Fine-Tuned Intrinsically *Ultra*-Microporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations

Raja Swaidan, Bader Ghanem, Ingo Pinnau*

Advanced Membranes and Porous Materials Center (AMPMC), Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, KSA

*Corresponding author: Al-Jazri Bldg. 4, Tel: +966-12-808-2406

E-mail address: ingo.pinnau@kaust.edu.sa (I. Pinnau)

Abstract

Intrinsically *ultra*-microporous (<7 Å) polymers (UPIMs) represent a new paradigm in materials development for membrane-based gas separation. In particular, UPIMs demonstrate that uniting *intra*-chain "rigidity" – the traditional design metric of highly permeable polymers of intrinsic microporosity (PIMs) – with gas-sieving *ultra*-microporosity yields high performance gas separation membranes. UPIMs have redefined the state-of-the-art in cornerstone air (e.g., O_2/N_2) and hydrogen recovery (e.g., H_2/N_2, H_2/CH_4) applications with unprecedented molecular sieving gas transport properties. Accordingly, presented herein are new 2015 permeability/selectivity "upper bounds" for large-scale commercial membrane-based air and hydrogen applications that accommodate the substantial performance enhancements of UPIMs over preceding polymers. A subtle balance between *intra*-chain rigidity and *inter*-chain spacing has been achieved in the amorphous microstructures of UPIMs, fine-tuned using unique bridged-bicyclic building blocks (i.e., triptycene, ethanoanthracene and Tröger's base) in both ladder and semi-ladder (e.g., polyimide) structures.

Main Text

Polymer membrane technology is a simple low-energy intensity alternative to traditional gas separation technologies such as cryogenic distillation and absorption.[1, 2] It is well established in various applications, with nearly two-thirds of the market comprising air enrichment (e.g., for nitrogen blanketing or oxygen-enhanced combustion) and hydrogen recovery (e.g., from ammonia purge gas and petrochemical refinery reactor streams).[3, 4] Membrane materials performance, and thus viability, is gauged by the polymer permeability and selectivity. In 1991 Robeson[5, 6] established that these two intrinsic material properties obey a trade-off relationship for polymers, whereby more permeable materials tend to be less selective and vice versa and, more recently, updated the database in 2008. Accordingly, the state of the art for a given gas pair is traditionally identified by a linear "upper bound" fit to the top performing materials on a log-log plot of available permeability/selectivity combinations. Freeman provided the fundamental theoretical basis of these upper bound gas pair relationships.[7] Highly selective but *low*-permeability commercially available polymers, such as cellulose acetate, polysulfone, polyimide and polycarbonate, continue to be industrially employed in air and hydrogen separations since the 1980s, and a key challenge driving research has been to develop new polymers that defy the "upper bound" trade-off relationships and unite *high* selectivities with *high* permeabilities.

Polymers of intrinsic microporosity (PIMs) are a rapidly expanding class of solution-processable amorphous glassy polymers designed for membrane separations. Traditionally, PIMs integrate microporosity (< 20 Å) by virtue of rigid and contorted macromolecular architectures that pack inefficiently in the solid state.[8-25] The earliest PIMs were principally based on such "rigid" design metrics and included substituted polyacetylenes. For example, poly(1-trimethylsilyl-1-

propyne) [PTMSP] was characterized by very high free volume (~30%), a high BET surface area of ~900 m^2g^{-1}, and gas diffusion coefficients three to six orders of magnitude higher than those of any known preceding polymers. Because of its large average *inter*-chain pore size, PTMSP still exhibits among the *highest* reported gas permeabilities which are, however, coupled with the *lowest* gas selectivities, making it an unattractive membrane material for air and hydrogen separations.[26]

