
37. Simmons, J. M.; Wu, H.; Zhou, W.; Yildirim, T., Carbon capture in metal–organic frameworks-A comparative study. *Energy & Environmental Science* **2011,** *4* (6), 2177-2185.
38. Zhou, W.; Wu, H.; Hartman, M. R.; Yildirim, T., Hydrogen and methane adsorption in metal−organic frameworks: A high-pressure volumetric study. *The Journal of Physical Chemistry C* **2007,** *111* (44), 16131-16137.
39. Autié Castro, G.; Jardim, E. D. O.; Reguera, E.; Vilarrasa-García, E.; Rodríguez-Castellón, E.; Cavalcante Jr, C. L., CH_4 and CO_2 Adsorption Study in ZIF-8 and Al-BDC MOFs. *Biological and Chemical Research* **2017,** 234-246.
40. Huang, H.; Zhang, W.; Liu, D.; Liu, B.; Chen, G.; Zhong, C., Effect of temperature on gas adsorption and separation in ZIF-8: A combined experimental and molecular simulation study. *Chemical engineering science* **2011,** *66* (23), 6297-6305.