



Swansea University
Prifysgol Abertawe



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in:
Chemistry - A European Journal

Cronfa URL for this paper:
<http://cronfa.swan.ac.uk/Record/cronfa41083>

Paper:

Sabetghadam, A., Liu, X., Orsi, A., Lozinska, M., Johnson, T., Jansen, K., Wright, P., Carta, M., McKeown, N., et. al. (2018). Towards High Performance Metal-Organic Framework-Microporous Polymer Mixed Matrix Membranes: Addressing Compatibility and Limiting Aging by Polymer Doping. *Chemistry - A European Journal*
<http://dx.doi.org/10.1002/chem.201803006>

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

<http://www.swansea.ac.uk/library/researchsupport/ris-support/>

Towards High Performance MOF – Microporous Polymer Mixed Matrix Membranes: Addressing Compatibility and Limiting Aging via Polymer Doping

Anahid Sabetghadam, Xinlei Liu,* Angelica F. Orsi, Magdalena M. Lozinska, Timothy Johnson, Kaspar M. B. Jansen, Paul A. Wright, Mariolino Carta, Neil B. McKeown, Freek Kapteijn and Jorge Gascon*

Abstract: Membrane separation for gas purification is an energy-efficient and environment-friendly technology. However, the development of high performance membranes is still a great challenge. In principle, mixed matrix membranes (MMMs) have the potential to overcome current materials limitations, but in practice there is no straightforward method to match the properties of fillers and polymers (the main components of MMMs) in such a way that the final membrane performance reflects the high performance of the microporous filler and the processability of the continuous polymer phase. This issue is especially important when high flux polymers are utilized. In this work, we demonstrate that the use of small amounts of a glassy polymer in combination with high performance PIM-1 allow for the preparation of MOF based MMMs with superior separation properties and low aging rates under humid conditions, meeting the commercial target for post-combustion CO₂ capture.

Membrane technologies for gas separation are attractive due to their relatively low energy penalty and benign environmental aspects.^[1] Currently, polymeric materials dominate the market for membrane gas separation thanks to ease of processing and mechanical strength.^[1b] However, the performance of polymeric membranes is limited by the fact that improvements in permeability are always at the expense of selectivity, and *vice*

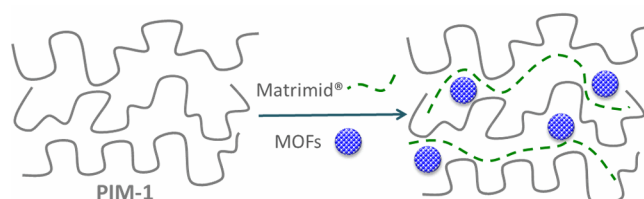
versa.^[2] This trade-off, defined by Robeson's upper bounds, still hampers the widespread application of membrane units.^[2] Recently, polymers of intrinsic microporosity (PIMs),^[3] a subfamily of microporous polymers, have been identified as attractive candidates for high performance gas separation membranes. A prototypical example is PIM-1.^[3d] The rigid and contorted ladder-like structure of PIM-1 leads to inefficient packing of polymer chains and to a high fractional free volume, providing highly permeable pathways for gas molecules but moderate selectivity and very fast physical aging.^[3b] Various strategies including crosslinking,^[4] post-modification^[5] and polymer blending^[6] have been employed to improve the membrane performance. Polymer blending has been recognized as a cost- and time-effective route,^[7] which combines the advantages of different polymers.

Besides the above strategies, mixed matrix membranes (MMMs) are proposed to have even more potential, provided that properties from embedded fillers and the economical processing features of polymers can be properly matched.^[8] ^[9] In the last few years, the effect of boosting gas adsorption^[10] and diffusion,^[10-11] incorporation of additional polymer chains^[12] and altering the matrix structure^[13] have been explored by using metal-organic frameworks (MOFs),^[10, 11b, 13] porous organic cages (POCs)^[11a] and porous aromatic frameworks (PAFs)^[12] as fillers. Nevertheless, simultaneous improvement of permeation and selectivity is challenging and there is not a large amount of data reported in literature showing this improvement. Table S1 shows data collected by Vinoba *et al.*^[14] on membranes that have so far demonstrated an increase in both permeability and selectivity for CO₂/N₂ separation. Moreover, in most cases low permeation polymers are used. When it comes to microporous polymers, the main challenge to overcome in the field of MMMs is mostly the poor interfacial compatibility between the two phases.^[15] As a result, performance improvements are marginal and membrane aging rates have been hardly reduced.