Importantly, polymer structure/property optimizations have recently revealed that exceptional molecular sieving transport, characterized by balanced combinations of permeability and selectivity, is attainable by a unique class of PIMs – herein referred to as *ultra*-microporous UPIMs – that augments the traditional focus on *intra*-chain "rigidity" with an emphasis on *inter*-chain spacing in the gas-sieving *ultra*-microporous domain. UPIMs demonstrated that integrating bridged-bicyclic contortion centers (Figure 1a) into "rigid," predominantly fused-ring, backbones resulted in exemplary ladder PIMs[17, 19, 23] and semi-ladder PIM-polyimides (PIM-PIs)[18, 22, 24] (Figure 1b) bridging the gap between high permeability *and* high selectivity for unprecedented performance in high-impact, energy-demanding air and hydrogen separations. Figure 1a illustrates the three most promising core building blocks currently employed in the design of a unique class of PIMs – here referred to as *ultra*-microporous PIMs (UPIMs) - namely 9,10-diisopropyl-triptycene, dimethyl-ethanoanthracene and Tröger's base, and highlights their nearly identical ~120° kinks. Indeed, the geometry of the contortion site has been increasingly emphasized given the inferior performances observed for analogous polymers containing traditional 90°-oriented spirobisindane-based contortion sites (e.g., in prototypical PIM-1 and PIM-7).[18, 19, 22]
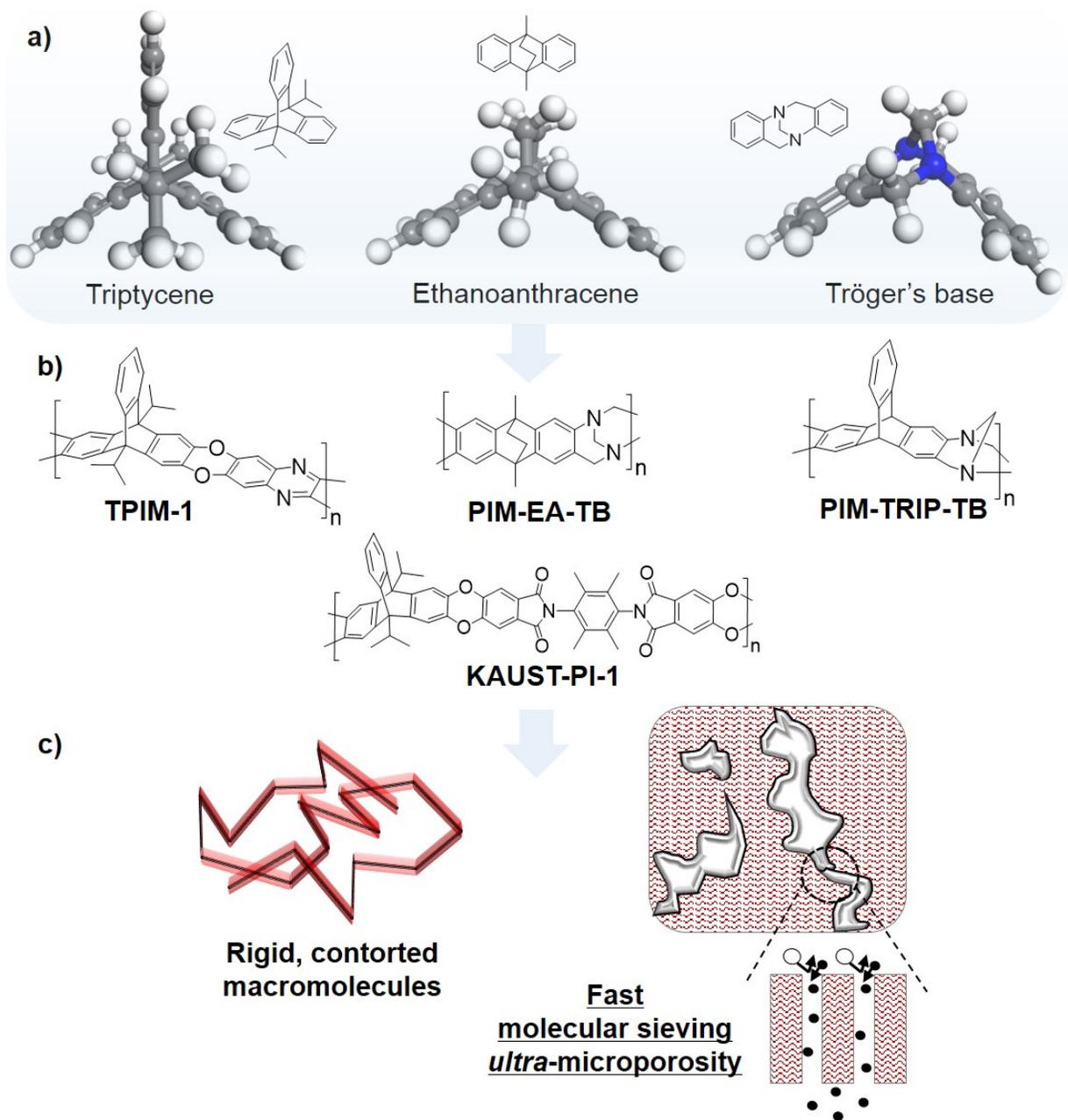
Figure 1. a) Three core bridged-bicyclic building blocks for intrinsically *ultra*-microporous PIMs. b) Exemplary ladder and semi-ladder PIMs recently derived from those building blocks that have redefined the state-of-the-art in membrane-based air and hydrogen separations. c) Schematic illustrating how rigid and contorted PIMs are envisioned to produce an amorphous

