Highly Permeable Polymers of Intrinsic Microporosity (PIM-1)-based Flat Dense and Hollow Fiber Membranes for Gas Separation

Wai Fen Yong, Tai-Shung Chung*
Department of Chemical and Biomolecular Engineering,
National University of Singapore, Singapore.

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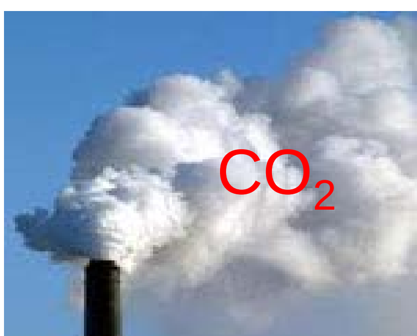




Outline

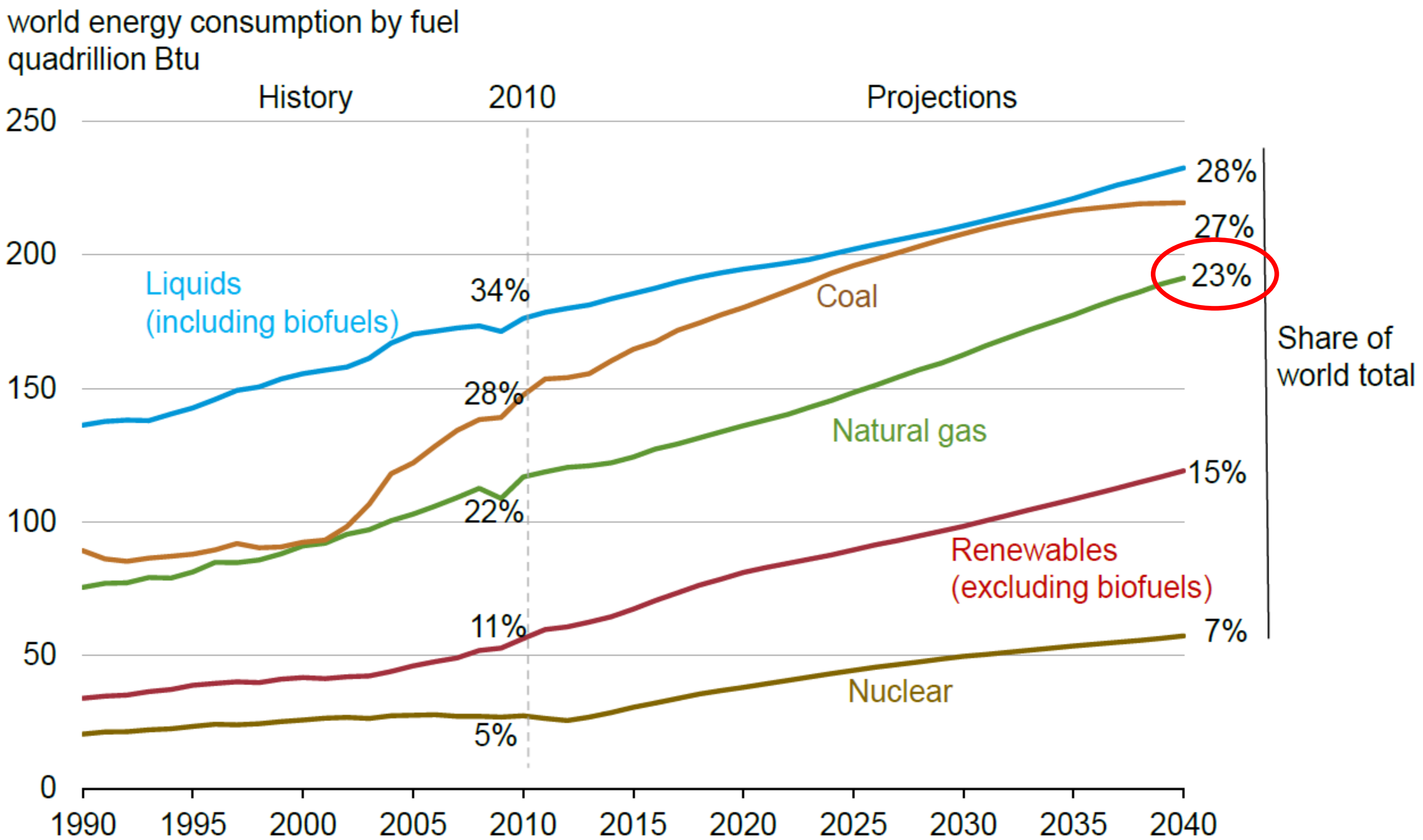
- Challenges and opportunities
- Our approach
- Research works
  - Miscibility study on dense membranes
  - Scale up to hollow fiber membranes
  - Properties alteration: from CO_2- to H_2-selective
- Summary

Crude Oil Price

- Increase in energy demand
- Higher in crude oil price
- Depletion of crude oil

- U.S. Energy Information Administration, released on Aug 4, 2014

Energy Consumption by Fuels

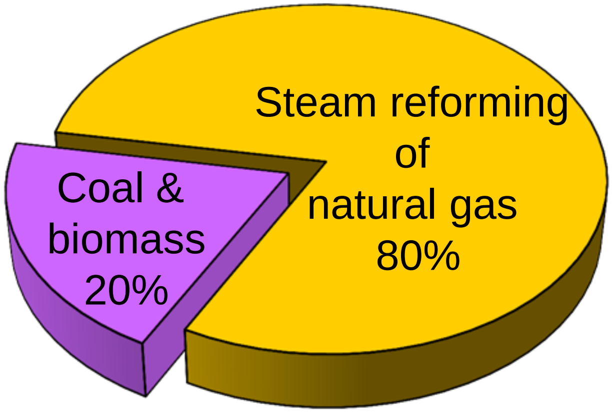


- U.S. Energy Information Administration, International Energy Outlook 2013

Hydrogen as Alternative Energy Source

- Clean energy carrier

- Hydrogen production:



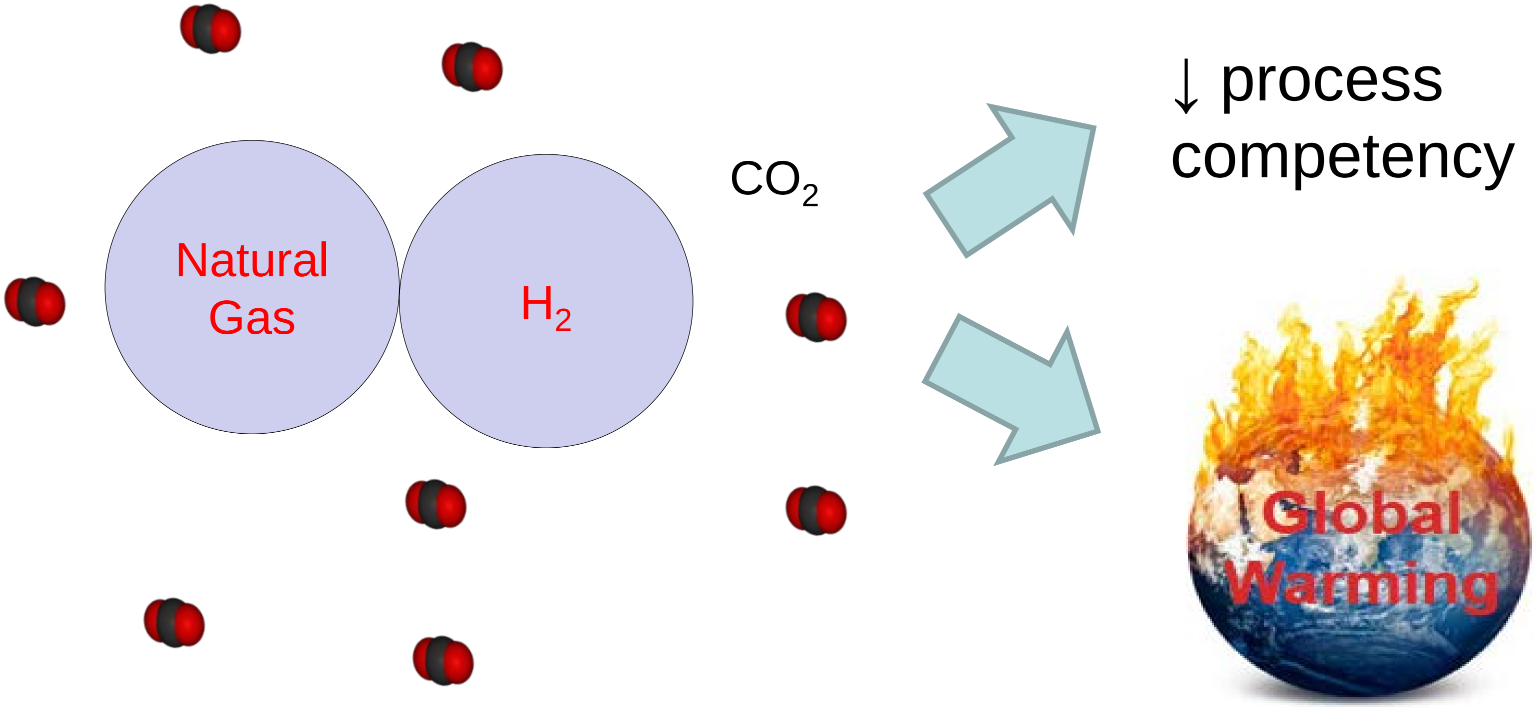
Steam reforming of natural gas coupled with water-gas shift reaction:

$$CH_4 + H_2O \xrightarrow{Catalyst} 3H_2 + CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

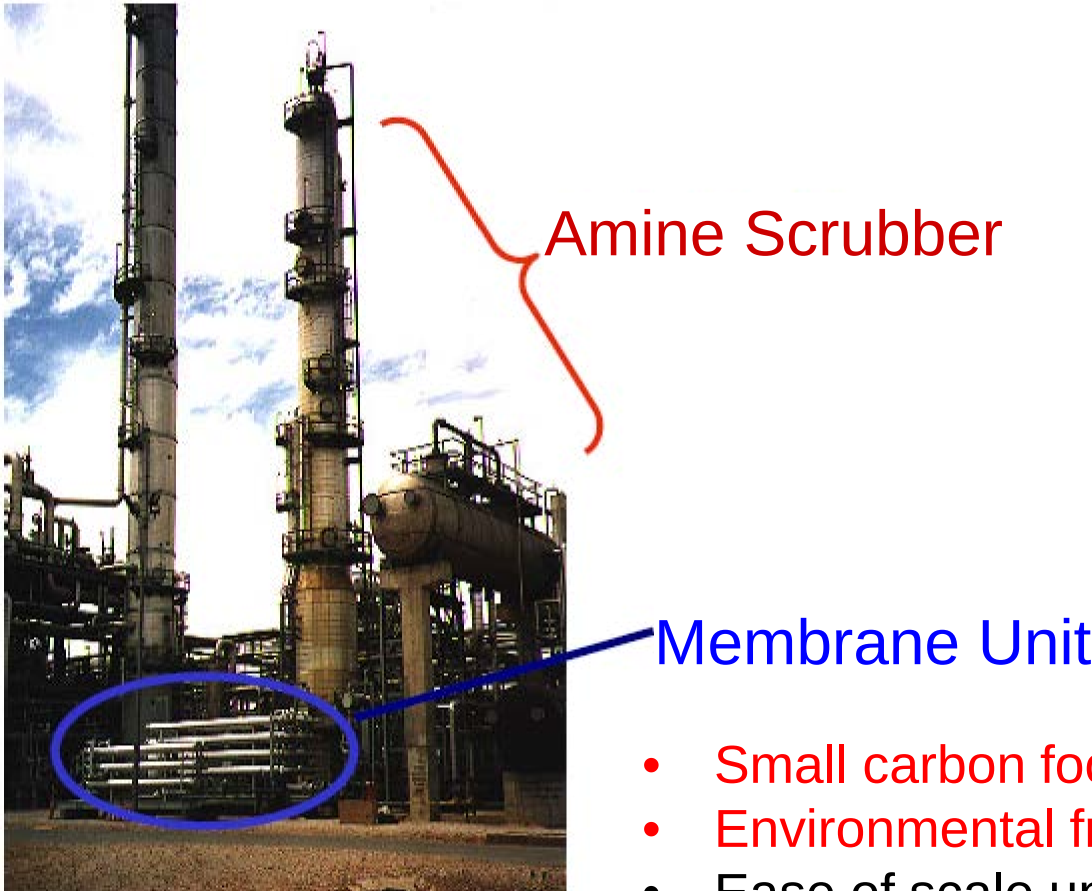
- Co-product CO_2 need to be removed

Contaminant CO_2 Need to be Removed



Gas treatment process is required!!