In this study, we demonstrate that the combination of doping glassy Matrimid[®] polymeric chains along with the addition of MOF fillers (e.g. NH₂-MIL-53(Al)) in PIM-1 (Scheme 1) results in both a substantial enhancement of CO₂ permeability and CO₂/N₂ selectivity under dry and humid conditions while greatly reducing aging. The obtained MMM performance transcends the 2008 Robeson upper bound limit and reaches the economic target region for post-combustion CO₂ capture,^[16] even after 17 months of aging.

[*] A. Sabetghadam, Dr. X. Liu, Prof. Dr. F. Kapteijn, Prof. Dr. J. Gascon
Catalysis Engineering, Department of Chemical Engineering,
Delft University of Technology, Van der Maasweg 9, 2629HZ Delft,
The Netherlands.
Email: x.liu-8@tudelft.nl
Prof. Dr. J. Gascon
KAUST Catalysis Center, King Abdullah University of Science and
Technology, Advanced Catalytic Materials, Thuwal 23955, Saudi
Arabia.
Email: jorge.gascon@kaust.edu.sa
A. F. Orsi, Dr. M. M. Lozinska, Prof. Dr. P. A. Wright
EaStCHEM School of Chemistry, University of St Andrews, Purdie
Building, North Haugh, St Andrews, Fife, KY16 9ST, United Kingdom.
Dr. T. Johnson
Johnson Matthey Technology Centre, Blount's Court Road, Sonning
Common, Reading, RG4 9NH, United Kingdom.
Prof. Dr. K. M. B. Jansen
Emerging Materials, Department of Design Engineering,
Delft University of Technology, Landbergstraat 15, 2628 CE Delft,
The Netherlands.
Dr. M. Carta
Department of Chemistry, College of Science,
Swansea University, Grove Building, Singleton Park, Swansea, SA2
8PP, United Kingdom.
Prof. Dr. N. B. McKeown
EaStCHEM, School of Chemistry, University of Edinburgh, Joseph
Black Building, David Brewster Road, Edinburgh, Scotland EH93FJ,
United Kingdom.

Supporting information for this article is given via a link at the end of the document.



Scheme 1. Scheme of doping Matrimid® and implanting MOFs into PIM-1 matrix.

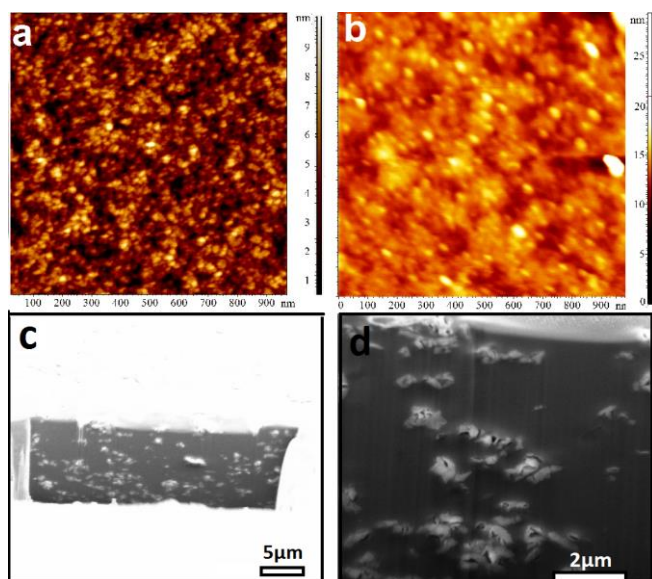


Figure 1. Tapping-mode AFM topographical image of the surface of a) PIMAT (9.1 wt.%) and b) PIMAT (40 wt.%). The height profile is shown for reference; FIB-SEM images of NH₂-MIL-53(AI)/PIMAT membrane: c) the trench created by FIB milling of the specimen and d) a representative cross-section of the membrane.

Matrimid®, in comparison to PIM-1, is a relatively flexible, and less contorted polymer that shows a higher degree of packing.^[17] This results in higher selectivity, lower permeance and a very slow aging rate. Following previous reports, we used a Matrimid®/PIM-1 blending weight ratio of 9.1/90.9 to achieve a miscible mixture for membrane preparation^[6]. Indeed, when using higher amounts of Matrimid® (Figure 1b, weight ratio 40/60), much rougher surfaces are observed by AFM than at the optimal ratio (Figure 1a). Such rough surfaces have been interpreted as phase segregation.^[6]