microstructure containing large, permeable "pores" linked with smaller, *ultra*-micropores to facilitate high permeability *with* high selectivity.

In general, relative to the microstructures of conventional low-free-volume polymers, a unique attribute of rigid, glassy PIM microstructures is a distribution of interconnected "porosity" that is permanent on the time-scale of gas permeation.[27] Therefore, in conventional polymers gas transport occurs via slow, thermally activated diffusion through transient chain openings. In PIMs, open "pores" derived from inefficient packing of rigid and contorted chains readily permit fast gas diffusion, and thus higher permeability. A major advantage of the UPIMs in Figure 1b, reported by the groups of McKeown et al. and Pinnau et al., is they simultaneously offer high selectivity owing to an interconnected porosity in the *ultra*-microporous (< 7 Å) domain critical to gas separation. Figure 1c illustrates how such molecular-sieving behavior may be realized in UPIMs, where larger, highly permeable pores are envisioned to be interconnected with smaller, selective *ultra*-micropores. That is, UPIMs feature a subtle balance between *intra*-chain rigidity and *inter*-chain spacing,[22] which has been long believed to be essential to realizing new heights in separation performance.[7, 28]

Figure 2a concisely presents key results from physisorption-based assessments of amorphous polymer microstructures that support the above discussion: (i) Large gas uptake at low pressures indicated high microporosity in rigid PIMs including PTMSP, PIM-1 and TPIM-1, whereas little was observed in efficiently packing low-free-volume polymers like poly(phenylene oxide) [PPO][29]; (ii) high free volumes were qualitatively indicated for the PIMs by nearly 2 orders of magnitude higher BET surface areas than for PPO; and (iii) more uptake in the ultra-low-