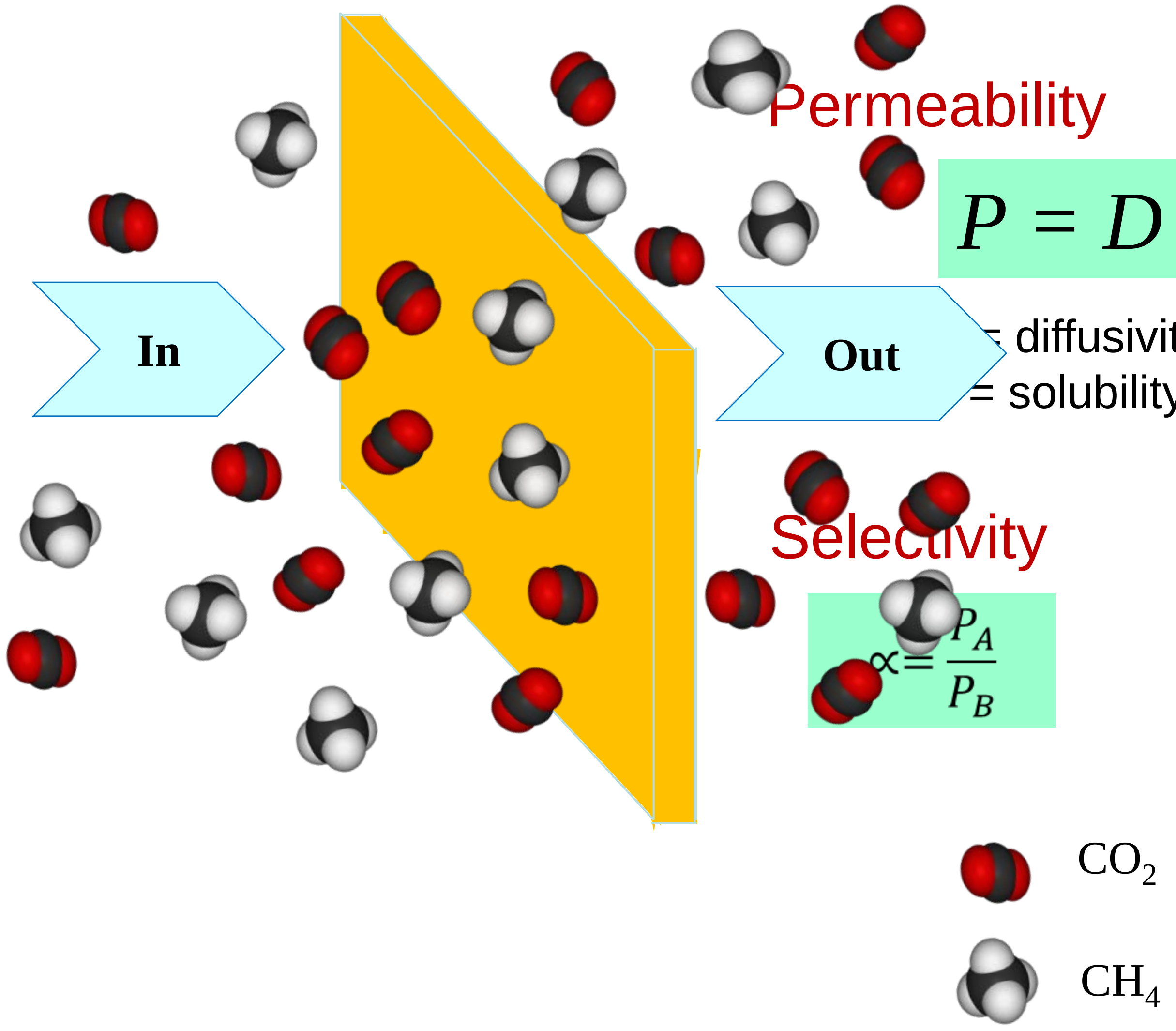
Why Membrane Separation?



- Small carbon footprint
- Environmental friendly
- Ease of scale up
- Low capital and operating costs
- High energy efficiency

Membrane Separation

Solution Diffusion



Permeability

$$P = D \times S$$

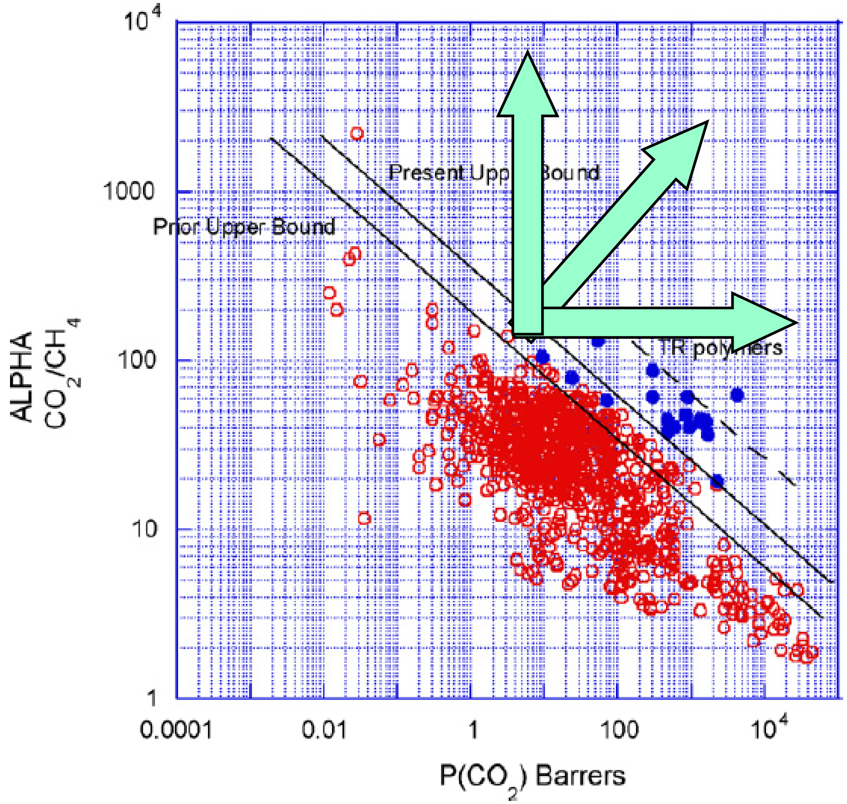
= diffusivity coefficient

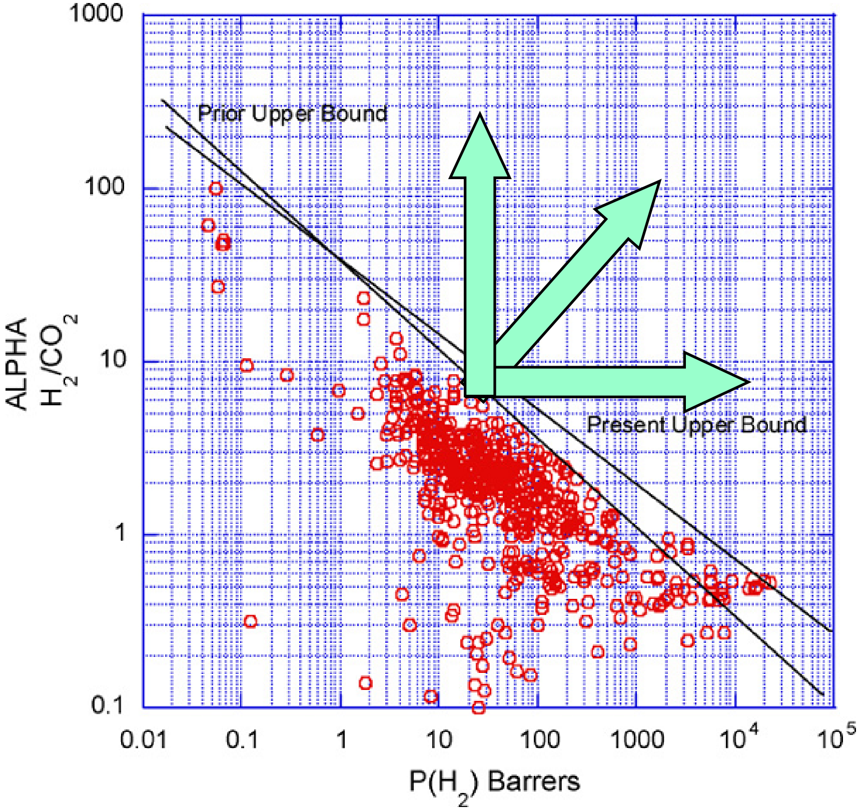
= solubility coefficient

Selectivity

$$\alpha = \frac{P_A}{P_B}$$

Trade-off Relation



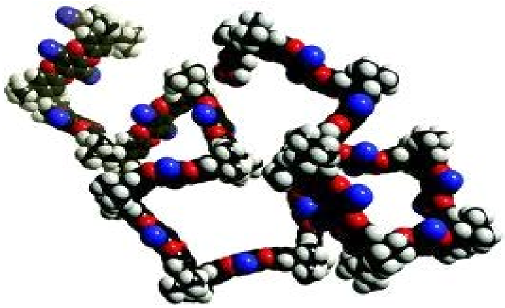


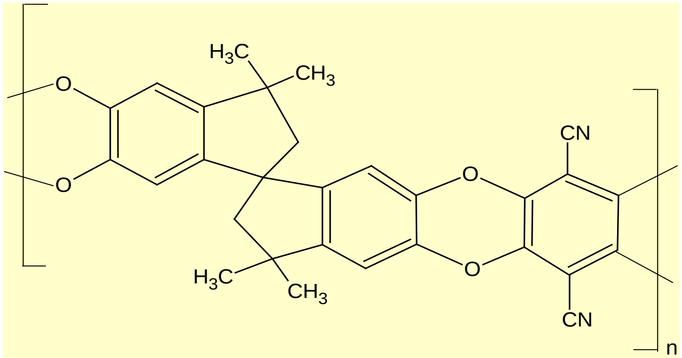
- High permeability and selectivity is desirable

L.M. Robeson, J. Membr. Sci. 320 (2008) 390-400.