NH₂-MIL-53,^[18] a promising MOF material, has been reported to display outstanding selectivity in the separation of CO₂ from N₂,^[19] thus making it a good candidate for constructing MMMs.^[20] Diamond and rod-shaped NH₂-MIL-53(AI) crystals with average particle size of 500 nm were prepared (Figure S1a). A relatively high filler content (25 wt.%, $W_{MOF}/(W_{MOF}+W_{PIMAT})$) was used. Surprisingly, the PIMAT composite is able to host high concentrations of MOF without compromising its structural properties. Indeed, such high loadings of filler in pure PIM-1 rendered brittle films with micro-cracks (Figure S2c, S2d, S3a and S3c). The filler dispersion and morphology of the as-synthesized composite membrane was studied by focused ion beam-scanning electronic microscopy (Figure 1c & d) and (Figure S3b and S3d). A homogeneous distribution of the MOF crystals in the PIMAT matrix along with no detectable gaps between the filler and matrix is clearly observed, illustrating a good adhesion between the filler and polymer phases.

CO₂ adsorption measurements on MOF materials and membranes were conducted at 273 K and up to 1.2 bar. As depicted in Figure 2a and S5, a slight drop of CO₂ uptake on PIM-1 is observed upon blending Matrimid®, indicating a higher packing efficiency of polymer chains in PIMAT. Given the good miscibility of both polymers, the free volume of PIM-1 could be partially occupied by the threading Matrimid®. Also the reduced N₂ uptake on PIMAT membranes suggests this (Figure S4). NH₂-MIL-53(AI) materials exhibit considerable CO₂ uptake even when its framework is in *np* configuration (Figure 2a).^[19] For comparison, the ideal adsorption isotherm of NH₂-MIL-53(AI)/PIMAT membrane was calculated from a linear combination of the isotherms of NH₂-MIL-53(AI) and PIMAT based on their mass contribution. Since the NH₂-MIL-53(AI) in the membrane is in a *lp-np* configuration, the experimental CO₂ uptake is overall higher than the linear combination of both isotherms.

The structures of the MOF powders and membranes were analyzed by XRD and the diffraction patterns are presented in Figure 2b and S6. NH₂-MIL-53 has a flexible framework, and displays a mixture of the narrow pore (*np*) and large pore (*lp*) configurations.^[19] As-prepared NH₂-MIL-53 crystals show a diffraction pattern coherent with the *np* framework configuration, but diffractions ascribed to the *lp* MOF structure emerge in the pattern of the casted PIMAT membrane. The intensity ratio of the *lp/np* reflections in the NH₂-MIL-53(AI)/PIMAT is higher than NH₂-MIL-53(AI)/PIM-1 membrane, suggesting, as previously reported by our group (Matrimid® in this case),^[21] the partial penetration of Matrimid® into the MOF pores (Figure 2b).

To get insight into the polymer-MOFs interaction, ATR-IR spectra of the MMMs were acquired and compared to the original spectra of the MOF powder (Figure 2c and S7). In case of NH₂-MIL-53(AI) MMMs, a slight shift in the stretching vibration of NH₂-MIL-53(AI) carboxylic groups was observed. The shift in asymmetric (1500 cm⁻¹: blue shift and 1580 cm⁻¹: red shift) and symmetric (1410 cm⁻¹: red shift) stretching vibration is attributed to the interaction of carboxylic and amine groups in NH₂-MIL-53(AI) as reported by Chen *et al* (Figure S7a).^[22] Moreover, the peaks at 3500 and 3387 cm⁻¹ are attributed to the asymmetric and symmetric amine stretchings of the MOF. The upward shift in the amine vibrations in PIMAT could be assigned to hydrogen bonding between MOF amine groups and free carbonyls in Matrimid® (Figure 2c).^[23] Considering ZIF-94 MMMs (Figure S7b), there is no shift in the peak of -N-H bond vibration of the ZIF-94 (1665 cm⁻¹) by loading in PIM-1 and PIMAT MMMs.

The mechanical properties of the PIM-1 and PIMAT based membranes were assessed by tensile tests. The results are presented in Figure S8 and Table S3. As it was observed by simple flexing of the samples, PIMAT was more flexible than PIM-1. Accordingly, the tensile results showed that by addition of Matrimid® to PIM-1, not only the sample shows more plastic deformation (shown in Figure S8), but also the strain in the fracture point was higher than PIM-1, showing the flexibility of PIMAT membranes. However, loading of NH₂-MIL-53(AI) and ZIF-94 would result in a lower fracture point which is attributed to the brittleness of the membranes in comparison to the neat polymeric membranes. Despite this issue, the elastic modulus (stress to strain ratio) of the PIMAT based MMMs is much higher than the

one measured for PIM-1 based MMMs, further demonstrating the benefits of polymer blending for the preparation of MMMs.^[24]