pressure region (inset Figure 2a) for triptycene-based TPIM-1 indicated the presence of a narrower microporosity than for spiro-based PIM-1, with PTMSP showing the lowest uptake and therefore, the largest micropores. Pore-size distributions derived via an NLDFT analysis of the isotherms (Figure 2b) qualitatively indicated a shift into the *ultra*-microporous domain for the highly permeable *and* selective TPIM-1, which is in contrast to a dominant contribution of larger pores to the microstructure in the highly permeable but poorly selective PTMSP.
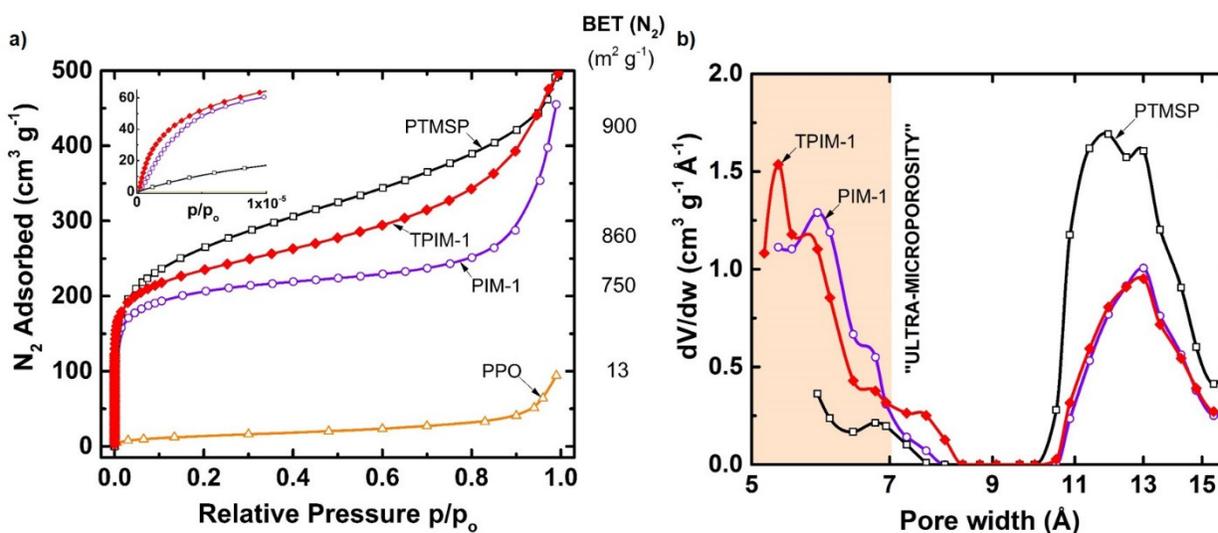

Figure 2. a) Nitrogen adsorption isotherms (77 K) by PIMs including PTMSP, TPIM-1 and PIM-1 and for conventional low-free-volume poly(phenylene oxide) [PPO]. The BET surface areas are listed beside the right axis. b) NLDFT-derived pore-size distribution analyses on the isotherms assuming carbon slit pores.

The outstanding O_2/N_2 separation properties for homogenous and isotropic films of notable PIMs reported to date are presented in Figure 3. The resulting scatter reaches significantly beyond the latest 2008 Robeson upper bound and thus warrants introduction of a new upper bound that defines a new state of the art.[6] Interestingly, a visual fit to the best performing PIMs (i.e., Figure

1b) yields a linear line over nearly 2 decades of permeability (i.e., via equation $P_i = k\alpha_{ij}^n$, where k is a front factor and n is the slope) with a slope practically identical to that reported in 1991 and 2008.[5, 6] This is consistent with Freeman's theoretical prediction that the slope of the upper bound should be fixed for a given gas pair (i.e., slope α $(d_j/d_i)^2$, where d_i may be the kinetic diameter of component i).[7, 30, 31] Also in line with Freeman's theory, a large increase in the front factor, k, which is a function of gas solubility,[7] is expected since the high-free-volume in the UPIMs defining the new line considerably boosts sorption capacity (e.g., Figure 2).[32] Furthermore, the shift from the 2008 line to the 2015 line is much greater than that between the 1991 and 2008 lines, illustrating the substantial impact of molecular sieving UPIMS. The discussion for the hydrogen separations is analogous and new 2015 H_2/N_2 and H_2/CH_4 upper bounds are shown in Figure 4a and 4b. Parameters for the new 2015 upper bounds are provided in Table 1. For validation, the permeabilities and selectivities of the UPIMs near to or defining the 2015 upper bounds are listed in Table 2.