New Class of Material

Polymer of Intrinsic Microporosity (PIM-1)



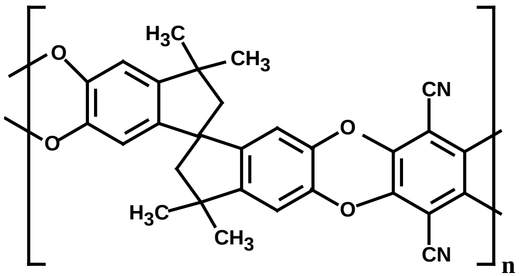


- Large surface area (600 – 900 m^2g^{-1})
- Rigid and contorted structure with no rotational freedom in the backbone → high fractional free volume
- Superior gas permeability, especially CO_2 (~4000 barrer)
- Moderate gas selectivity, $\alpha_{CO2/\,CH4}$ = 14, $\alpha_{CO2/\,N2}$ = 20
- Soluble in tetrahydrofuran, dichloromethane

P.M. Budd et al., Adv. Mater. 16 (2004) 456-459.
N.B. McKeown et al., International patent, (2005) WO05012397.

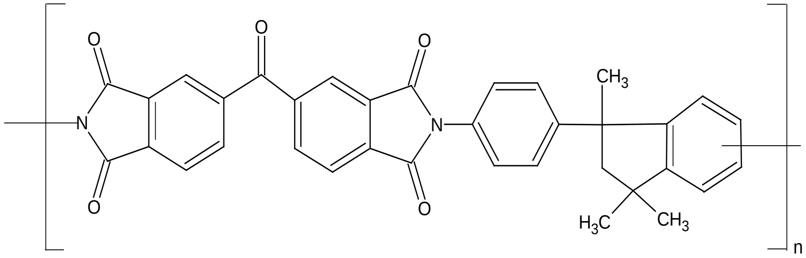
Our Approach: Polymer blends

Polymers of Intrinsic Microporosity (PIM-1)

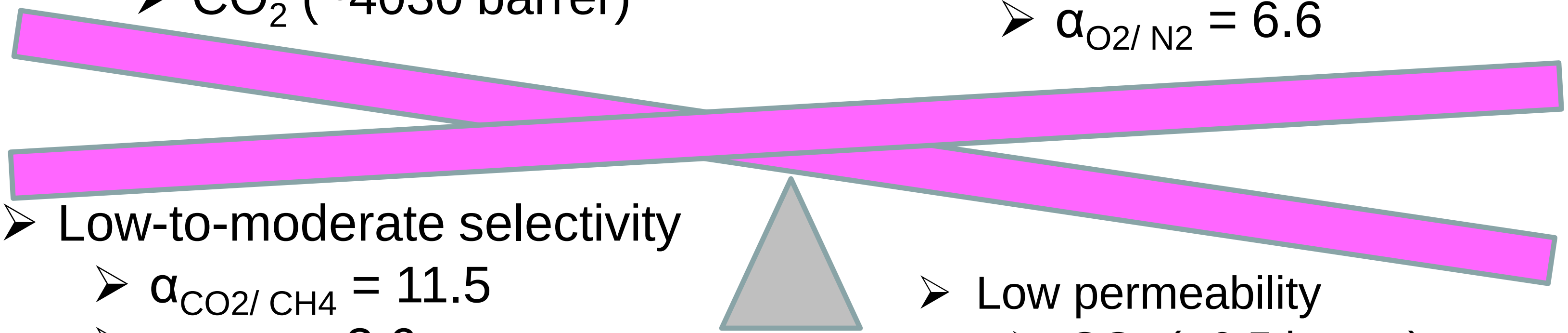


- High permeability[1,2,3]
  - H_2 (~2920 barrer)
  - CO_2 (~4030 barrer)

Matrimid



- High thermal stability
- Good processibility
- High selectivity[4]
  - $\alpha_{CO2/\ CH4} = 34$
  - $\alpha_{O2/\ N2} = 6.6$

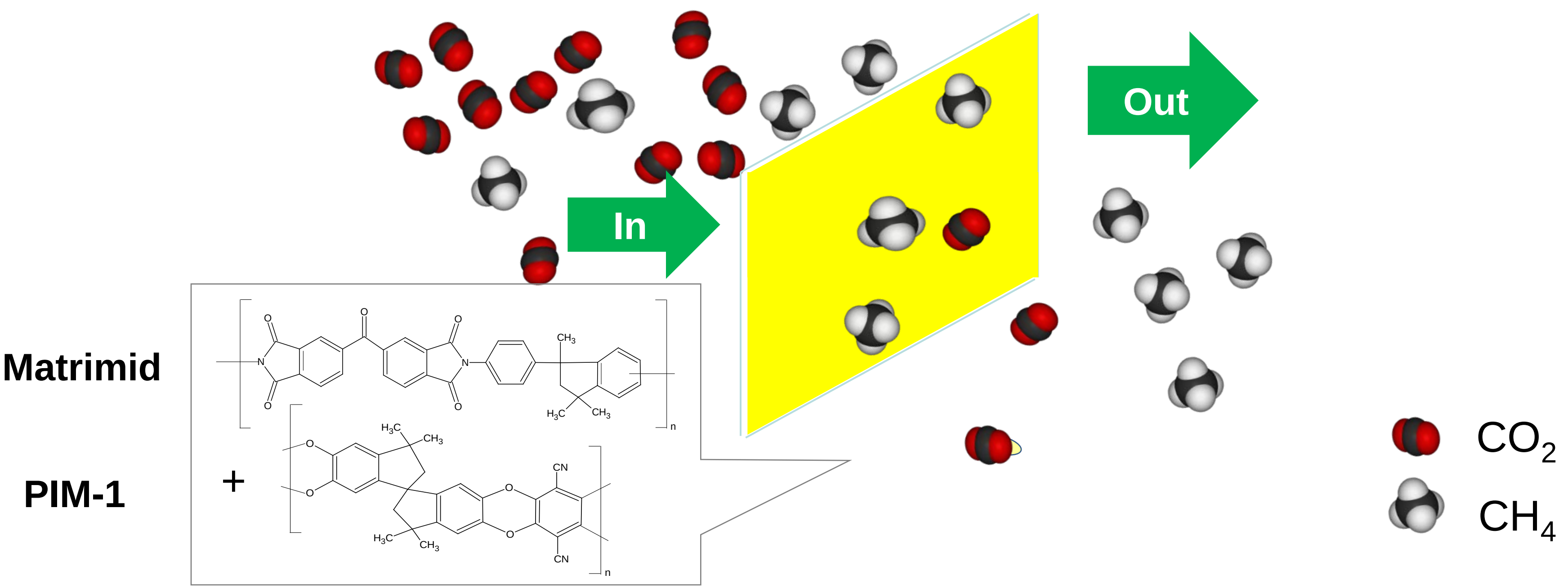


- Low-to-moderate selectivity
  - $\alpha_{CO2/\ CH4} = 11.5$
  - $\alpha_{O2/\ N2} = 3.6$

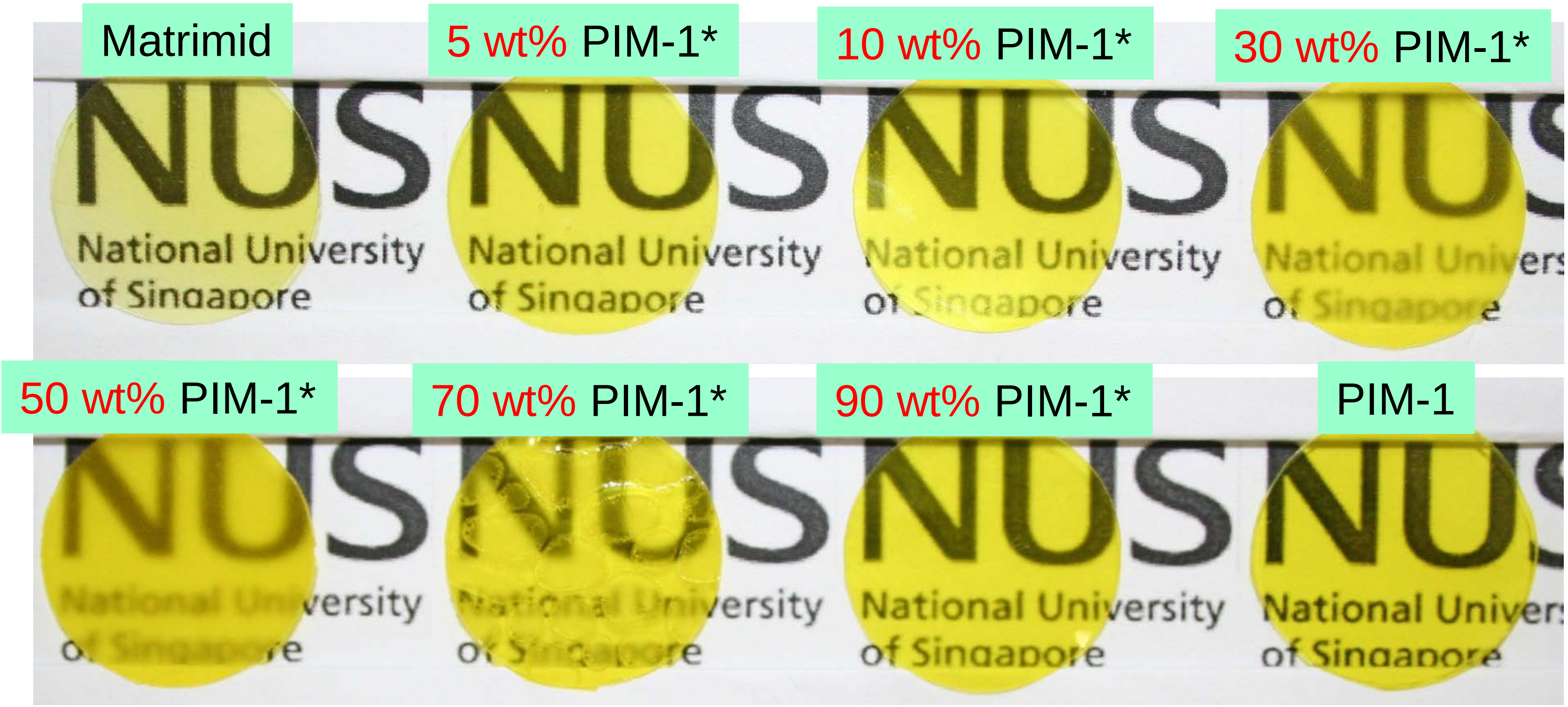
- Low permeability
  - CO_2 (~6.5 barrer)
  - O_2 (~1.7 barrer)

[1] P.M. Budd et al., Adv. Mater. 16 (2004) 456-459.
[2] N.B. McKeown et al., International patent, (2005) WO05012397.
[3] C. Liu and S.T. Wilson, US Pat 7,410,525 B1 (2008).
[4] A. Bos et al., J. Polym. Sci. B: Polym. Phys. 36 (1998) 1547-1556.