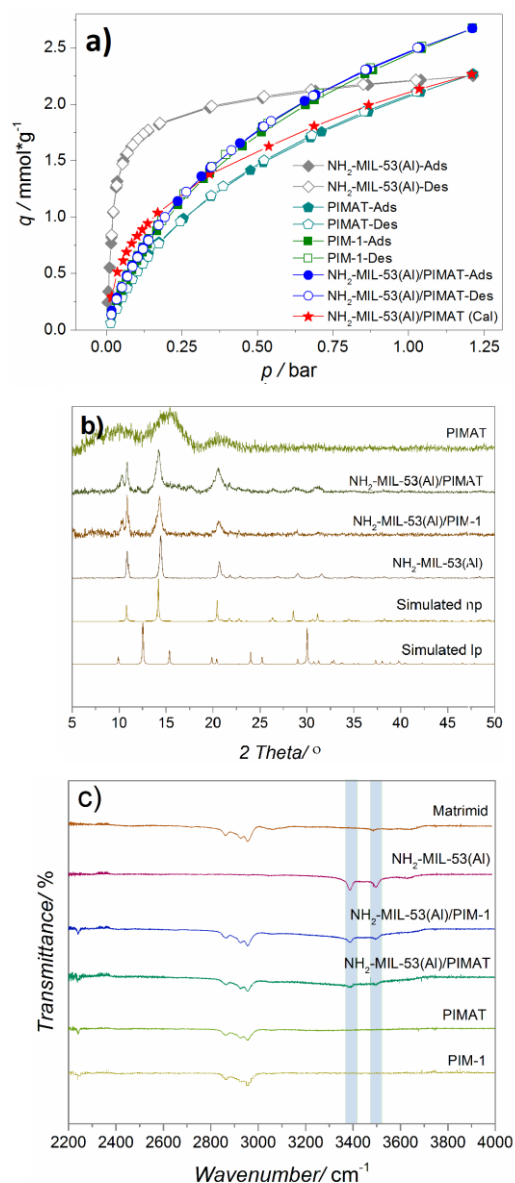


Figure 2. a) Experimental CO₂ adsorption (solid symbols) and desorption (open symbols) isotherms of NH₂-MIL-53(Al) and membranes at 273 K. The MOF particle loading in PIMAT is 25 wt. %. The Matrimid[®] loading in PIM-1 is 9.1 wt.%. The calculated isotherm is gained from a linear combination of the isotherms of NH₂-MIL-53(Al) and PIMAT based on their weight contribution, b) XRD patterns of NH₂-MIL-53(Al), PIMAT, NH₂-MIL-53(Al)/PIM-1 and NH₂-MIL-53(Al)/PIMAT. The simulated lp and np XRD patterns of NH₂-MIL-53(Al) are shown for reference, c) ATR-IR spectra between 2200-4000 cm⁻¹ of NH₂-MIL-53(Al), Matrimid[®], PIMAT, PIM-1 and their MMMs.

The as-synthesized membranes were sealed in home-made modules and evaluated in the separation of CO₂ from N₂ at conditions relevant to pre-combustion CO₂ capture (CO₂/N₂=15/85 mol/mol mixture at 298 K and 2 bar absolute feed pressure (see the Supporting Information)). The performance is

shown in Figure 3a and Figure S9. The neat PIM-1 membrane exhibits a CO₂ permeability of ~3780 Barrer (1 Barrer = 1*10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹) and a CO₂ / N₂ selectivity of ~19, in line with previous reports.^[6, 13] Upon threading the Matrimid[®], a ~32% enhancement of gas selectivity was observed at the expense of ~41% reduction in CO₂ permeability, further confirming the higher polymer packing efficiency in PIMAT. By the addition of NH₂-MIL-53(Al) filler to PIMAT, the CO₂ permeability nearly doubled (~97% increase relative to PIMAT) with a slight drop in selectivity. This synergistic effect generates a simultaneous increase of selectivity (to 23) and CO₂ permeability (to 4380 Barrer) relative to PIM-1, driving the membrane separation performance over the Robeson upper bound limit (2008)^[2] and reaching the economic target region.^[16] For comparison, the performance of a NH₂-MIL-53(Al)/PIM-1 membrane was evaluated. As shown in Figure 3a, the membrane permeability increased by a 160% with 26% drop in selectivity relative to neat PIM-1. This is most probably the generation of micro-cracks in the polymer matrix due to the relatively high MOF loading (*vide supra*).