An important point must be made regarding film preparation and the determination of gas transport properties in PIMs, which is relevant to the positioning of the new 2015 upper bounds. Upon slow evaporative casting, the films were all soaked in a non-solvent (e.g., methanol) to exchange residual casting solvent trapped in the micropores. Because the soak imparts significant excess non-equilibrium free volume to the films, freshly measured permeability and selectivity data taken are transient-state data and not meaningful to be placed on upper bounds. Therefore, sufficient time *must* be allowed for (i) the structures to relax into a "quasi-equilibrium" state and (ii) for consistent measurement of the intrinsic permeation properties of the films to be reported.[22, 24, 33] That is, reporting PIM transport data just after methanol treatment

8

is *inappropriate* given that the physically aging polymer structure is in a dynamic state. Figure S1, S2 and S3 (Supporting Information) illustrate the evolution of KAUST-PI-1, TPIM-1, TPIM-2, PIM-1, SBFDA-DMN PIM-EA-TB and PIM-Trip-TB gas transport properties in days after methanol treatment for the various gas pairs. Importantly, beyond two weeks, the trajectories begin to parallel the presented 2015 upper bounds, thereby further validating their positioning with the given data. This observation withstanding, the "ages" of the samples used to construct the upper bounds are provided in parentheses next to the labels in Figure 3 and 4.
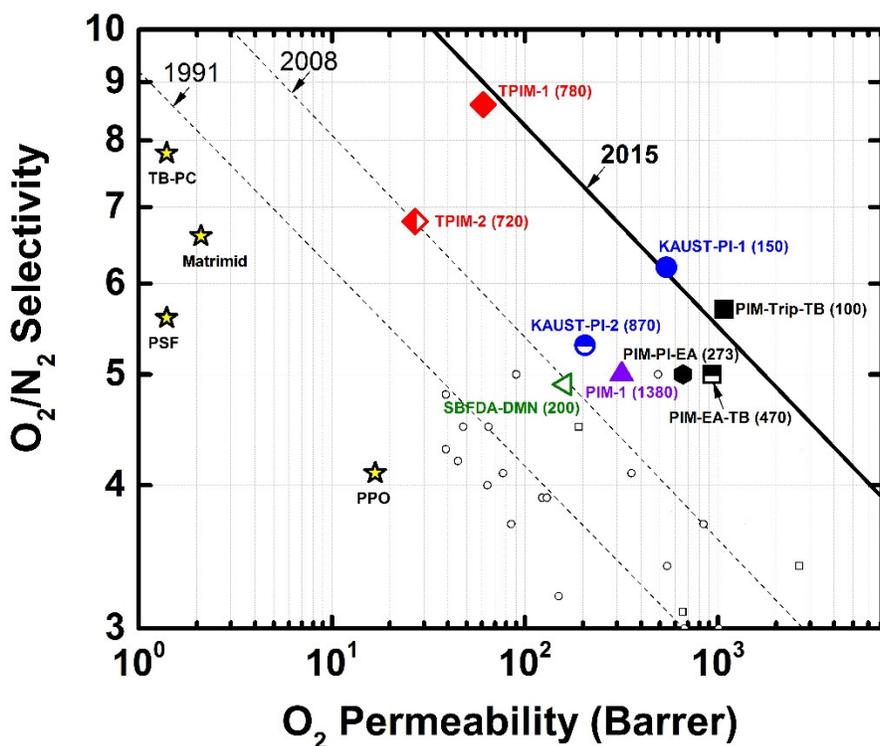

Figure 3. The 2015 "upper bound" to polymer membrane performance in O_2/N_2 separation, defined by outstanding UPIMs. Previous 1991 and 2008 upper bounds (dashed lines) are included to evidence the substantial shift in the state-of-the-art. The "age" of the polymer after methanol treatment is indicated in parentheses. The yellow stars indicate commercially used

membrane materials. The small open circles and squares represent other semi-ladder PIM-polyimides and ladder PIMs.

