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Synthesis and Preparation of Asymmetric PSf/ZIF-8 Mixed Matrix Membrane for CO₂/CH₄ Separation

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Graphical abstract
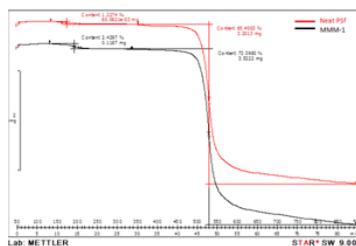
Abstract

Utilizing nano-size filler into polymer matrix would overcome challenges in developing MMM by providing good dispersion in polymer matrix, high contact polymer-filler even at low filler loading. Asymmetric neat Polysulfone (PSf) and PSf/Zeolitic Imidazole Framework-8 (PSf/ZIF-8) mixed matrix membrane was prepared using dry/wet inversion method. Membrane prepared was coated with 3wt% of polydimethylsiloxane (PDMS) in n-hexane and undergoes heat treatment. The membranes was characterized using x-ray diffraction (XRD), thermagravimetric analysis (TGA), differential scanning calorimetry (DSC), and gas permeation test at 4 bar. XRD pattern revealed that ZIF-8 was successfully synthesis with crystal size around 73nm. Lowered membrane Tg after embodiment of ZIF-8 suggests that additional free volume form, while thermal stability up to 350°C related to ZIF-8 stability. Neat PSf prepared shows CO_2 permeance at 4.97 GPU with CO_2/CH_4 selectivity at 7.52. Interestingly, incorporation of ZIF-8 showing improvement for both CO_2 permeance and CO_2/CH_4 selectivity up to 51% and 47% respectively. Thus, employing nano ZIF-8 as filler into PSf matrix has resultant promising membrane for CO_2/CH_4 separation.

Keywords: Mixed matrix membrane; PSf/ZIF-8; CO_2/CH_4 separation

■1.0 INTRODUCTION

Separation of CO_2 based on polymeric membrane emerges as potential approach to replace conventional techniques. Due to low capital cost, modest energy requirement and ease to fabricate, research on polymeric membrane has gain lots of attention in the last decades. Although polymeric membranes provide many advantages, its performance is bounded by Robeson's trade-off limit between selectivity and permeability [1]. Incorporating inorganic filler, such as zeolite, carbon nanotube, activated carbon and carbon molecular sieve, into polymer matrices to surpass Robeson's trade-off limit, called mix matrix membrane (MMM).

Several guidelines have been highlighted in developing high performance MMM, most importantly is high intrinsic separation properties of both polymer and filler. Inorganic fillers such as zeolite and carbon molecular sieve, posses separation properties surpass Robeson's trade-off limit, were among the first to be incorporated into polymer matrix. However, inorganic fillers has poor interaction with polymer matrix and often leads to defective membrane. Developing MMM defect-free membrane remain biggest challenges. Polymer-filler incompatibility defected membrane through particle agglomeration, un-selective voids formation, filler pore blockage and "sieve-in-cage" morphology leads to low

separation properties. Metal organic frameworks (MOFs) emerge as potential filler due to organic linkers exist in its structure have good interaction with polymer. Besides, MOFs consist of large surface area, high adsorption capacity, ease to modifications and high affinity towards certain gas gives the edge for MOFs to be implemented as filler. Among MOFs, zeolitic imidazole framework-8 (ZIF-8) is one of the most investigated MOFs. ZIF-8 is porous crystalline structure with M-Im-M angle (M=metal) near to 145°, coincident with the Si–O–Si angle found in many zeolites. ZIF-8 show good chemical stability against polar and nonpolar solvents [2], reorientation of its structure at high pressure [3, 4] and high mechanical strength [5].

Another concern regarding MMM is the amount of filler loading. High filler loading would provide higher penetrant-filler interaction and increase MMM separation properties. However, it also likely leads to particles agglomeration. Literatures suggest that increased filler loading increase its separation performance, but eventually leads to particles to agglomerate and deteriorating its performance[6, 7]. It should be noted that high filler loading would directly reflect on membrane production cost. In contrast, incorporating small amount of filler give insignificant improvement on membrane separation properties, but highly unlikely for particles to agglomerate. Minimum filler loading with significant

improvement of membrane performance would be the ideal MMM. The study by Hashemifard *et al.* [8] showed that significant enhancement of membrane separation properties can be achieved even at low loading. In the study, 0.5wt% (total solid) of clay mineral (Cloisite 15A) shows CO_2 permeance and CO_2/CH_4 selectivity increased to 24% and 28%, respectively due to combination of polymer chain disruption and tortuous path for CH4 to permeate. In other words, layered clay minerals is exfolaited into nano layer [9] provide lower external surface area to volume ratio and ease to interact with polymer chain [10-13].Therefore, significant improvement of membrane separation properties can be achieved using nano filler even at low filler loading.

