



Supplementary Materials: Mixed Matrix Membranes Based on Torlon® and ZIF-8 for High-Temperature, Size-Selective Gas Separations

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Figure S1. Pictures of the membranes produced: Torlon, Torlon/6 ZIF-8, Torlon/25 ZIF-8.

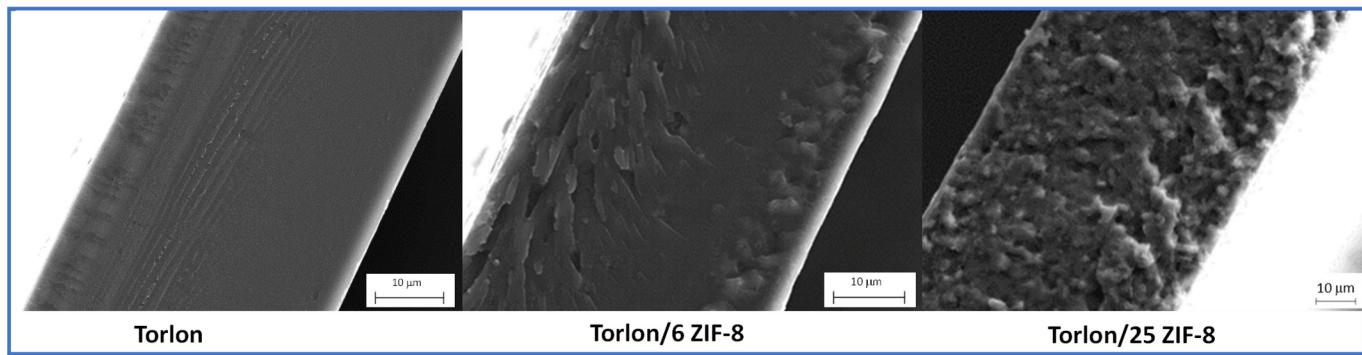


Figure S2. SEM images of cross sections of Torlon, Torlon/6 ZIF-8, Torlon/25 ZIF-8 samples.

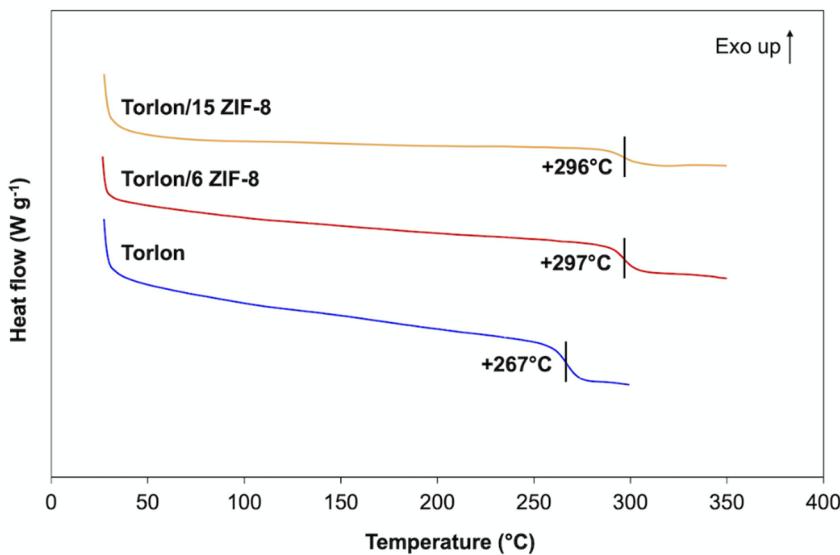


Figure S3. DSC thermograms of Torlon, Torlon/6 ZIF-8 and Torlon/15 ZIF-8 samples.

Table S1. MMM samples produced, thickness and tests performed.

| ZIF-8 Weight % | Sample ID | Thickness (μm) | Permeability Tests | SEM Tests | DSC Tests |
|----------------|-----------------|----------------|---|-----------|-----------|
| 0 | Torlon | 10.5±1.4 | He, CO ₂ , 35°C, 65°C | x | x |
| 6 | Torlon/6 ZIF-8 | 45.5±1.9 | He, H ₂ , CO ₂ , 35°C, 65°C | x | x |
| 15 | Torlon/15 ZIF-8 | - | - | - | x |
| 25 | Torlon/25 ZIF-8 | 64.7±5.0 | He, CO ₂ , 35°C, 65°C | x | - |

Table S2. Gas permeability data in Torlon® flat sheet membranes from this work and the literature.

| Polymer Density | Permeability (Barrer) | | | | | | | Source | Notes |
|-----------------|-----------------------|----------------|----------------|----------------|-----------------|-----------------|----|-----------|-------|
| | He | H ₂ | O ₂ | N ₂ | CH ₄ | CO ₂ | T | | |
| °C | | | | | | | | | |
| 1.252 | - | 3.730 | 0.130 | 0.018 | 0.013 | 0.541 | 35 | [1] | a |
| n.r. | 5.53 | 4.44 | 0.212 | 0.037 | 0.030 | 0.83 | 35 | [2] | b |
| n.r. | 4.4±0.2 | - | 0.12±0.006 | 0.014±0.0007 | 0.009±0.0004 | 0.47±0.02 | 35 | [3] | c |
| 1.252 [1] | 3.9±0.6 | - | - | - | - | 0.47±0.06 | 35 | This work | d |

^a Torlon 4000 TF, solvent NMP, dense films 50 microns, thermal treatment at 250°C for 12 h, upstream pressure 3.5 atm

^b Torlon 4000 T, solvent NMP, upstream pressure 10 atm

^c Torlon 4000T-LV, dense film, solvent NMP, membrane treated at 310°C for 1d

^d Torlon 4000TF, dense film, solvent NMP, membrane treated at 200°C under vacuum overnight, upstream pressure 1.3 bar, downstream pressure vacuum.