Research Work 1:
Miscibility Study of PIM-1/ Matrimid Membranes



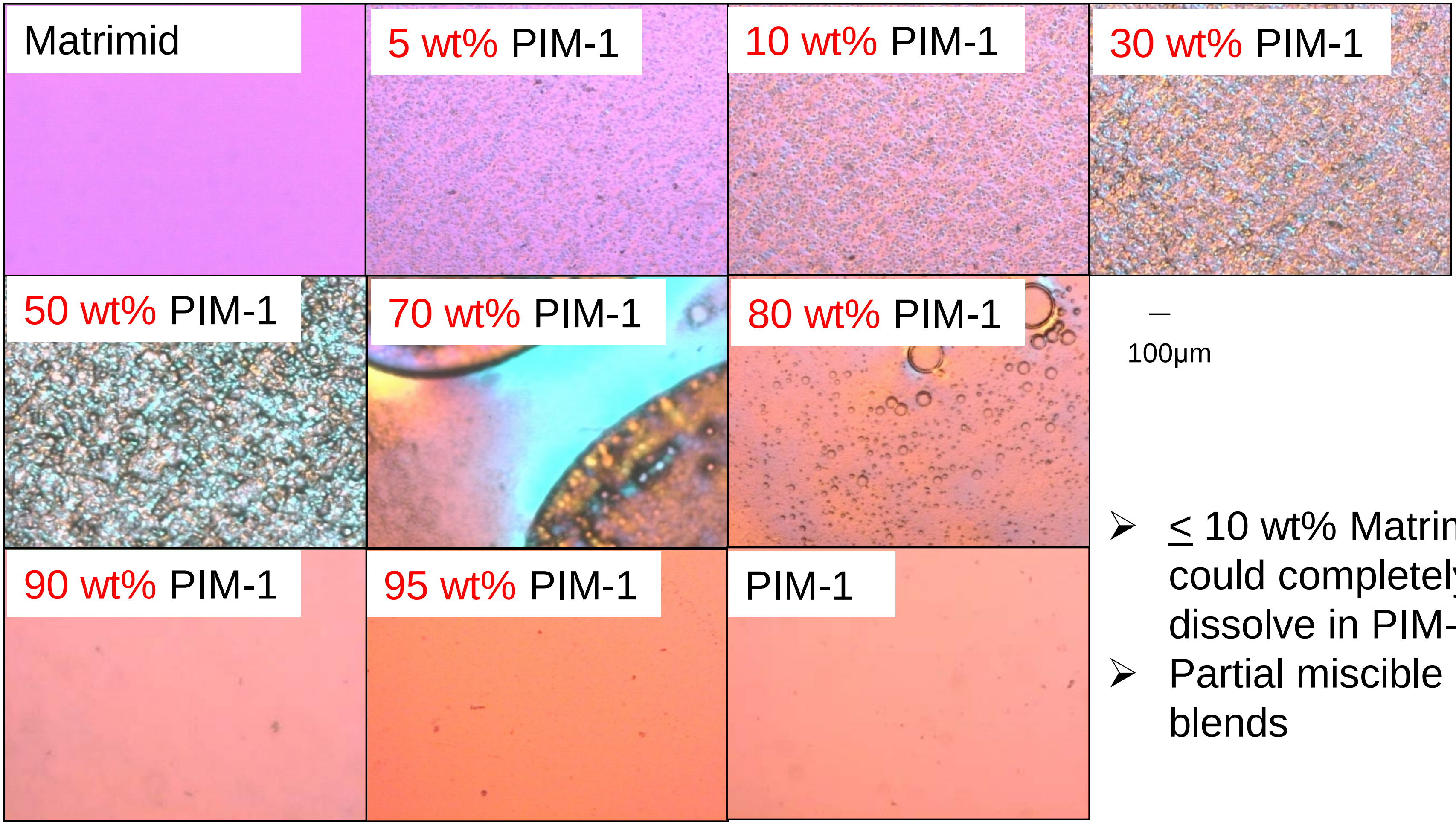
Appearance of the Dense Membranes



* wt% PIM-1 in Matrimid

- Translucent for 30 wt % PIM-1 in Matrimid blend.
- Opaque for 50-70 wt% PIM-1 in Matrimid blend.

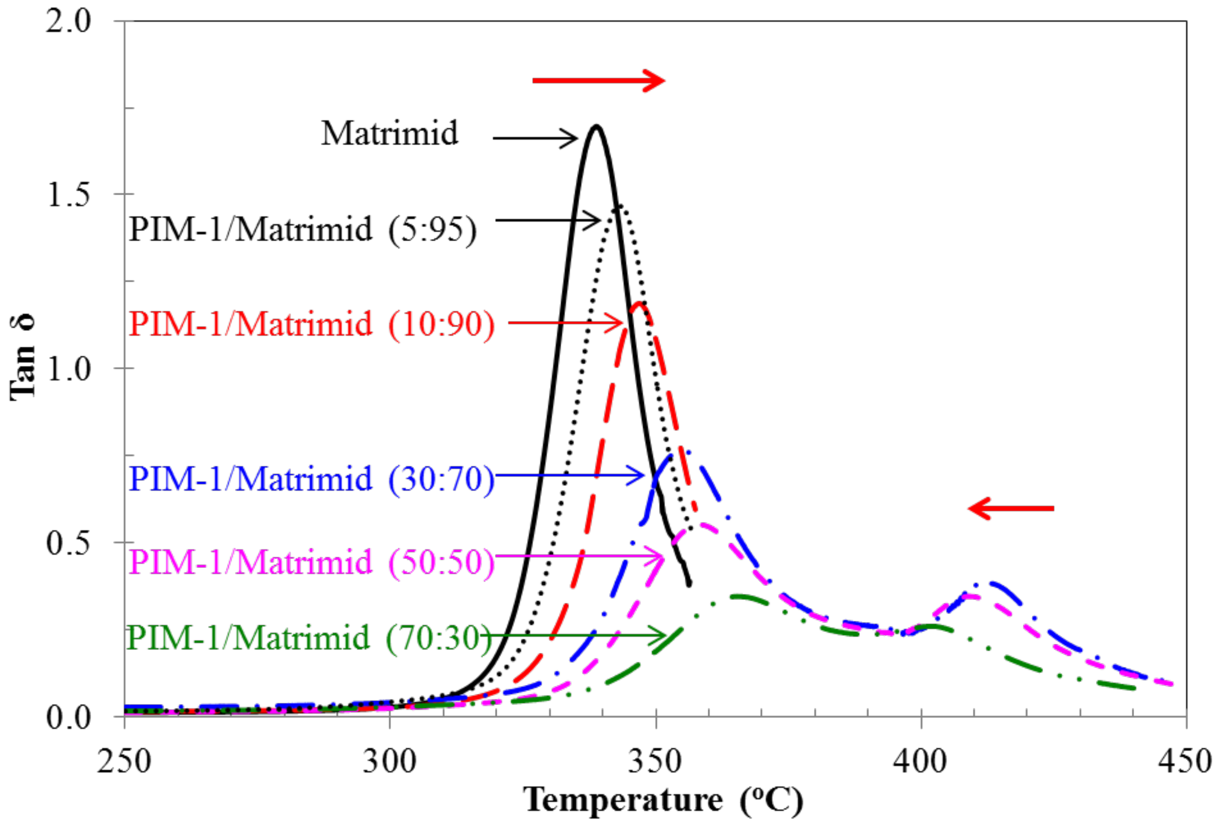
Effects of Blend Ratio under Miscroscope



- ≤ 10 wt% Matrimid could completely dissolve in PIM-1
- Partial miscible blends

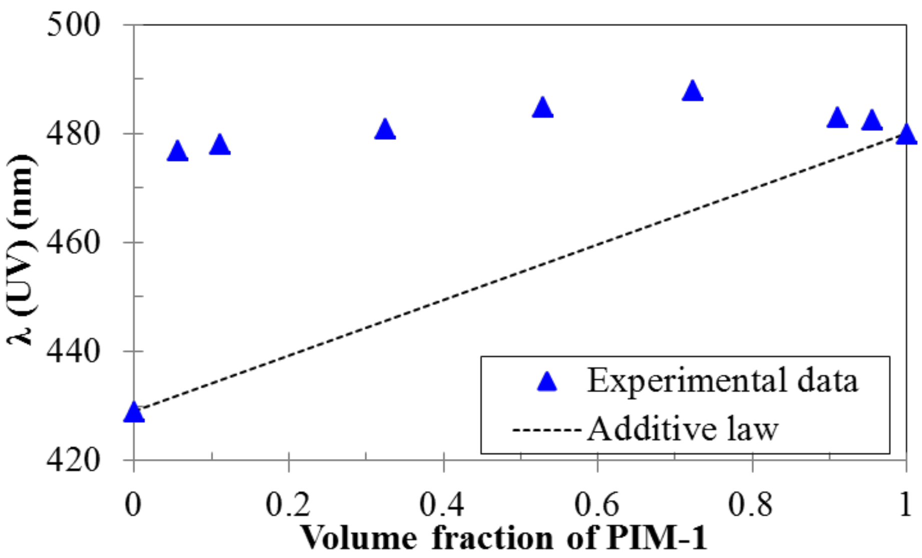
* wt% PIM-1 in Matrimid

Changes on Glass Transition Temperature (T_g)