In order to develop high performance MMM at low filer loading, nano filler with good polymer-filer interaction is necessary. Thus, this study aims to develop nano-size ZIF-8 using aqueous system method[14] with base-type. Addition of triethylamine (TEA) as base-type additive during synthesis step show nano-size ZIF-8 can be produce due to deprotonated ligands. The influence of nano ZIF-8 dispersed in polymer matrix is investigated. Up to this date, the development of MMM-MOF mainly focused on dense membrane [15-18]. This study also provides the preparation of asymmetric MMM using dry/wet inversion method for CO_2/CH_4 separation.

■2.0 EXPERIMENTAL

2.1 Materials

Zinc nitrate hexahydrate $(Zn(NO_3)_2.6H_2O)$, 2-methylimidazole (H-MeIM) and triethylamine (TEA) was purchased from Sigma Aldrich. Polysulfone (PSfUdel® P-3500) was purchased from Solvay Plastic. N,N-methylpyrrolidone (NMP), tetrahydrofurane (THF) and ethanol was purchased from Merk. For coating solution, polydimethylsiloxane (PDMS) was purchased from Sigma Aldrich and n-hexane was purchased from Merk. All chemicals were used without further purification.

2.2 ZIF-8 Synthesis

ZIF-8 was prepared using aqueous system method [14] with base additive. Briefly, Zinc nitrate (10g) was dissolved into deionized water (100g) while H-MeIM (16.56g) was dissolve into TEA (10ml) in 400g of deionized water. Zinc nitrate solution was added to the H-MeIM solution and cloudy solution formed upon mixing the solutions. The solution was stirred continuously for 30 minutes. The solution was centrifuge to remove separate the mixture and washed with deionized water several times to remove reactants. The solution was dried in oven at 60°C overnight. The powder formed was collected and weighted to calculate mass yield

2.3 Membrane Preparation

Asymmetric flat sheet neat membranes was prepared by casting solution consisted of polysulfone (30 wt%), NMP (35 wt%), THF (30 wt%) and EtOH (5 wt%). Casting process was performed by hand-casting at ambient atmosphere. Then, membrane was remained free standing at atmosphere for a certain period before immersion in an aqueous bath and remained there for 1 day. Finally, the washed membrane was solvent-exchanged with methanol for 2 h, followed by n-hexane for 2 h and then air-dried for 1 day.

Asymmetric flat sheet MMM was prepared by casting solution consisted of polysulfone (30 wt%), NMP (35 wt%),

THF (30 wt%), EtOH (5 wt%) and ZIF-8 (1 wt% from total solid). Approximately 10% of polymer solution was then added to the MOFs suspension to priming the MOFs particles. Remaining polymer was added until dissolved. The solution was left at ambient to check solution homogeneity. Casting process was performed by hand-casting at ambient atmosphere. Then, membrane was left for free standing at atmosphere for a certain period before immersion in an aqueous bath and remained there for 1 day. Finally, the washed membrane was solvent-exchanged with methanol for 2 h, followed by n-hexane for 2 h and then air-dried for 1 day. MMM with 1wt% of ZIF-8 is marked as MMM-1.

Membranes were dip-coated for 10 minutes in 3wt% PDMS in n-hexane to seal possible pinhole on membrane surface. Then, membrane undergoes "curing" at 60°C overnight.

2.1 Characterization

Differential scanning calorimeter (DSC) is used to determine the glass transition temperature (Tg) of prepared membranes using Mettler Toledo DSC 822e. The membrane sample was cut into small pieces, weighed and placed into pre-weighed aluminium crucible. Then, the sample was heated from 50 to 400^0C at a heating rate of 10^0C min^{-1} in the first cycle to remove the thermal history. The sample was cooled from 400 to 30^0C at the rate of 10^0C min^{-1}. The same heating protocol was repeated in the next heating cycle. Tg of the sample was determined as the midpoint temperature of the transition region in the second heating cycle.

