Electronic Supplementary Material (ESI) for Energy & Environmental Science


Supplementary information for Thornton *et al*.

# Feasibility for Zeolitic Imidazolate Frameworks as Gas Separation Membranes in Clean Energy Applications

**TABLE S1**: van der Waals forcefield values for calculating solubility coefficients. Framework atoms were modified from the Dreiding FF database according the parameterization technique outlined by Dubbeldam *et al.* [69] resulting in the following scaling factors (0.95 × kinetic diameter, 0.85 × well depth). Note that the unmodified Dreiding FF database is used for diffusivity coefficients.

| | kinetic diameter (Å) | well depth (K) |
|---|---|---|
| *Gases* | | |
| H2 | 2.958 | 36.7 |
| CH4 | 3.73 | 148 |
| O_CO2 | 3.05 | 79 |
| C_CO2 | 2.80 | 27 |
| N_N2 | 3.31 | 36 |
| O_O2 | 2.99 | 52 |

| | kinetic diameter (Å) | well depth (K) |
|---|---|---|
| *Framework atoms* | | |
| Zn | 3.84 | 23.1 |
| O | 2.88 | 40.2 |
| N | 3.10 | 29.2 |
| C | 3.30 | 39.9 |
| H | 2.71 | 6.38 |

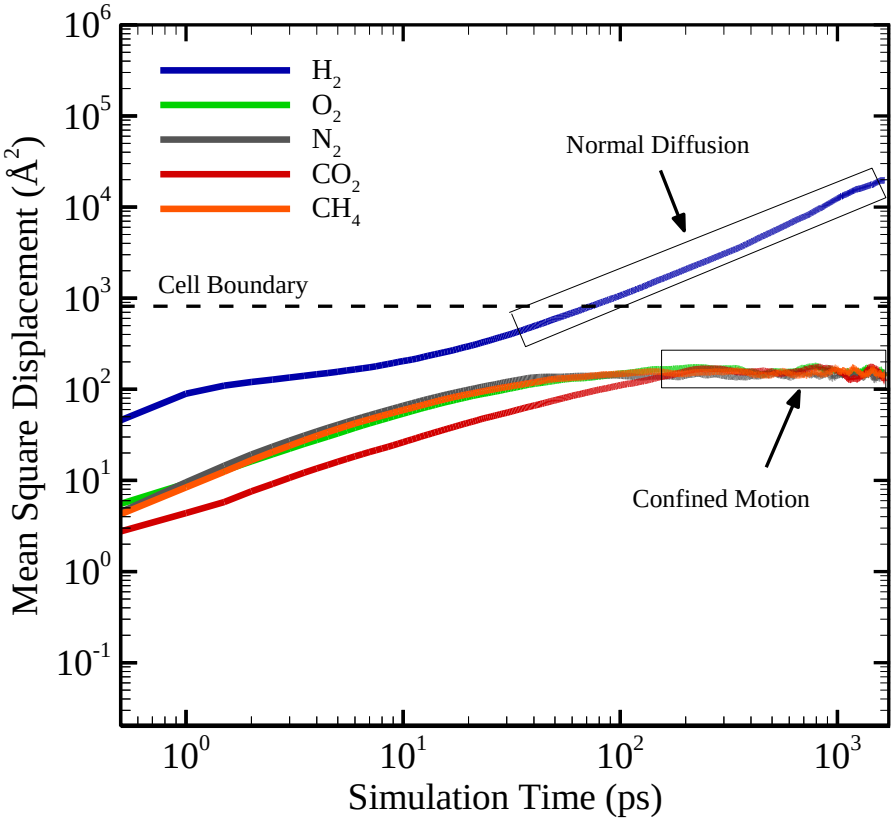


**FIGURE S1**: Our calculated Mean Squared Displacement (MSD) of gas molecules from molecular dynamics simulation within ZIF-11. This indicates the strong preference for transport of hydrogen over other gases, which reach a plateau in MSD, indicating that they are confined within the cell

**TABLE S2**: Accessible surface area (using center of probe with nitrogen radius = 1.84 Å), ore volume (using Connolly probe with helium radius = 1.3 Å), helium void fraction (Widom Insertion method), cavity size and window size.

| | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Void fraction (-) | Cavity size 1 (Å) | Window Size 1a (Å) | Window Size 1b (Å) | Cavity Size 2* (Å) | Window Size 2a (Å) | Window Size 2b (Å) |
|---|---|---|---|---|---|---|---|---|---|
| ZIF-7 | 230 | 0.235 | 0.274 | 4.31 | 2.9 | - | 4.8 | 1.8 | - |
| ZIF-8 | 1344 | 0.554 | 0.465 | 11.6 | 3.14 | - | - | - | - |
| ZIF-11 | 1140 | 0.457 | 0.469 | 14.6 | 3.10 | - | 12.5 | 3.08 | - |
| ZIF-69 | 967 | 0.392 | 0.418 | 6.6 | 4.2 | - | 7.6 | 5.4 | - |
| ZIF-71 | 1007 | 0.452 | 0.512 | 16.5 | 3.65 | 4.7 | 17.0 | 3.65 | 4.75 |
| ZIF-77 | 331 | 0.203 | 0.309 | 4.7 | 3.74 | 3.6 | - | - | - |
| ZIF-90 | 1360 | 0.561 | 0.498 | 10.8 | 2.86 | - | - | - | - |

*** The second cavity is due to the ligands asymmetry.**

**TABLE S3**: Equilibrium gas concentrations at 298 K and 10 bar calculated with software package RASPA. Gases are labeled with their Lennard-Jones well depth values (K).

| | Simulated Concentration ($mol/m^3$) | | | | |
|---|---|---|---|---|---|
| | $H_2$ (60 K) | $CO_2$ (195 K) | $O_2$ (107 K) | $N_2$ (71 K) | $CH_4$ (149 K) |
| ZIF-7 | 378 | 3407 | 2828 | 2469 | 3211 |
| ZIF-7 (498 K) | 73 | 1218 | 427 | 305 | 872 |
| ZIF-8 | 304 | 4528 | 1177 | 974 | 2253 |
| ZIF-11 | 297 | 8203 | 5310 | 4402 | 6152 |
| ZIF-69 | 297 | 4852 | 1760 | 1318 | 2962 |
| ZIF-71 | 342 | 4268 | 1520 | 1190 | 2185 |
| ZIF-77 | 281 | 4324 | 2082 | 1508 | 3143 |
| ZIF-90 | 313 | 4557 | 1182 | 964 | 2160 |
| ZIF-90 (498 K) | 120 | 415 | 230 | 206 | 335 |

**TABLE S4**: Diffusivities at 298 K and 10 bar calculated with Forcite module within Accelrys package. Gases are labeled with their Lennard-Jones kinetic diameter values (Å)

| | Simulated Diffusivity ($m^2$/sec) x $10^{-8}$ | | | | |
|---|---|---|---|---|---|
| | $H_2$ (2.89 Å) | $CO_2$ (3.30 Å) | $O_2$ (3.46 Å) | $N_2$ (3.64 Å) | $CH_4$ (3.87 Å) |
| ZIF-7 | 0.16 | < 0.0001 | < 0.0001 | < 0.0001 | < 0.0001 |
| ZIF-7 (498 K) | 1.33 | 0.0025 | 0.0012 | 0.00187 | 0.0013 |
| ZIF-8 | 5.82 | 0.19 | 0.50 | 0.13 | 0.03 |
| ZIF-11 | 0.72 | < 0.0001 | < 0.0001 | < 0.0001 | < 0.0001 |
| ZIF-69 | 2.94 | 0.12 | 0.11 | 0.16 | 0.08 |
| ZIF-71 | 10.02 | 0.42 | 1.30 | 0.58 | 0.76 |
| ZIF-77 | 11.43 | 0.54 | 0.62 | 1.14 | 0.09 |
| ZIF-90 | 4.75 | 0.08 | 0.36 | 0.10 | 0.03 |
| ZIF-90 (498 K) | 5.54 | 0.12 | 0.37 | 0.15 | 0.04 |