Figure 4. The 2015 "upper bound" to polymer membrane performance in a) H_2/N_2 and b) H_2/CH_4 separations defined by outstanding UPIMs. Previous 1991 and 2008 upper bounds (dashed lines) are included to evidence the substantial shift in the state-of-the-art. The "age" of the polymer after methanol treatment is indicated in parentheses. The yellow stars indicate commercially used membrane materials. The small open circles and squares represent other semi-ladder PIM-polyimides and ladder PIMs.
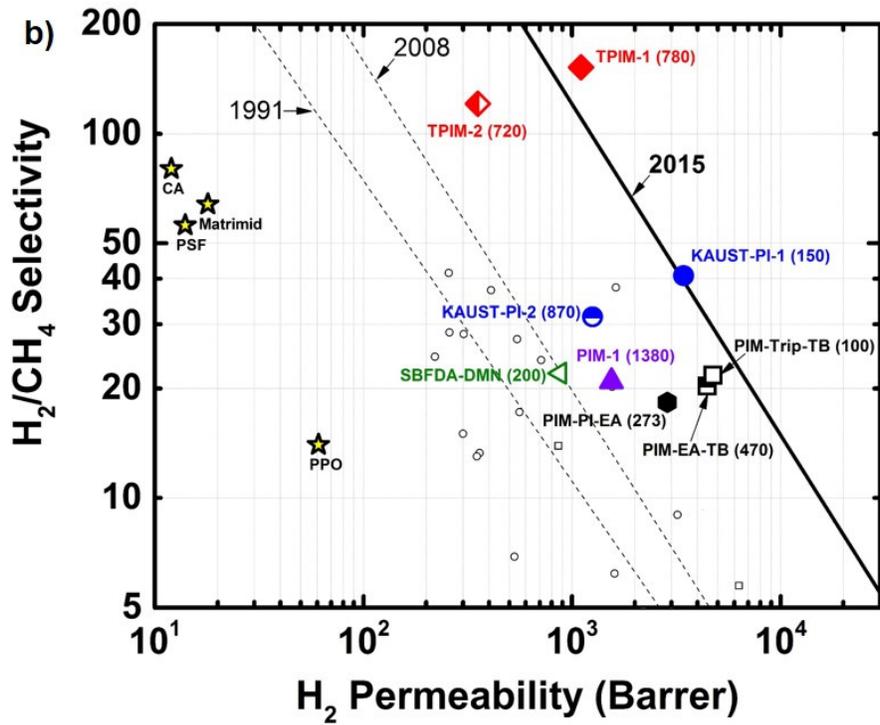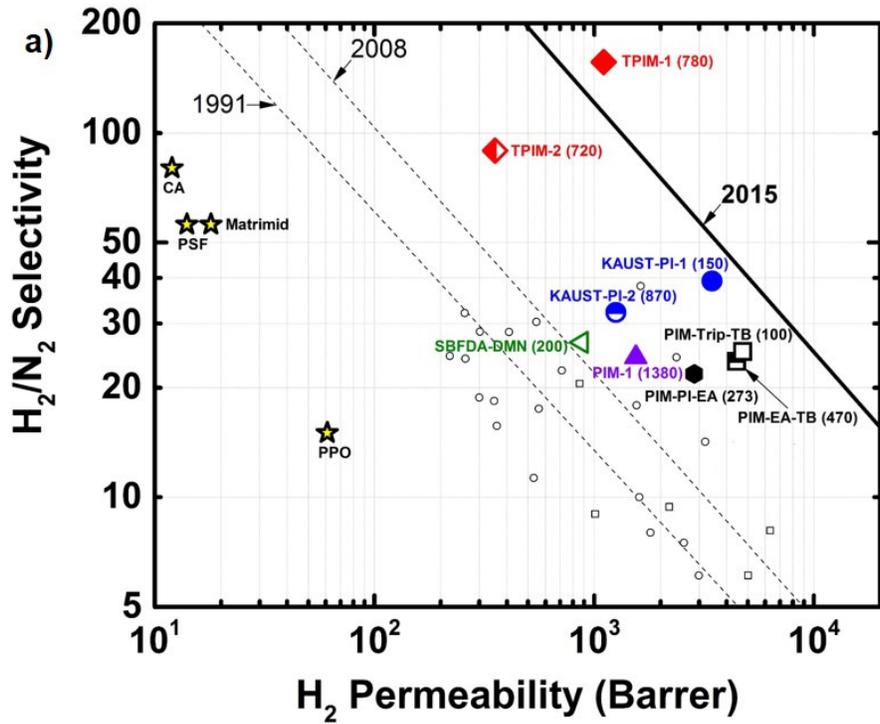
Table 1. Overview of "upper bound" line parameters, where $P_i=k\alpha_{ij}^n$ (i.e., P_i is permeability of *i* in Barrer, k is the front factor in Barrer, α_{ij} is the selectivity for i/j and *n* is the slope), for key polymer membrane-based air and hydrogen separations.