Thermogravimetric analysis (TGA) uses to characterize thermal stability of prepared samples. TGA records the weight changes of sample when heated continuously. The samples were heated from 50 to 900^0C at the heating rate of 10^0C min^{-1} under nitrogen atmosphere with a nitrogen flow rate of 20 mL min^{-1}.

XRD analysis use to confirm the phase of ZIF-8 similar with literature. X-Ray Diffraction (XRD) analysis using Siemens D5000 Difractometer is non-destructive analysis to measuring wavelength of samples and identifies its structure. The XRD will emit x-rays to the sample and the x-rays diffracted at different angles and intensity by using CuKα radiation with a wavelength (λ) = 1.54Å at room temperature. Particle size estimation was calculated using Williamson-Hall equation [19, 20].

Gas permeation tests were performed with a permeation cell by using pure methane (CH_4) and carbon dioxide (CO_2), respectively. Circular membrane discs with an effective permeation area of 13.5 cm^2 were used. Feed pressure was controlled at 4 bar while permeate side was opened to atmosphere. Experiments were carried out at ambient temperature. Permeance are calculated using Equation (1)

$$\left(\frac{P_i}{l}\right) = \frac{1}{A\Delta p} \times \frac{dV_i}{dt} \tag{1}$$

where *i* represents the gas penetrant *i*, *Vi* is the volume of gas permeated through the membrane (cm^3, STP), *A* the effective membrane area (cm^2), *t* the permeation time (s) and *Δp* is the transmembrane pressure drop (cmHg). Permeances is expressed in gas permeation units, GPU, where

1 GPU = 1×10^{-6} cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1}.

Selectivity was obtained using Equation (2):

$$\alpha_{i/j} = \frac{(P_i/l)}{(P_j/l)} \tag{2}$$

■3.0 RESULTS AND DISCUSSION

3.1 Characterization

The synthesized ZIF-8 was first characterized by XRD to identify phase purity and crystal structure. XRD pattern of synthesized ZIF-8 was shown in Figure 1 and the prepared ZIF-8 shows high crystalline structure. Compared to the Basolite Z1200, the intensity of the as-synthesized peak, especially on 2θ = 7.25, are significantly lower. The differences can be related to guest molecule occupying ZIF-8 pores caused pattern destructive and retarded gas uptake capacity [21, 22]. Besides, the BET surface area of prepared ZIF-8 is 413.97 m^2/g, significantly lower than Basolite Z1200 (1223.19 m^2/g) are also related to the occupied ZIF-8 pore. Particle size of synthesized ZIF-8 is estimated around 73 nm using Williamson-Hall plot. ZIF-8 crystal then further confirmed by FTIR, indicate no foreign chemical bond exist in the molecule to cause the destructive pattern of XRD (Figure 1b).
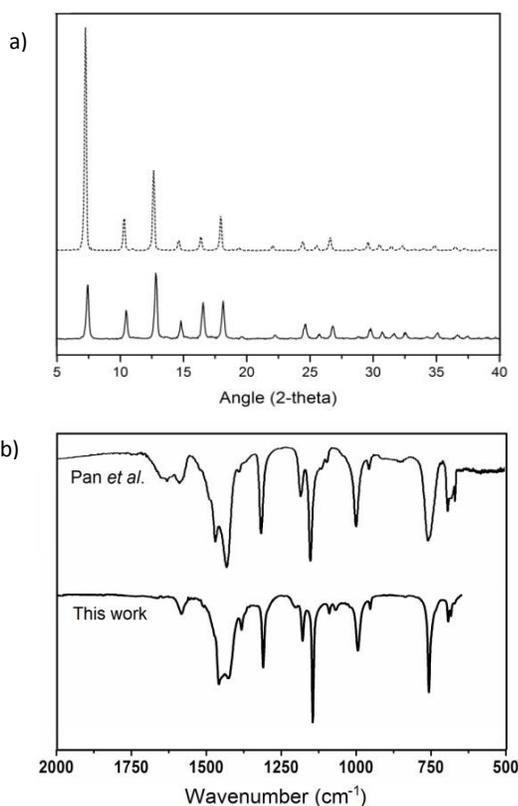
Figure 1 a) XRD pattern of as-synthesized ZIF-8 (solid line) and compared with Basolite Z1200 (dashed line), b) comparison between FTIR transmittance of synthesized ZIF-8 and literature [14]