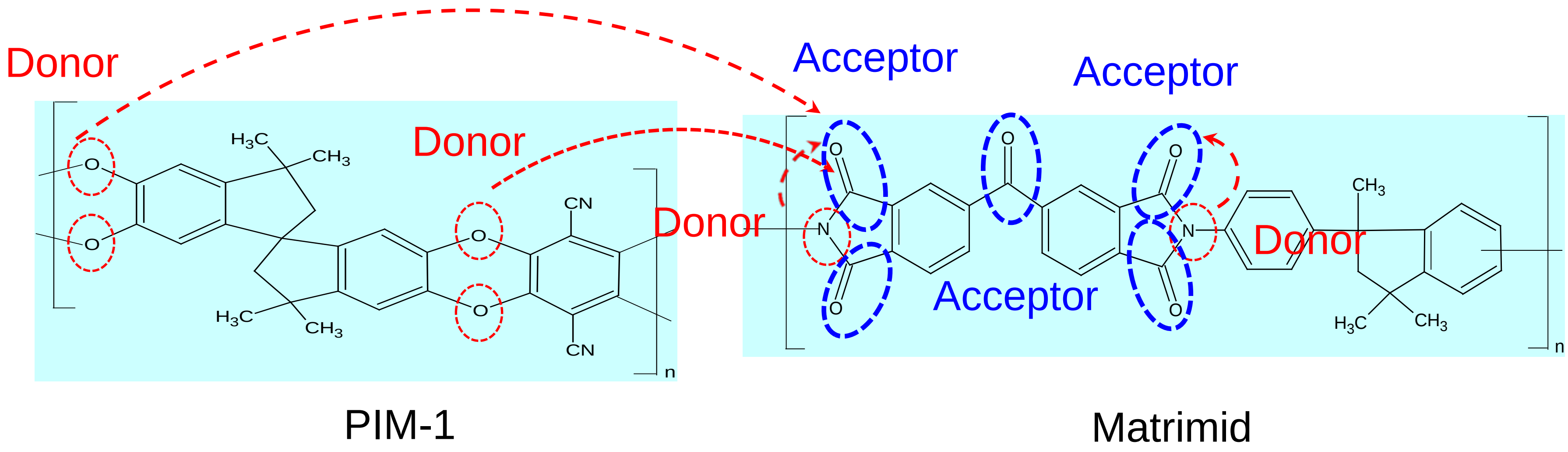


- T_g shift towards each other → partial miscible

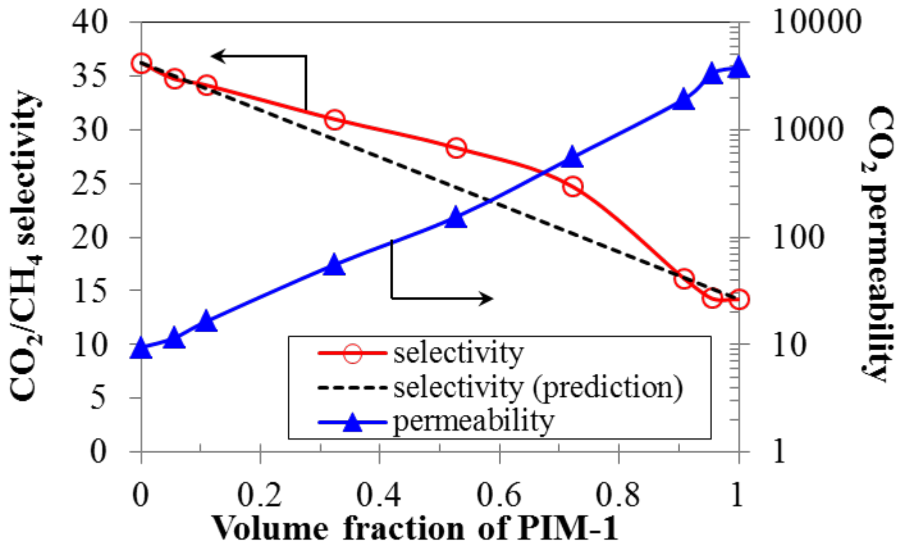
Interaction between PIM-1 and Matrimid



- Development of charge transfer complexes (CTC)
- Attributed to electron transfer interaction between electron acceptor and donor



Pure Gas Performance for CO_2/CH_4 Separations



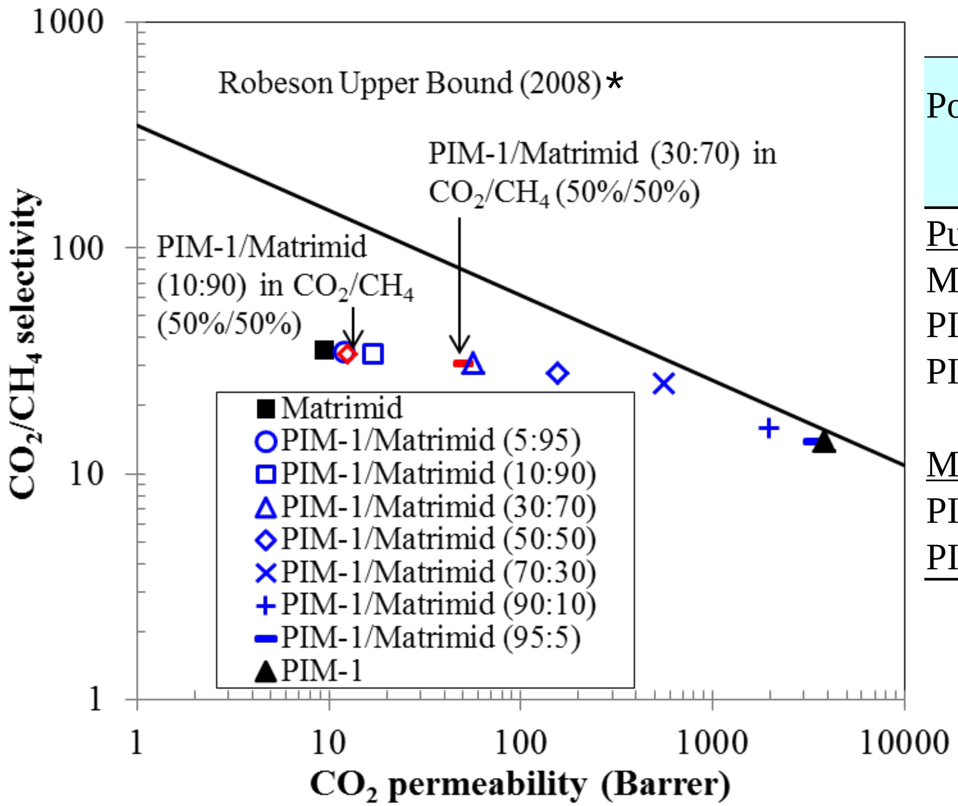
- Additions of 5 and 10 wt% PIM-1 into Matrimid, permeability increases by 25% and 77%, respectively without compromising its CO_2/CH_4 selectivity.

Polymer blends	Permeability (Barrer[a]) CO_2	Ideal Selectivity CO_2/CH_4
Pure gas test (35 °C, 3.5 atm)		
Matrimid	9.6 ± 0.7	36 ± 0.4
PIM-1/Matrimid (5:95)	12 ± 0.7	35 ± 0.5
PIM-1/Matrimid (10:90)	17 ± 0.6	34 ± 1.6
PIM-1/Matrimid (30:70)	56 ± 3.3	31 ± 1.8
PIM-1/Matrimid (50:50)	155 ± 4.0	28 ± 0.1
PIM-1/Matrimid (70:30)	558 ± 1.8	25 ± 1.1
PIM-1/Matrimid (90:10)	1953 ± 4.8	16 ± 0.1
PIM-1/Matrimid (95:5)	3355 ± 1.8	14 ± 0.2
PIM-1	3815 ± 2.5	14 ± 0.1

↑ **25%**

↑ **77%**

CO_2/CH_4 Tradeoff Relations

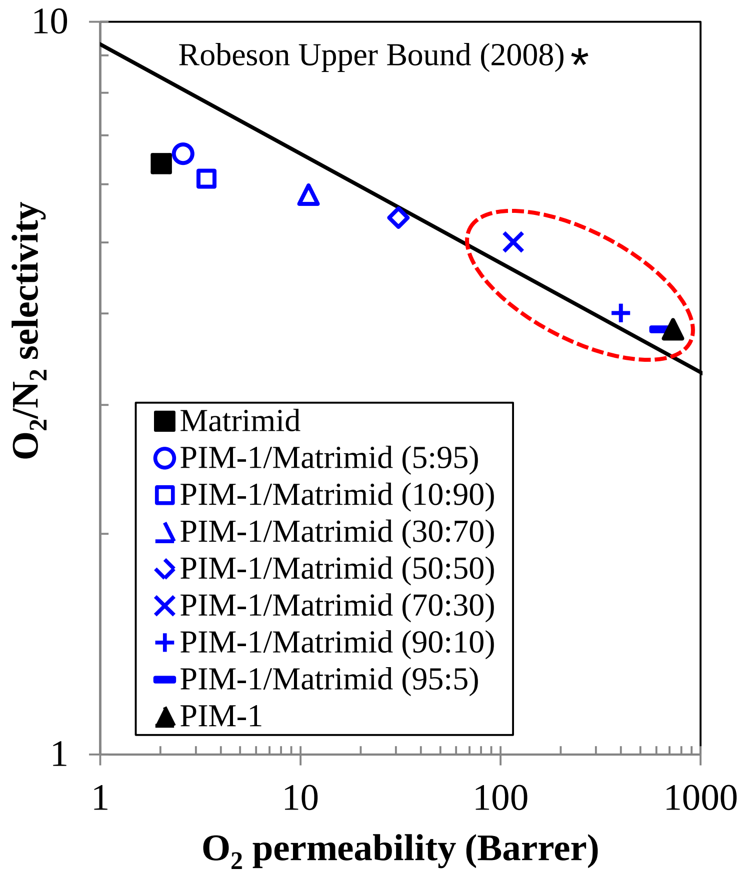


Polymer blends	Permeability (Barrer[a]) CO_2	Selectivity CO_2/CH_4
Pure gas test (35 °C, 3.5 atm)		
Matrimid	9.6 ± 0.7	36 ± 0.4
PIM-1/Matrimid (10:90)	17 ± 0.6	34 ± 1.6
PIM-1/Matrimid (30:70)	56 ± 3.3	31 ± 1.8
Mixed gas test CO_2/CH_4 (50%/50%) (35 °C, 7 atm)		
PIM-1/Matrimid (10:90)	12 ± 1.3	34 ± 1.4
PIM-1/Matrimid (30:70)	50 ± 4.2	31 ± 1.5

- Goes along with upper bound line when PIM-1 loading increases.
- For mixed gas tests, 30 wt% PIM-1 in Matrimid membrane has a CO_2 permeability of 50 Barrer and a CO_2/CH_4 selectivity of 31.

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

O_2/N_2 Tradeoff Relations



- Incorporation of a small amount (5-30 wt% of Matrimid) drives the overall gas separation performance approaches closes or surpasses the upper bound.

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

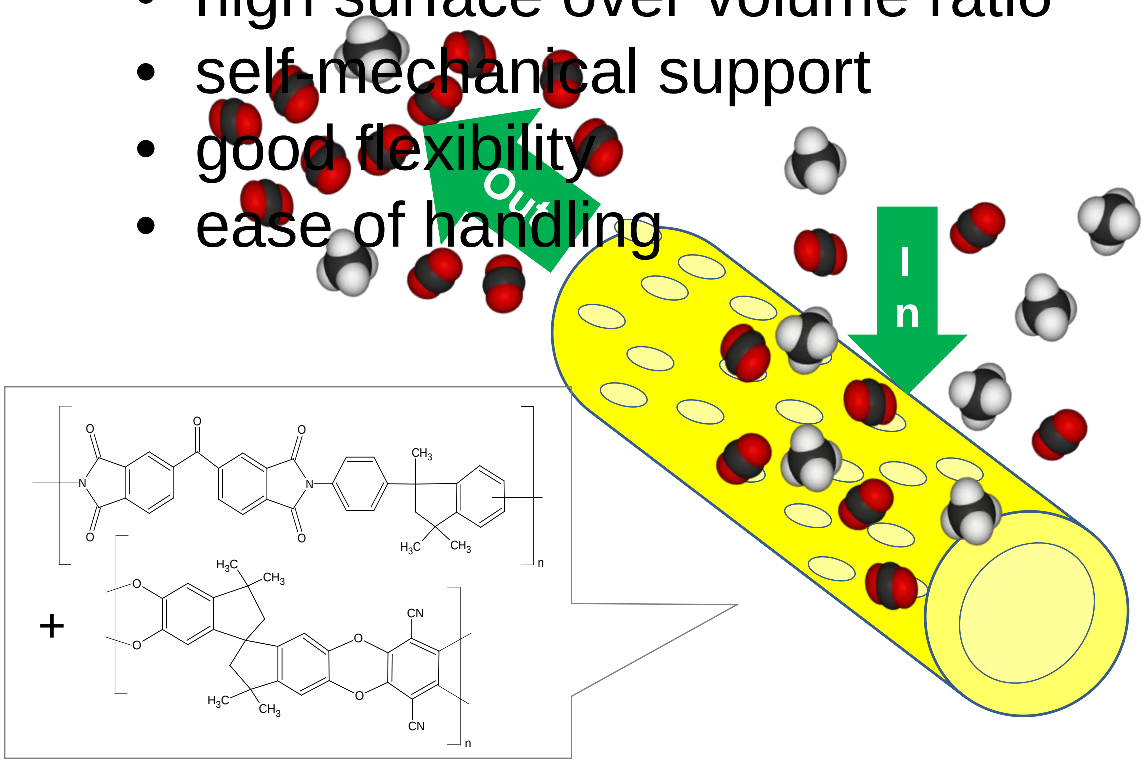
Research Work 2:

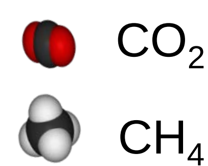
PIM-1/ Matrimid Hollow Fiber Membranes

- high surface over volume ratio
- self-mechanical support
- good flexibility
- ease of handling

Matrimid

PIM-1





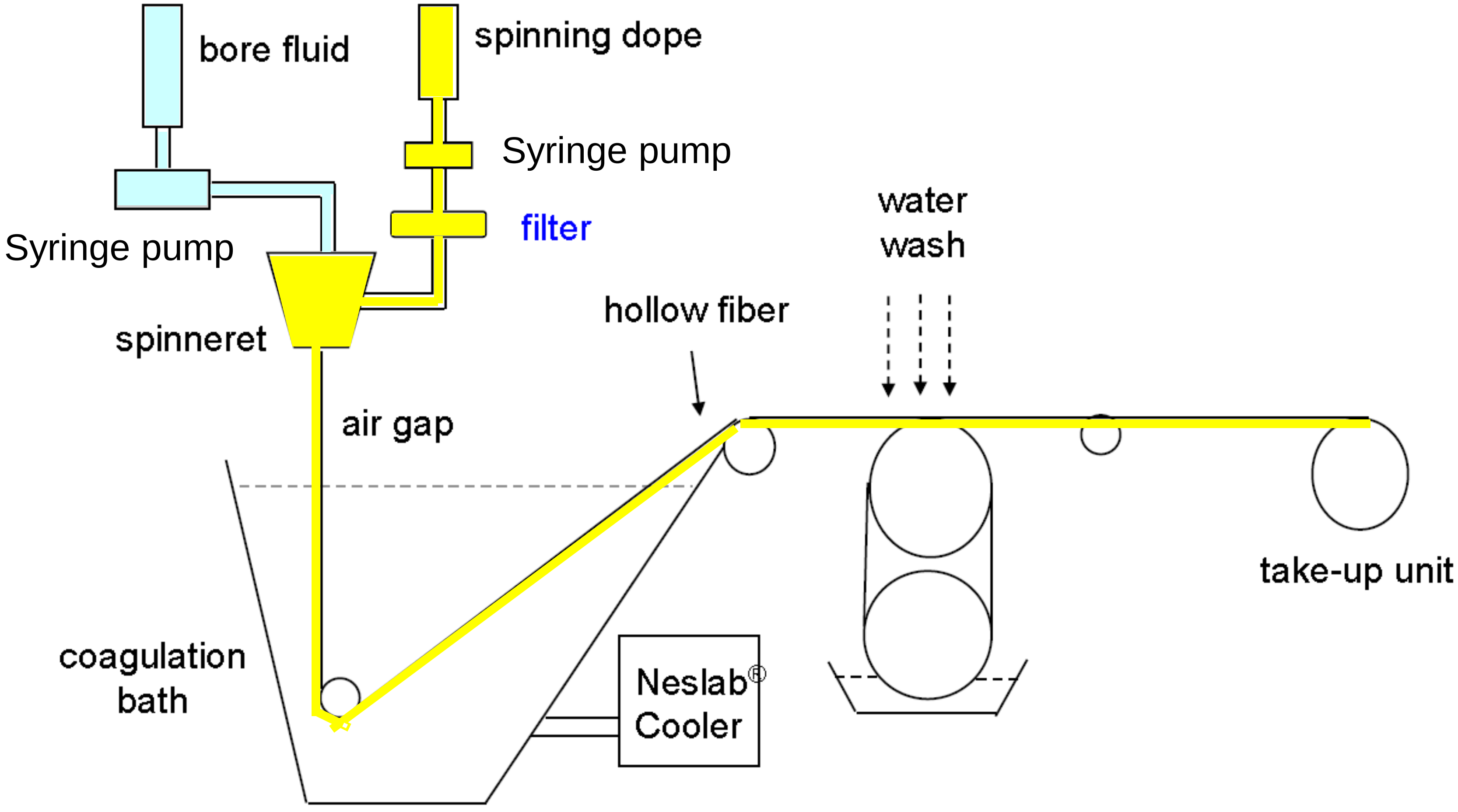
Why PIM-1/Matrimid Hollow Fibers

Polymer blends	Permeability (Barrer[a,b])			Ideal Selectivity		
	O_2	CO_2		O_2/N_2	CO_2/N_2	CO_2/CH_4
Pure gas test (35 °C, 3.5 atm)						
Matrimid	2.1 ± 0.1	9.6 ± 0.7		6.4 ± 0.6	30 ± 2.5	36 ± 0.4
PIM-1/Matrimid (5:95)	2.6 ± 0.2	12 ± 0.7	↑25%	6.6 ± 0.1	29 ± 2.7	35 ± 0.5
PIM-1/Matrimid (10:90)	3.4 ± 0.0	17 ± 0.6	↑77%	6.1 ± 0.4	30 ± 0.9	34 ± 1.6
PIM-1/Matrimid (15:85)	4.4 ± 0.3	21 ± 0.8	↑118%	5.9 ± 0.5	28 ± 0.7	32 ± 1.3

[a] 1 Barrer = 1 × 10^{-10} cm^3 (STP)cm/cm^2s cmHg.

W.F. Yong et al., J. Membr. Sci. 407– 408 (2012) 47–57.

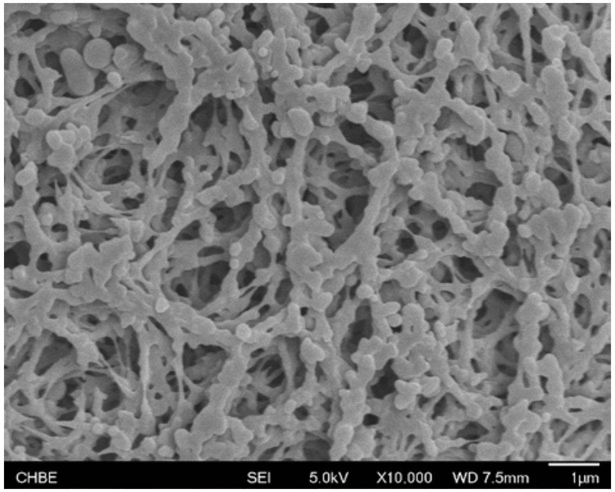
Schematic Diagram for Hollow Fiber Spinning

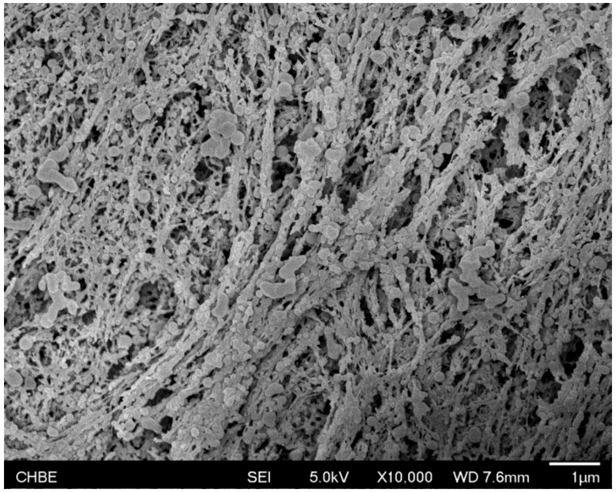


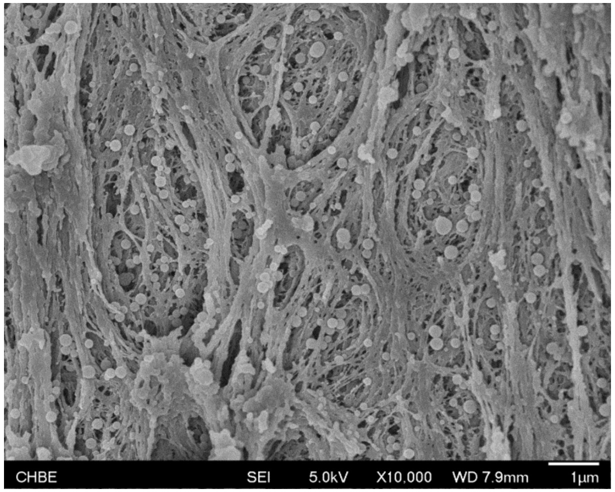
Effect of Bore Fluid Concentration on Inner Surface Morphology

Bore fluid

NMP/water (95:5)	NMP/water (80:20)	NMP/water (50:50)