In order to gain insight into the influence on aging, membrane performance was evaluated after exposing the membranes to ambient conditions for 3 months. Results are shown in Figure 3a and Figure S9. It is well known that during physical aging, the polymer chains of PIM-1 tend to pack more efficiently,^[25] leading to a decrease in permeability (75%) and an increase in selectivity from 19 to 25. In contrast, in case of PIMAT, where Matrimid[®] occupies part of this free volume, CO₂ permeability decreases only by a 56% and selectivity slightly increases to 27. In case of NH₂-MIL-53(Al)/PIM-1, where a large fraction of permeability is due to the presence of micro-cracks, only a 26% drop in CO₂ flux is observed. Despite the substantial decrease (48%) in CO₂ permeability for the NH₂-MIL-53(Al)/PIMAT membrane upon aging, its performance, with a CO₂ permeability of 2260 Barrer and CO₂/N₂ selectivity of 27 lies on the Robeson upper bound (2008). This performance clearly improved over that observed for the fresh PIMAT and is better both in terms of selectivity and permeability than that of aged PIM-1.

In order to demonstrate the scope of our approach, we prepared additional membranes using ZIF-94(Zn) as filler, in virtue of its high CO₂ uptake at low pressure (Figure S5).^[26] However, upon loading 25 wt.% ZIF-94(Zn) into PIM-1, very brittle membranes were obtained with no separation selectivity. As anticipated, a more selective ZIF-94(Zn)/PIMAT membrane was formed with the assistance of Matrimid[®] threading (Figure 3a). After 3 months aging, although the CO₂ permeability of ZIF-94(Zn)/PIMAT decreased by 60%, it is still higher than the aged PIM-1 with a comparable selectivity. These results further demonstrate the significance of our approach for composite membrane preparation.

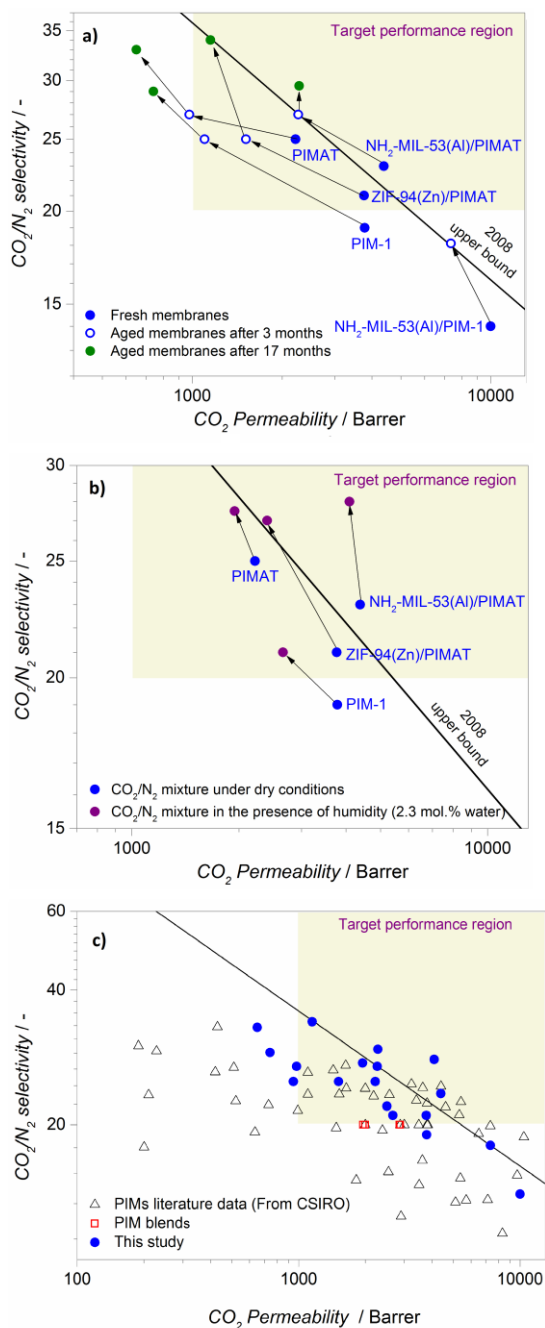


Figure 3. a) Robeson plot of CO₂/N₂ separation performance of the fresh (blue closed), aged membranes after 3 months (blue open symbols) and 17 months (green closed squares) tested under dry conditions. b) Robeson plot of CO₂/N₂ separation performance of the fresh (blue symbols) membranes tested under dry and humid (2.3 mol.% water in feed, purple symbols) conditions. c) Robeson plot of CO₂/N₂ mixed gas separation performance of this study (the fresh/aged membranes in dry and humid condition) and the literature data of microporous polymers taken from Commonwealth Scientific and Industrial Research Organization (CSIRO).^[27] The Robeson upper bound (2008)^[2] is shown for reference, as well as the target performance region for CO₂ capture from flue gas from Merkel *et al.*^[16] assuming a membrane thickness of 1 μm . The MOF particle loading in PIMAT is 25 wt. %. The Matrimid® loading in PIM-1 is 9.1 wt. %. All the measurements were conducted at 298 K with 2 bar absolute feed pressure (mixed gases). 1 Barrer = 1×10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹.