The thermal stability of membranesare illustrated in Figure 2. At temperature 130°C-350°C, weight loss is evident in both membrane, withneat PSf at 1.23 % while MMM-1at 2.43 %. The weight loss are attribute to residual solvent evaporation. MMM-1 shown greater weight loss compared to neat PSf results from residual solvent trapped in ZIF-8's [23]. At temperature above 350°C, the second weight loss occurred in regards to degradation of polymer matix. MMM-1 shows greater weight loss than neat PSf due to the oxidation of ZIF-8 and turn to ZnO [24].The change in membrane Tg is evident at low ZIF-8

loading, where Tg of MMM-1 is 155°C while neat PSf is 165°C. The decrease in membrane Tg indicate that Disruption of polymer chain, creating flexible intermediate phase between polymer and nano ZIF-8 [16, 23].
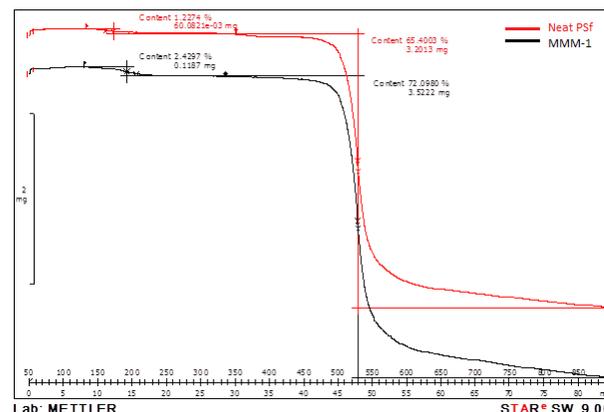
Figure 2 Thermal stability of neat PSf membrane and MMM-1

The gas permeation was conducted to evaluate ideal separation properties of both membranes are presented in Table 1. The gas permeation of MMM-1shows better in both CO_2 permeance and CO_2/CH_4 selectivity. Increased in CO2 permeance with incorporated ZIF-8 create more free volume among polymer chain [28, 29] as supported by lowered membrane Tg. Thus, increase flux for both tested gases are evident. Significant increment in CO_2/CH_4selectivity suggest that CO_2 preferred to access filler's pore rather than bypassing it due to interaction between quadrupole moment of CO2 and unsaturated metal sites in ZIF-8 [30, 31]. Table 2 shows relative comparison between this work to literature data using different polymer-filler combination. Although small amount of filler incorporated in polymer matrix was implement in this study, significant improvement of both CO2 permeance and CO2/CH4 selectivity somehow comparable with literature data. It is expected since synthesized ZIF-8 in nano-scale providelower external surface area to volume ratio and ease to interact with polymer chain [10-13]. Significant improvement of MMM performances using nano-sized ZIF-8 also suggest that better dispersion of filler into polymer matrix ease interaction between filler-penetrant.

Table 1 CO_2 and CH_4 permeation for neat PSf and PSf/ZIF-8

Membrane	$P_{\cdot CH4}$ (GPU)	$P_{\cdot CO2}$ (GPU)	α CO_2/CH_4
Neat PSf	0.66 ±0.30	4.97 ±0.12	7.52
MMM-1	0.68 ± 0.06	7.50 ±1.81	11.03

*the gas permeation was conducted at 4 bar, 27°C

Table 2 Comparison between literatures

Polymer	Filler	Loading (%)	Δ $P_{\cdot CO2}$	Δ $\alpha_{CO2/CH4}$	Reference (s)
PPEES	ZIF-8	10	1.393	1.29	[15, 16]
PSf	MIL-53(Al)	25	1.2	1.84	[13]
PVAc	Zeolite 4A	56	1.009	1.624	[25]
PI	Zeolite FAU/FMT	25	2.497	0.861	[26]
PSf/PI	Silica Sol	13	2.58	2.027	[27]
PSf	ZIF-8	1	1.51	1.467	This work

◼4.0 CONCLUSION

Nano-size ZIF-8 has been successfully synthesized and incorporated intoPSf matrix.The membrane was characterized via TGA and DSC has shown that ZIF-8 altered PSf membrane properties. Besides, improvement in both CO_2 permeance and CO_2/CH_4 selectivity are showndue to good interaction between quadrupole moment of CO_2, molecular sieving effect and unsaturated metal sites in ZIF-8. Besides, nano-ZIF-8 use in this study provide better dispersion through polymer phase, which evident through significant increase separation properties. Thus, the MMM prepared with nano-filler show great potential to be further improvement and commercialized.