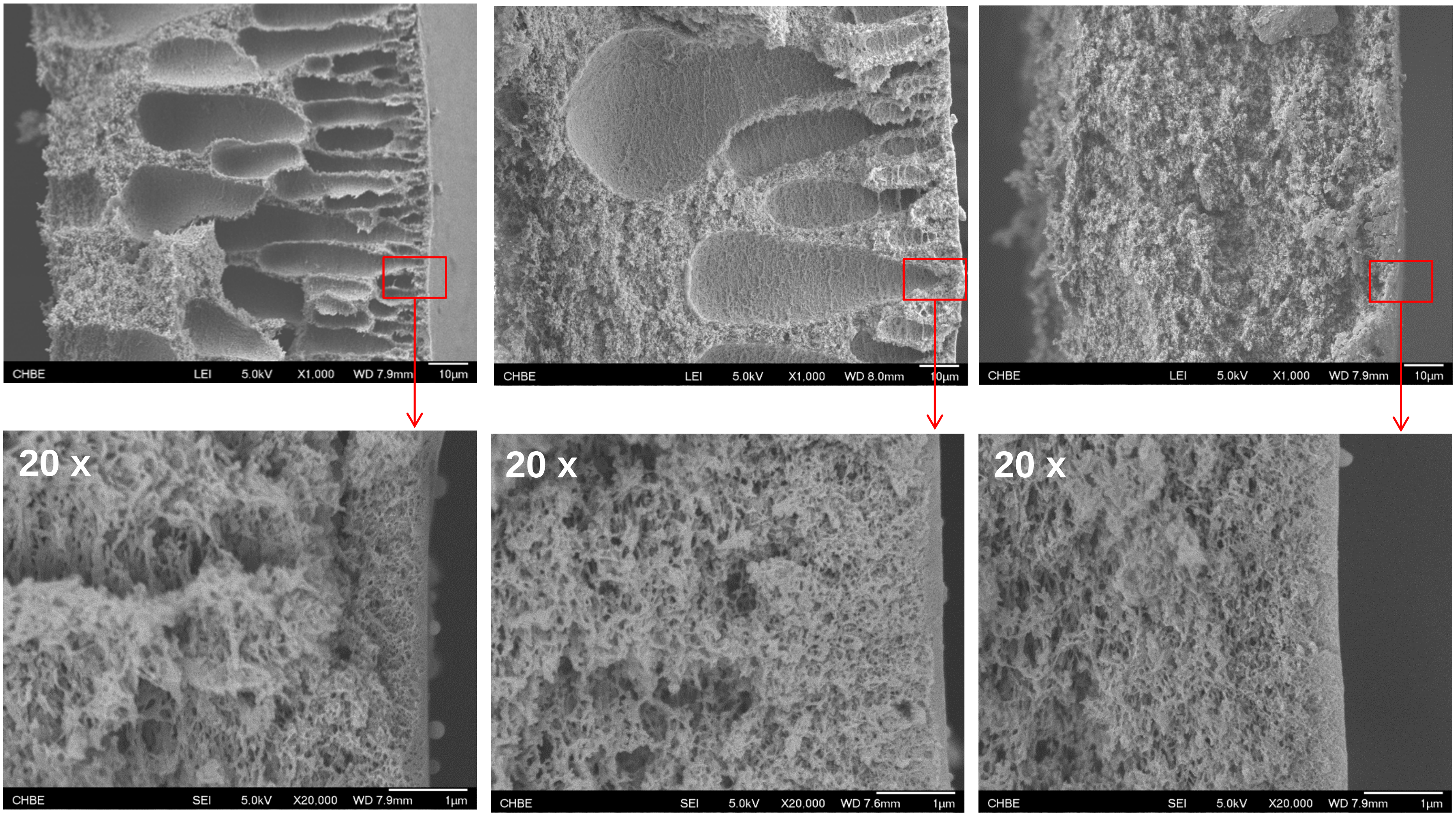


* PIM-1/Matrimid (15:85)