Further, we have tested the aged PIM and PIMAT neat and MMM samples after 17 months. The aging after 3 months mainly resulted predominantly in a decrease in permeation while after 17 months the aging shifted towards an increase in selectivity for the PIMAT membranes. In contrast, the PIM-1 membrane continued the trend of reduction in permeability after 17 months of aging. Interestingly, after 17 months of membranes aging in ambient conditions the PIMAT MMMs performance surpasses the upper bound.

The separation performance of PIM-1 and PIMAT neat and mixed matrix membranes was evaluated under humid conditions (2.3 mol.% water in feed) and compared with dry conditions (Figure 3b). PIMAT based membranes showed less reduction in permeability than PIM-1, while in both cases the selectivity increased by two points. However, the NH₂-MIL-53(Al)/PIMAT composites nearly preserved its high permeability of 4000 Barrer and improved CO₂/N₂ selectivity up to 28, the highest of all samples.

The results of this study (blue circles) demonstrate a superior performance in comparison to other PIMs (black open circles) and PIM blended (red open circles) membranes (Figure 3c). This confirms the influence of MOF loading in blended polymers and enhancing the CO₂/N₂ separation performance relative to the upper bound.

In summary, by utilizing a second, less permeable polymer, in combination with a high performance PIM-1 microporous polymer, we were able to manufacture MOF-based mixed matrix membranes with enhanced phase compatibility, and consequently the membrane separation performance and anti-aging properties were improved simultaneously. The versatility of the developed method was evidenced by using different MOF fillers, which can potentially incorporate in other rigid microporous polymer membranes.

Experimental Section

MOF/PIMAT membrane preparation: to prepare the mixture of polymers, 0.10 g PIM-1 was dissolved in 4.0 mL chloroform (Sigma Aldrich, anhydrous $\geq 99.99\%$) and then 0.010 g Matrimid® (Huntsman Advanced Materials, Mw: 80,000) was added and stirred for 2 h. Meanwhile, a certain amount of MOF NH₂-MIL-53(Al) or ZIF-94(Zn) (degassed at 373 K, 0.037 g) was dispersed in 1.5 mL of chloroform, followed by ultrasonication and stirring for 90 min. To attain a better MOF dispersion, firstly a 10 % of the dissolved polymers solution was added to the MOF solution. After stirring, the remaining amount of polymer solution was added and stirred overnight. The homogeneous MOF/PIMAT solution was casted on a glass plate by Doctor Blade technique with a gap of 80 μm and covered with a top-drilled box and dried overnight under chloroform-saturated atmosphere. Finally, the dried membranes were peeled off and heat-treated under vacuum at 393 K for 24 h. The MOF content in both fabricated PIMAT membranes was kept at 25 wt.% ($W_{\text{MOF}}/(W_{\text{MOF}}+W_{\text{PIMAT}})$) for consistency. As reference, neat PIM-1, PIMAT ($W_{\text{Mat}}/(W_{\text{Mat}}+W_{\text{PIM}})=9.1$ wt.%), MOF/PIM-1 ($W_{\text{MOF}}/(W_{\text{MOF}}+W_{\text{PIM}})=25$ wt.%) membranes were prepared with the same approach. The thickness of all membranes was around 30-40 μm , measured by a digital micrometer (Mitutoyo, Japan, 1 μm) at different locations of each membrane.

More experimental (preparation of MOFs and PIM-1) and characterization details (adsorption measurements, FIB-SEM, TEM, XRD, AFM and gas permeation evaluation) are described in the Supporting Information.

Acknowledgements

The authors gratefully acknowledge the financial support from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013), M4CO2 project (608490).

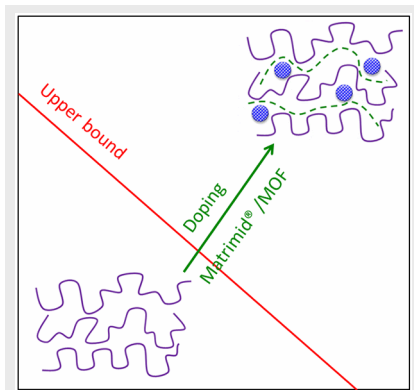
Conflict of interest

The authors declare no conflict of interest.