References

[1] L. M. Robeson. 2008. The Upper Bound Revisited. *Journal of Membrane Science*. 320: 390–400.
[2] K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, and O. M. Yaghi. 2006. Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks. *Proc Natl Acad Sci U S A*. 103: 10186–91.
[3] S. A. Moggach, T. D. Bennett, and A. K. Cheetham. 2009. The Effect of Pressure on ZIF-8: Increasing Pore Size with Pressure and the Formation of a High-Pressure Phase at 1.47 GPa. *Angew Chem Int Ed Engl*. 48: 7087–9.
[4] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, and T. Duren. 2011. Opening the Gate: Framework Flexibility in ZIF-8 Explored by Experiments and Simulations. *J Am Chem Soc.* 133: 8900–2.
[5] J. C. Tan, T. D. Bennett, and A. K. Cheetham. 2010. Chemical Structure, Network Topology, and Porosity Effects on the Mechanical Properties of Zeolitic Imidazolate Frameworks. *Proceedings of the National Academy of Sciences*. 107: 9938–9943.
[6] A. Car, C. Stropnik, and K.-V. Peinemann. 2006. Hybrid Membrane Materials with Different Metal–organic Frameworks (MOFs) for Gas Separation. *Desalination*. 200: 424–426.
[7] Y. Zhang, K. J. Balkus, I. H. Musselman, and J. P. Ferraris. 2008. Mixed-matrix Membranes Composed of Matrimid® and Mesoporous ZSM-5 Nanoparticles. *Journal of Membrane Science*. 325: 28–39.
[8] S. A. Hashemifard, A. F. Ismail, and T. Matsuura. 2011. Effects of Montmorillonite Nano-clay Fillers on PEI Mixed Matrix Membrane for CO2 Removal. *Chemical Engineering Journal*. 170: 316–325.
[9] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, and D. R. Paul. 2001. Effect of Melt Processing Conditions on the Extent of Exfoliation in Organoclay-based Nanocomposites. *Polymer*. 42: 9513–9522.
[10] F. Li, Y. Li, T.-S. Chung, and S. Kawi. 2010. Facilitated Transport by Hybrid POSS®–Matrimid®–Zn2+ Nanocomposite Membranes for the Separation of Natural Gas. *Journal of Membrane Science*. 356: 14–21.
[11] Y. Li and T.-S. Chung. 2010. Molecular-level Mixed Matrix Membranes Comprising Pebax® and POSS for Hydrogen Purification via Preferential CO2 Removal. *International Journal of Hydrogen Energy*. 35: 10560–10568.
[12] S. Basu, A. Cano-Odena, and I. F. J. Vankelecom. 2010. Asymmetric Matrimid®/[Cu3(BTC)2] mixed-matrix Membranes for Gas Separations. *Journal of Membrane Science*. 362: 478–487.
[13] B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, and F. Kapteijn. 2011. Functionalized Flexible MOFs as Fillers in Mixed Matrix Membranes for Highly Selective Separation of CO2 from CH4 at Elevated Pressures. *Chem Commun (Camb)*. 47: 9522–4.
[14] Y. Pan, Y. Liu, G. Zeng, L. Zhao, and Z. Lai. 2011. Rapid Synthesis of Zeolitic Imidazolate Framework-8 (ZIF-8) Nanocrystals in an Aqueous System. *Chem Commun (Camb)*. 47: 2071–3.
[15] K. Díaz, L. Garrido, M. López-González, L. F. del Castillo, and E. Riande. 2010. CO2 Transport in Polysulfone Membranes Containing Zeolitic Imidazolate Frameworks as Determined by Permeation and PFG NMR Techniques. *Macromolecules*. 43: 316–325.
[16] K. Díaz, M. López-González, L. F. del Castillo, and E. Riande. 2011. Effect of Zeolitic Imidazolate Frameworks on the Gas Transport Performance of ZIF8-poly(1,4-phenylene ether-ether-sulfone) Hybrid Membranes. *Journal of Membrane Science*. 383: 206–213.