	1991		2008		2015	
Gas pair	k (Barrer)	N	k (Barrer)	n	k (Barrer)	n
O_2/N_2	3.89×10^5	-5.800	1.40×10^6	-5.666	1.67×10^7	-5.70
H_2/N_2	5.29×10^4	-1.5275	9.77×10^4	-1.484	1.10×10^6	-1.46
H_2/CH_4	1.85×10^4	-1.2112	2.72×10^4	-1.107	1.95×10^5	-1.10

Table 2. Performance of UPIMs near to or defining the new 2015 upper bounds for key polymer membrane-based air (e.g., O_2/N_2) and hydrogen (e.g., H_2/N_2, H_2/CH_4) separations.

	Air		Hydrogen		
Polymer	O_2 Permeability (Barrer)	O_2/N_2 Selectivity	H_2 Permeability (Barrer)	H_2/N_2 Selectivity	H_2/CH_4 Selectivity
TPIM-1	61	8.6	1105	156	152
KAUST-PI-1	542	6.2	3431	39	41
PIM-TRIP-TB	1073	5.7	4740	25	22
PIM-EA-TB	933	5.0	4442	24	20

In conclusion, the new 2015 permeability/selectivity upper bound lines presented herein reflect the substantial progress UPIMs contribute to the state of the art in membrane-based air and hydrogen separations. The combination of rigidity and *ultra*-microporosity, which is fine-tuned via the use of bridged-bicyclic building blocks, allows UPIMs to bridge the gap between the high permeabilities of standard PIMs and the high selectivities of low-free-volume commercial-type materials. Importantly, the UPIMs defy trade-off relationships in matching the *practical* selectivities of commercial materials with *desired* orders-of-magnitude higher permeabilities. The resulting performance represents a major step forward in material development and offers great potential to expand the industrial horizons of polymer membrane-based gas separation technology.

Associated Content

The evolution of gas transport properties over time for methanol-treated PIMs is provided on permeability/selectivity maps for O_2/N_2, H_2/N_2 and H_2/CH_4 separations. This material is provided free of charge via the internet at http://pubs.acs.org.

Acknowledgments

References

1. Sanders, D. E.; Smith, Z. P.; Guo, R. L.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. *Polymer* **2013,** 54, 4729-4761.

2. Materials research for separations technologies: energy and emission reduction opportunities. US Department of Energy, USA, 2004.

3. Baker, R. W. *Ind. Eng. Chem. Res.* **2002,** 41, 1393-1411.

4. Baker, R. W.; Low, B. T. *Macromolecules* **2014,** 47, 6999-7013.

5. Robeson, L. M. *J. Membr. Sci.* **1991,** 62, 165-185.

6. Robeson, L. M. *J. Membr. Sci.* **2008,** 320, 390-400.

7. Freeman, B. D. *Macromolecules* **1999,** 32, 375-380.

8. McKeown, N. B. *ISRN Materials Science* **2012,** 2012, 16.

9. Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230-231.