Table S3. Gas permeability data in Torlon/ZIF-8 mixed matrix membranes from this work and for ZIF-8 from the literature. Data marked with an asterisk are estimated values based on linear interpolation between permeability and kinetic diameter in each matrix.

| Permeability (Barrer) | He | H ₂ | CO ₂ | He | H ₂ | CO ₂ |
|-----------------------|-----------|----------------|-----------------|----------|----------------|-----------------|
| | 35°C | | | 65°C | | |
| Torlon | 3.9±0.6 | 2.43* | 0.47±0.06 | 6.4±1.0 | 3.97* | 0.72±0.09 |
| Torlon/6 ZIF-8 | 5.3±0.2 | 3.8±0.2 | 0.97±0.04 | 9.0±0.4 | 7.0±0.3 | 1.4±0.1 |
| Torlon/25 ZIF-8 | 10.0±0.9 | 6.66* | 2.20±0.2 | 19.6±1.6 | 13.0* | 4.2±0.4 |
| 20-35°C | | | | | | |
| ZIF-8 [4,5] | 3000±1322 | | 1640±712 | | | |

Table S4. Ideal selectivity values in Torlon/ZIF-8 mixed matrix membranes from this work and 8 from the literature.

| Ideal Selectivity | He/CO ₂ | H ₂ /CO ₂ | He/CO ₂ | H ₂ /CO ₂ |
|-------------------|--------------------|---------------------------------|--------------------|---------------------------------|
| | 35°C | | 65°C | |
| Torlon | 8.2 | 5.2* | 8.9 | 5.5* |
| Torlon/6 ZIF-8 | 5.4 | 3.9 | 6.6 | 5 |
| Torlon/25 ZIF-8 | 5.0 | 3.0* | 4.6 | 3.1* |
| 20–35°C | | | | |
| ZIF-8 [4,5] | 1.8 | 3.9 | | |

Table S5. Gas diffusivity and ideal diffusivity-selectivity in Torlon/ZIF-8 mixed matrix membranes.

| | Diffusivity (cm ² /s) | | | | Diffusivity-Selectivity α_D | |
|-----------------|-------------------------------------|-----------------------------|----------------------------|----------------------------|---------------------------------------|------|
| | He | CO ₂ | He | CO ₂ | He/CO ₂ | |
| | 35°C | | 65°C | | 35°C | 65°C |
| Torlon | (1.6±0.4)×10 ⁻⁷ | (3.5±1)×10 ⁻¹⁰ | (1.6±0.4)×10 ⁻⁷ | (1.4±0.4)×10 ⁻⁹ | 448 | 116 |
| Torlon/6 ZIF-8 | (4.4±0.4)×10 ⁻⁷ | (9.6±0.8)×10 ⁻¹⁰ | (4.5±0.4)×10 ⁻⁷ | (2.3±0.2)×10 ⁻⁹ | 457 | 198 |
| Torlon/25 ZIF-8 | (6.6±1)×10 ⁻⁷ | (2.3±0.4)×10 ⁻⁹ | (1.3±0.2)×10 ⁻⁶ | (9.3±1.4)×10 ⁻⁹ | 290 | 139 |

References

- W.F.; Yong, F.Y.; Li, T.S.; Chung, Y.W.; Tong, Molecular interaction, gas transport properties and plasticization behavior of cPIM-1/Torlon blend membranes, *J. Memb. Sci.* 462 (2014) 119–130. <https://doi.org/10.1016/j.memsci.2014.03.046>.
- S.S.; Hosseini, T.S.; Chung, Carbon membranes from blends of PBI and polyimides for N₂/CH₄ and CO₂/CH₄ separation and hydrogen purification, *J. Memb. Sci.* 328 (2009) 174–185. <https://doi.org/10.1016/j.memsci.2008.12.005>.
- M.R.; Kosuri, W.J.; Koros, Defect-free asymmetric hollow fiber membranes from Torlon®, a polyamide-imide polymer, for high-pressure CO₂ separations, *J. Memb. Sci.* 320 (2008) 65–72. <https://doi.org/10.1016/j.memsci.2008.03.062>.
- H.; Bux, F.; Liang, Y.; Li, J.; Cravillon, M.; Wiebcke, J.; Caro, Zeolitic Imidazolate Framework Membrane with Molecular Sieving Properties by Microwave-Assisted Solvothermal Synthesis, *J. Am. Chem. Soc.* 131 (2009) 16000–16001. <https://doi.org/10.1021/ja907359t>.
- K.S.; Park, Z.; Ni, A.P.; Cote, J.Y.; Choi, R.; Huang, F.J. Uribe-Romo, H.K.; Chae, M. O’Keeffe, O.M.; Yaghi, Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, *Proc. Natl. Acad. Sci.* 103 (2006) 10186–10191. <https://doi.org/10.1073/pnas.0602439103>.
- Q.; Song, S.K.; Nataraj, M. V.; Roussenova, J.C.; Tan, D.J.; Hughes, W.; Li, P.; Bourgoin, M.A.; Alam, A.K.; Cheetham, S.A. Al-Muhtaseb, E.; Sivaniah, Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation, *Energy Environ. Sci.* 5 (2012) 8359. <https://doi.org/10.1039/c2ee21996d>.