[17] C. Zhang, Y. Dai, J. R. Johnson, O. Karvan, and W. J. Koros. 2012. High Performance ZIF-8/6FDA-DAM Mixed Matrix Membrane for Propylene/Propane Separations. *Journal of Membrane Science*. 389: 34–42.
[18] O. G. Nik, X. Y. Chen, and S. Kaliaguine. 2012. Functionalized metal Organic Framework-polyimide Mixed Matrix Membranes for CO2/CH4 Separation. *Journal of Membrane Science*. 413–414: 48–61.
[19] G. K. a. H. Williamson, W. H. 1953. X-ray Line Broadening from Filed Aluminium and Wolfram. *Acta Metallurgica*. 1: 22–31.
[20] V. D. Mote, Y. Purushotham, and B. N. Dole. 2012. Williamson-Hall Analysis in Estimation of Lattice Strain in Nanometer-sized ZnO Particles. *Journal of Theoretical and Applied Physics*. 6: 1–8. 2012/07/02.
[21] Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, and R. Q. Snurr. 2008. Separation of CO2 from CH4 Using Mixed-Ligand Metal−Organic Frameworks. *Langmuir*. 24: 8592–8598, 2008/08/01.
[22] E. V. Perez, K. J. Balkus, J. P. Ferraris, and I. H. Musselman. 2009. Mixed-matrix Membranes Containing MOF-5 for Gas Separations. *Journal of Membrane Science*. 328: 165–173.
[23] J. Ploegmakers, S. Japip, and K. Nijmeijer. 2013. Mixed Matrix Membranes Containing MOFs for Ethylene/ethane Separation—Part B: Effect of Cu3BTC2 on Membrane Transport Properties. *Journal of Membrane Science*. 428: 331–340.
[24] X. C. Huang, Y. Y. Lin, J. P. Zhang, and X. M. Chen. 2006. Ligand-directed Strategy for Zeolite-type Metal-organic Frameworks: Zinc(II) Imidazolates with Unusual Zeolitic Topologies. *Angew Chem Int Ed Engl*. 45: 1557–9.
[25] R. T. Adams, J. S. Lee, T.-H. Bae, J. K. Ward, J. R. Johnson, C. W. Jones, S. Nair, and W. J. Koros. 2011. CO2–CH4 Permeation in High Zeolite 4A Loading Mixed Matrix Membranes. *Journal of Membrane Science*. 367: 197–203.
[26] O. G. Nik, X. Y. Chen, and S. Kaliaguine. 2011. Amine-functionalized Zeolite FAU/EMT-polyimide Mixed Matrix Membranes for CO2/CH4 Separation. *Journal of Membrane Science*. 379: 468–478.
[27] S. Rafiq, Z. Man, A. Maulud, N. Muhammad, and S. Maitra. 2012. Separation of CO2 from CH4 using Polysulfone/polyimide Silica Nanocomposite Membranes. *Separation and Purification Technology*. 90: 162–172.
[28] L. Ge, Z. Zhu, and V. Rudolph. 2011. Enhanced Gas Permeability by Fabricating Functionalized Multi-walled Carbon Nanotubes and Polyethersulfone Nanocomposite Membrane. *Separation and Purification Technology*. 78: 76–82.
[29] M. J. C. Ordoñez, K. J. Balkus, J. P. Ferraris, and I. H. Musselman. 2010. Molecular Sieving Realized with ZIF-8/Matrimid® Mixed-matrix Membranes. *Journal of Membrane Science*. 361: 28–37.
[30] R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, and O. M. Yaghi. 2009. Control of Pore Size and Functionality in Isoreticular Zeolitic Imidazolate Frameworks and Their Carbon Dioxide Selective Capture Properties. *J Am Chem Soc.* 131: 3875–7.
[31] R. Adams, C. Carson, J. Ward, R. Tannenbaum, and W. Koros. 2010. Metal Organic Framework Mixed Matrix Membranes for Gas Separations. *Microporous and Mesoporous Materials.* 131: 13–20.