10. Budd, P. M.; McKeown, N. B.; Fritsch, D. *J. Mater. Chem.* **2005,** 15, 1977-1986.

11. Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanem, B. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. *J. Membr. Sci.* **2005,** 251, 263-269.

12. Budd, P. M.; McKeown, N. B.; Ghanem, B. S.; Msayib, K. J.; Fritsch, D.; Starannikova, L.; Belov, N.; Sanfirova, O.; Yampolskii, Y.; Shantarovich, V. *J. Membr. Sci.* **2008,** 325, 851-860.

13. Maier, G. *Angew. Chem. Int. Ed.* **2013,** 52, 4982-4984.

14. Guiver, M. D.; Lee, Y. M. *Science* **2013,** 339, 284-285.

15. Du, N. Y.; Park, H. B.; Robertson, G. P.; Dal-Cin, M. M.; Visser, T.; Scoles, L.; Guiver, M. D. *Nat. Mater.* **2011,** 10, 372-375.

16. Thomas, S.; Pinnau, I.; Du, N. Y.; Guiver, M. D. *J. Membr. Sci.* **2009,** 333, 125-131.

17. Carta, M.; Croad, M.; Malpass-Evans, R.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; Friess, K.; Lanč, M.; McKeown, N. B. *Adv. Mater.* **2014,** 26, 3526-3531.

18. Rogan, Y.; Malpass-Evans, R.; Carta, M.; Lee, M.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; Tocci, E.; Friess, K.; Lanc, M.; McKeown, N. B. *J. Mater. Chem. A.* **2014,** 2, 4874-4877.

19. Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. *Science* **2013,** 339, 303-307.

20.   Bezzu, C. G.; Carta, M.; Tonkins, A.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. *Adv. Mater.* **2012,** 24, 5930-5933.

21.   Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Selbie, J. D.; Fritsch, D. *Adv. Mater.* **2008,** 20, 2766-2771.

22.   Swaidan, R.; Al-Saeedi, M.; Ghanem, B.; Litwiller, E.; Pinnau, I. *Macromolecules* **2014,** 47, 5104-5114.

23.   Ghanem, B. S.; Swaidan, R.; Ma, X.; Litwiller, E.; Pinnau, I. *Adv. Mater.* **2014,** 26, 6696-6700.

24.   Ghanem, B. S.; Swaidan, R.; Litwiller, E.; Pinnau, I. *Adv. Mater.* **2014,** 26, 3688-3692.

25.   Ma, X. H.; Swaidan, R.; Belmabkhout, Y.; Zhu, Y. H.; Litwiller, E.; Jouiad, M.; Pinnau, I.; Han, Y. *Macromolecules* **2012,** 45, 3841-3849.

26.   Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983,** 105, 7473-7474.

27.   Wijmans, J. G.; Baker, R. W. *J. Membr. Sci.* **1995,** 107, 1-21.

28.   Kim, T. H.; Koros, W. J.; Husk, G. R.; Obrien, K. C. *J. Membr. Sci.* **1988,** 37, 45-62.

29.   Ilinitch, O. M.; Fenelonov, V. B.; Lapkin, A. A.; Okkel, L. G.; Terskikh, V. V.; Zamaraev, K. I. *Micropor Mesopor Mat* **1999,** 31, 97-110.

30.   Robeson, L. M.; Smith, Z. P.; Freeman, B. D.; Paul, D. R. *J. Membr. Sci.* **2014,** 453, 71-83.

31.   Robeson, L. M.; Freeman, B. D.; Paul, D. R.; Rowe, B. W. *J. Membr. Sci.* **2009,** 341, 178-185.

32.   Robeson, L. M.; Liu, Q.; Freeman, B. D.; Paul, D. R. *J. Membr. Sci.* **2015,** 476, 421-431.

33.   Hill, A. J.; Pas, S. J.; Bastow, T. J.; Burgar, M. I.; Nagai, K.; Toy, L. G.; Freeman, B. D. *J. Membr. Sci.* **2004,** 243, 37-44.