Keywords: membranes • gas separation • microporous polymer • metal-organic frameworks • compatibility

- [1] a) W. J. Koros, R. P. Lively, *AIChE J.* **2012**, *58*, 2624-2633; b) D. F. Sanders, Z. P. Smith, R. Guo, L. M. Robeson, J. E. McGrath, D. R. Paul, B. D. Freeman, *Polymer* **2013**, *54*, 4729-4761.
- [2] L. M. Robeson, *J. Membr. Sci.* **2008**, *320*, 390-400.
- [3] a) X. Zhu, C. Tian, S. M. Mahurin, S. H. Chai, C. Wang, S. Brown, G. M. Veith, H. Luo, H. Liu, S. Dai, *J. Am. Chem. Soc.* **2012**, *134*, 10478-10484; b) S. Wang, X. Li, H. Wu, Z. Tian, Q. Xin, G. He, D. Peng, S. Chen, Y. Yin, Z. Jiang, M. D. Guiver, *Energy Environ. Sci.* **2016**, *9*, 1863-1890; c) M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli, N. B. McKeown, *Science* **2013**, *339*, 303-307; d) N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675-683; e) P. M. Budd, E. S. Elabas, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall, D. Wang, *Adv. Mater.* **2004**, *16*, 456-459; f) I. Rose, C. G. Bezzu, M. Carta, B. Comesana-Gandara, E. Lasseuguette, M. C. Ferrari, P. Bernardo, G. Clarizia, A. Fuoco, J. C. Jansen, K. E. Hart, T. P. Liyana-Arachchi, C. M. Colina, N. B. McKeown, *Nat. Mater.* **2017**, *16*, 932-937.
- [4] Q. Song, S. Cao, R. H. Pritchard, B. Ghalei, S. A. Al-Muhtaseb, E. M. Terentjev, A. K. Cheetham, E. Sivaniah, *Nat. Commun.* **2014**, *5*, 4813.
- [5] N. Du, H. B. Park, G. P. Robertson, M. M. Dal-Cin, T. Visser, L. Scoles, M. D. Guiver, *Nat. Mater.* **2011**, *10*, 372-375.
- [6] W. F. Yong, F. Y. Li, Y. C. Xiao, P. Li, K. P. Pramoda, Y. W. Tong, T. S. Chung, *J. Membr. Sci.* **2012**, *407-408*, 47-57.
- [7] D. R. Paul, S. Newman, *Polymer Blends*, Academic Press, New York, **1978**.
- [8] a) J. Dechnik, J. Gascon, C. J. Doonan, C. Janiak, C. J. Sumbly, *Angew. Chem. Int. Ed.* **2017**, *56*, 9292-9310; b) B. Seoane, J. Coronas, I. Gascon, M. Etxeberria Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascon, *Chem. Soc. Rev.* **2015**, *44*, 2421-2454; c) T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, I. X. F. X. Llabres, J. Gascon, *Nat. Mater.* **2015**, *14*, 48-55.
- [9] a) T. H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones, S. Nair, *Angew. Chem. Int. Ed.* **2010**, *49*, 9863-9866; b) W. J. Koros, C. Zhang, *Nat. Mater.* **2017**, *16*, 289-297; c) X. L. Liu, Y. S. Li, G. Q. Zhu, Y. J. Ban, L. Y. Xu, W. S. Yang, *Angew. Chem. Int. Ed.* **2011**, *50*, 10636-10639.
- [10] N. Tien-Binh, H. Vinh-Thang, X. Y. Chen, D. Rodrigue, S. Kaliaguine, *J. Membr. Sci.* **2016**, *520*, 941-950.
- [11] a) A. F. Bushell, P. M. Budd, M. P. Attfield, J. T. Jones, T. Hasell, A. I. Cooper, P. Bernardo, F. Bazzarelli, G. Clarizia, J. C. Jansen, *Angew. Chem. Int. Ed.* **2013**, *52*, 1253-1256; b) Q. Song, S. Cao, R. H. Pritchard, H. Qiblawey, E. M. Terentjev, A. K. Cheetham, E. Sivaniah, *J. Mater. Chem. A* **2016**, *4*, 270-279.
- [12] a) C. H. Lau, P. T. Nguyen, M. R. Hill, A. W. Thornton, K. Konstas, C. M. Doherty, R. J. Mulder, L. Bourgeois, A. C. Liu, D. J. Sprouster, J. P. Sullivan, T. J. Bastow, A. J. Hill, D. L. Gin, R. D. Noble, *Angew. Chem. Int. Ed.* **2014**, *53*, 5322-5326; b) C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* **2015**, *54*, 2669-2673.
- [13] a) B. Ghalei, K. Sakurai, Y. Kinoshita, K. Wakimoto, Ali P. Isfahani, Q. Song, K. Doitomi, S. Furukawa, H. Hirao, H. Kusuda, S. Kitagawa, E. Sivaniah, *Nat. Energy* **2017**, *2*, 17086; b) S. J. Smith, B. P. Ladewig, A. J. Hill, C. H. Lau, M. R. Hill, *Sci. Rep.* **2015**, *5*, 7823.
- [14] M. Vinoba, M. Bhagiyalakshmi, Y. Alqaheem, A. A. Alomair, A. Pérez, M. S. Rana, *Sep. Purif. Technol.* **2017**, *188*, 431-450.
- [15] a) S. J. D. Smith, C. H. Lau, J. I. Mardel, M. Kitchin, K. Konstas, B. P. Ladewig, M. R. Hill, *J. Mater. Chem. A* **2016**, *4*, 10627-10634; b) Z. Wang, D. Wang, S. Zhang, L. Hu, J. Jin, *Adv. Mater.* **2016**, *28*, 3399-3405.
- [16] T. C. Merkel, H. Lin, X. Wei, R. Baker, *J. Membr. Sci.* **2010**, *359*, 126-139.
- [17] Y. D. Y. Xiao, T. S. Chung, M. D. Guiver, *Macromolecules* **2005**, *38*, 10042-10049.
- [18] J. Gascon, U. Aktay, M. Hernandezalonso, G. Vanklink, F. Kapteijn, *J. Catal.* **2009**, *261*, 75-87.
- [19] E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, F. Kapteijn, *Langmuir* **2011**, *27*, 3970-3976.
- [20] a) T. Rodenas, M. van Dalen, E. García-Pérez, P. Serra-Crespo, B. Zornoza, F. Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2014**, *24*, 249-256; b) A. Sabetghadam, B. Seoane, D. Keskin, N. Duim, T. Rodenas, S. Shahid, S. Sorribas, C. L. Guillouzer, G. Clet, C. Tellez, M. Daturi, J. Coronas, F. Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2016**, *26*, 3154-3163.
- [21] A. Sabetghadam, X. Liu, M. Benzaqui, E. Gkaniatsou, A. Orsi, M. M. Lozinska, C. Sicard, T. Johnson, N. Steunou, P. A. Wright, C. Serre, J. Gascon, F. Kapteijn, *Chem. Eur. J.* **2018**, *24*, 7949-7956.
- [22] X. Y. Chen, V.-T. Hoang, D. Rodrigue, S. Kaliaguine, *RSC Adv.* **2013**, *3*, 24266.
- [23] X. Y. Chen, H. Vinh-Thang, D. Rodrigue, S. Kaliaguine, *Ind. Eng. Chem. Res.* **2012**, *51*, 6895-6906.
- [24] I. S. Flyagina, E. M. Mahdi, K. Titov, J.-C. Tan, *APL Materials* **2017**, *5*, 086104.
- [25] X. Q. Cheng, K. Konstas, C. M. Doherty, C. D. Wood, X. Mulet, Z. Xie, D. Ng, M. R. Hill, L. Shao, C. H. Lau, *ACS Appl. Mater. Interfaces* **2017**, *9*, 14401-14408.
- [26] a) W. Morris, N. He, K. G. Ray, P. Klonowski, H. Furukawa, I. N. Daniels, Y. A. Houndonougbo, M. Asta, O. M. Yaghi, B. B. Laird, *J. Phys. Chem. C* **2012**, *116*, 24084-24090; b) M. Etxeberria-Benavides, O. David, T. Johnson, M. M. Łozińska, A. Orsi, P. A. Wright, S. Mastel, R. Hillenbrand, F. Kapteijn, J. Gascon, *J. Membr. Sci.* **2018**, *550*, 198-207.
- [27] <https://membrane-australasia.org/polymer-gas-separation-membranes/>.

Soft helps hard: by utilizing a second, relative flexible polymer, in combination with rigid PIM-1 microporous polymer, we were able to manufacture MOF based mixed matrix membranes with enhanced phase compatibility, and consequently the membrane separation performance and anti-aging properties were improved simultaneously.



A. Sabetghadam, X. Liu, A. F. Orsi, M. M. Lozinska, T. Johnsen, K. M. B. Jansen, P. A. Wright, M. Carta, N. B. McKeown, F. Kapteijn and J. Gascon**

Page No. – Page No.

Towards High Performance MOF – Microporous Polymer Mixed Matrix Membranes: Addressing Compatibility and Limiting Aging via Polymer Doping