Increase NMP content, inner surface becomes more porous

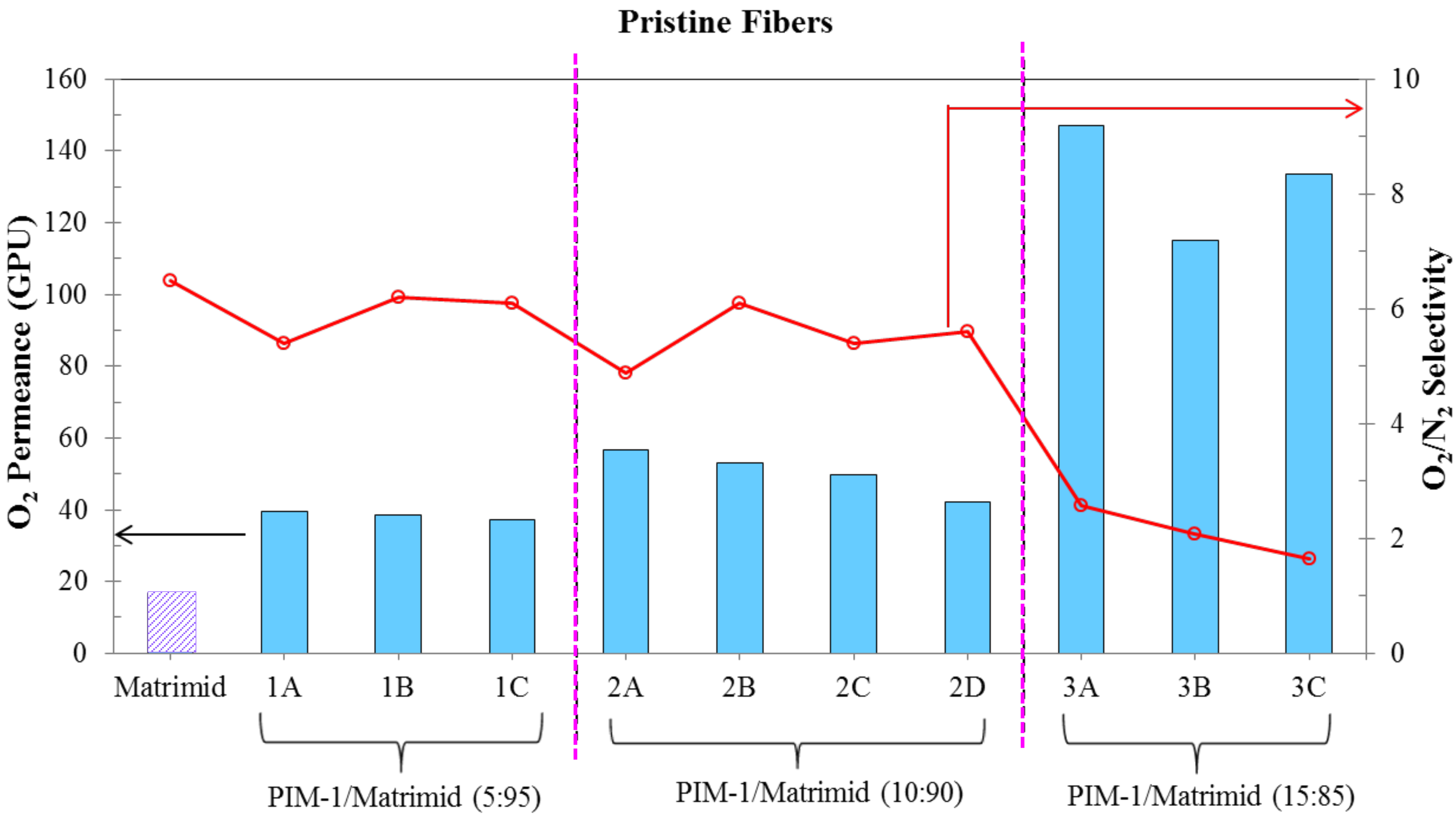
Dense-selective Layer Thickness

Dope | 5 wt % PIM-1 | 10 wt % PIM-1 | 15 wt % PIM-1

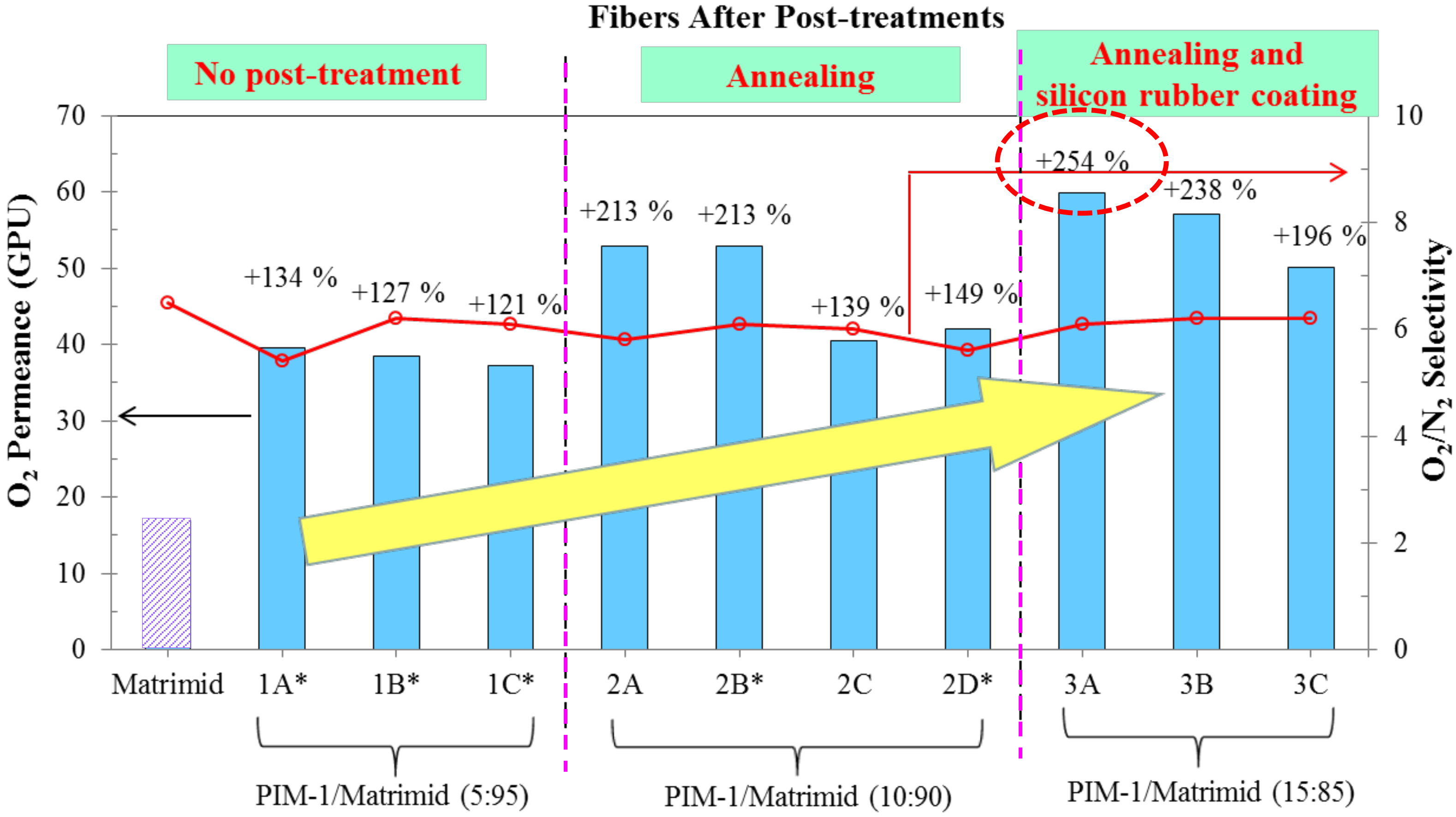


- ultrathin dense layer thickness

Effect of PIM-1 Concentration on Gas Separation Performance



Effect of Different Post-treatment Conditions on Gas Separation Performance



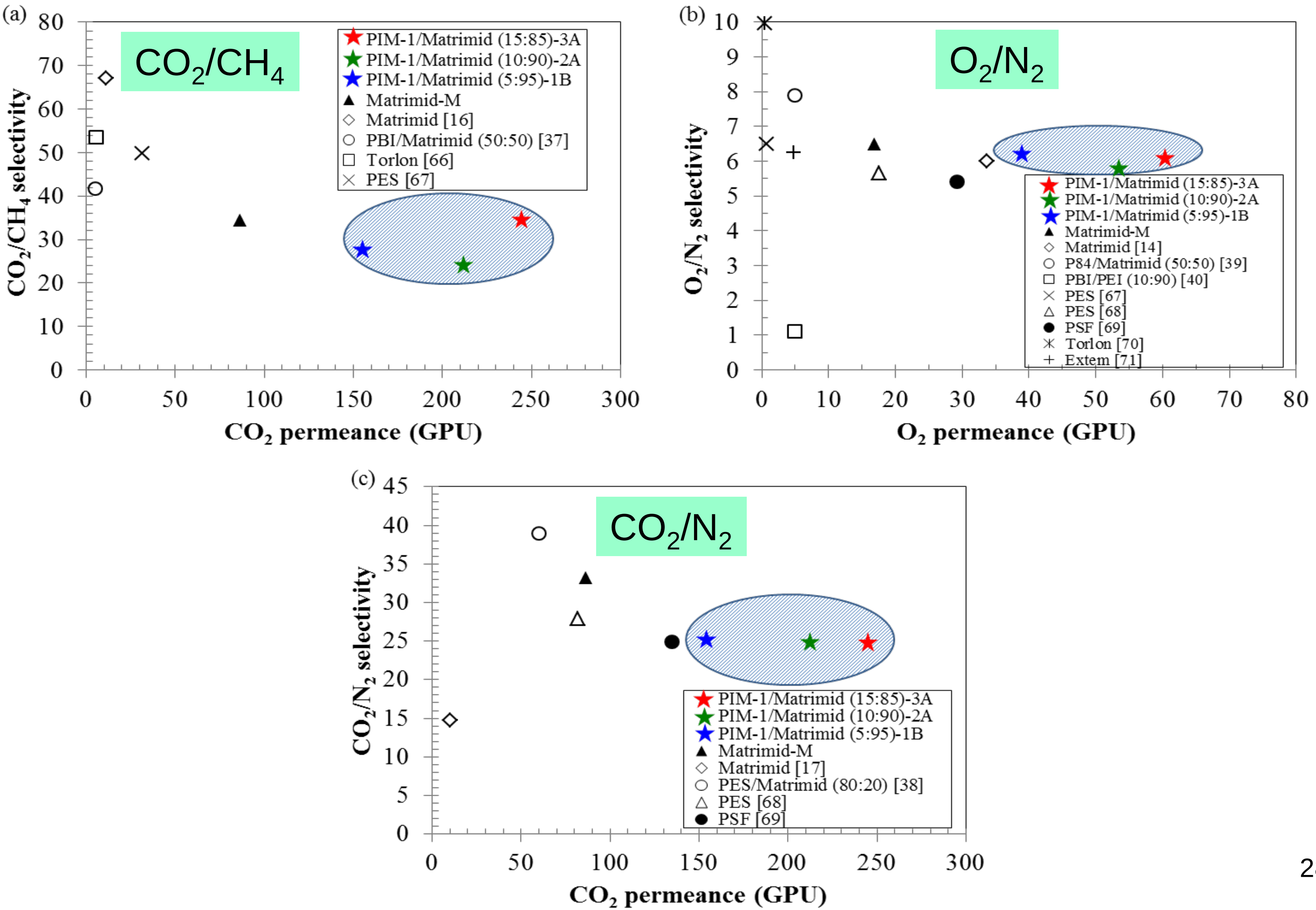
* is the pristine fibers without post-treatment.

CO_2/CH_4 Pure and Mixed Gas Performance

Hollow fibers ID	Pure gas[a] Permeance (GPU)			Pure gas[a] Selectivity	Binary gas[a] Permeance (GPU)		Binary gas[a] Selectivity
	CH_4	CO_2		CO_2/CH_4	CH_4	CO_2	CO_2/CH_4
Matrimid	2.5	86.3		34.5	-	-	-
PIM-1/Matrimid (5:95)-1B	5.4	153.4	+78%	28.4	-	-	-
PIM-1/Matrimid (10:90)-2B	8.1	212.4	+146%	26.2	6.9	159.7	23.1
PIM-1/Matrimid (15:85)-3A	7.1	243.2	+182%	34.3	6.6	188.9	28.8

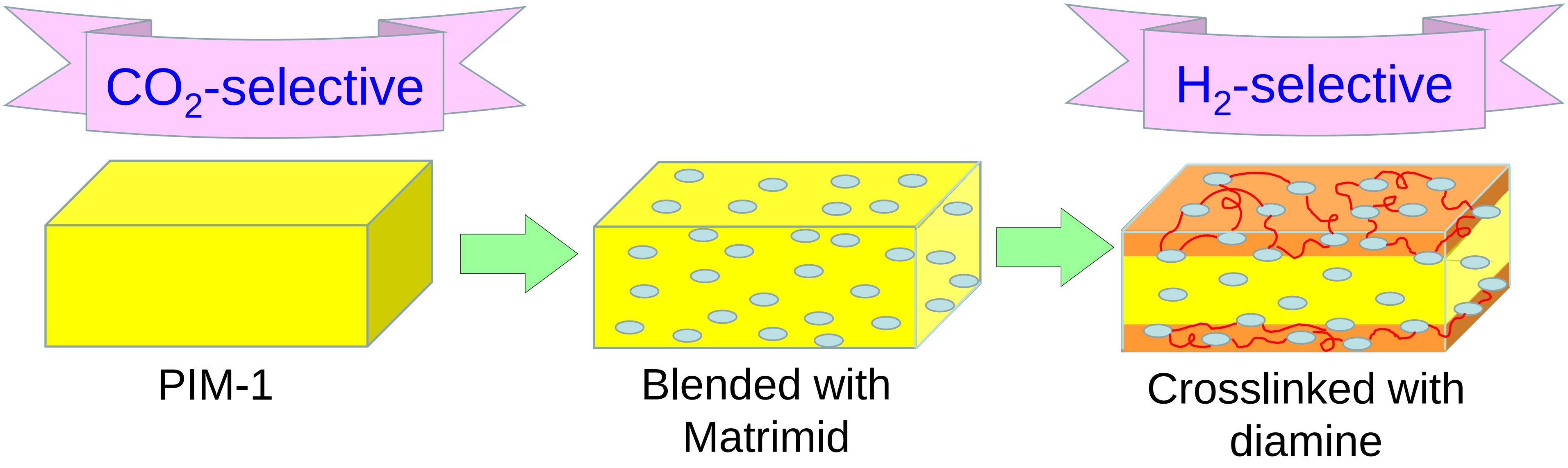
[a] After silicon rubber coating.
Pure gas and binary gas conducted at ambient temperature with 1 atm and 2 atm, respectively.

Comparison with Commercial Materials

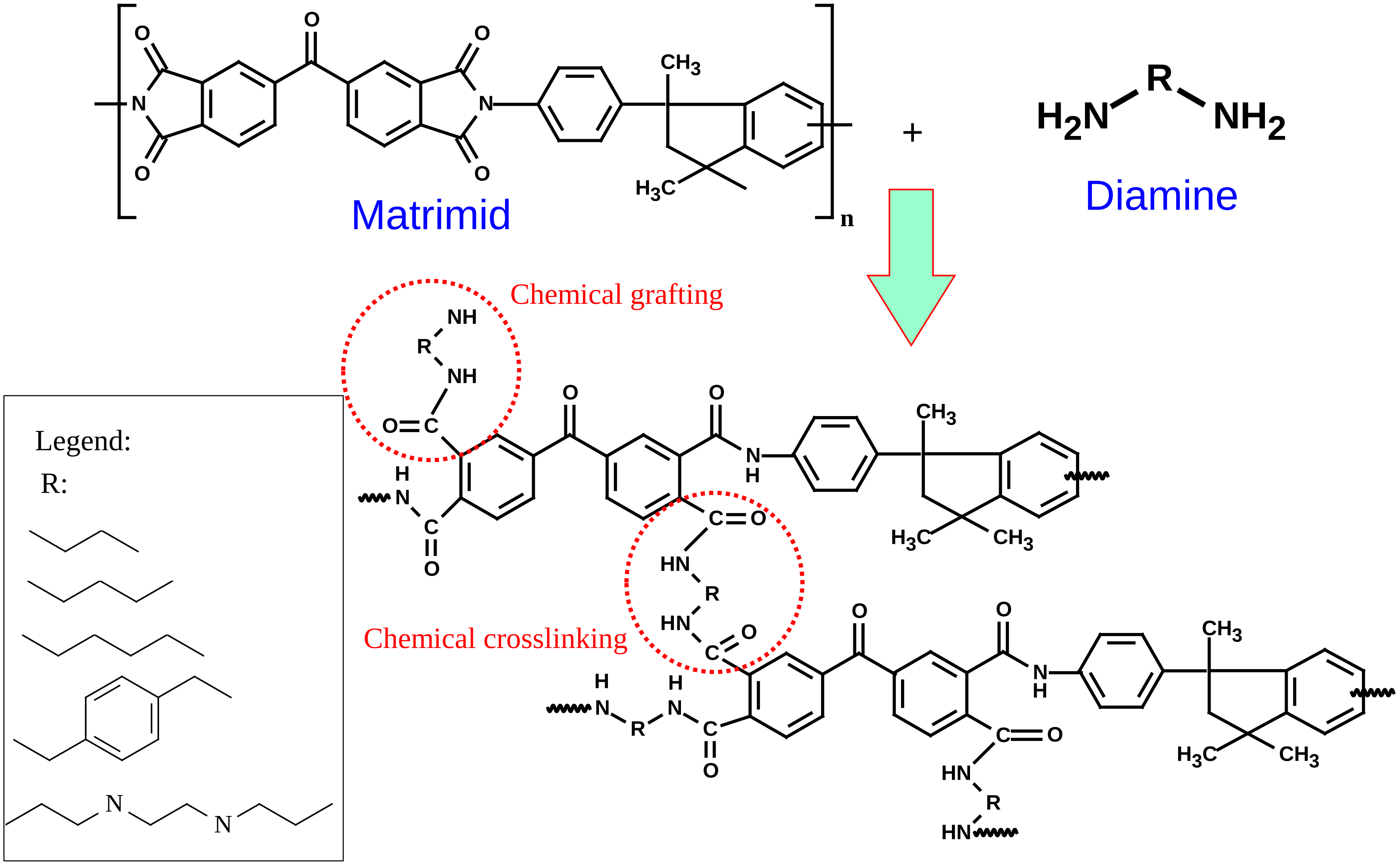


Research Work 3:

PIM-1/ Matrimid and Diamine Modified Membranes from CO_2-selective to H_2-selective



Cross-linking Mechanism



Effect of Diamine Structure on Pure Gas Performance

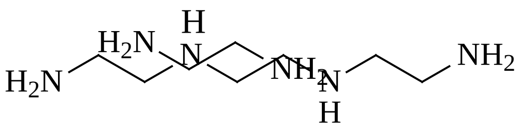
Membranes ID	Permeability (Barrer)[a,b]					Ideal Selectivity					
	H_2	O_2	N_2	CH_4	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2	CO_2/CH_4	H_2/CH_4	H_2/CO_2
PIM-1	2918	735	192	268	3825	15.2	3.8	19.9	14.3	10.9	0.8
PIM-1/Matrimid (90:10)	2118	575	144	173	2855	14.7	4.0	19.8	16.5	12.2	0.7
PIM-1/Matrimid (90:10) membranes modified with											
2 hr EDA	2783	930	269	374	4572	10.3	3.5	17.0	12.2	7.4	0.6
2 hr TMEDA	1776	326	62.6	63.4	1157	28.4	5.2	18.5	18.2	28.0	1.5
2 hr pXDA	823	124	20.8	17.2	388	39.6	6.0	18.6	22.5	47.8	2.1
2 hr BuDA	1015	136	23.0	22.0	341	44.1	5.9	14.8	15.5	46.1	3.0
2 hr TETA	395	32	4.3	3.4	41	91.9	7.4	9.5	12.1	116.2	9.6

H_2/N_2 ↑ 525%; O_2/N_2 ↑ 85%; H_2/CH_4 ↑ 852%; H_2/CO_2 ↑ 1271%

[a] 1 Barrer = 1 × 10^{-10} cm^3 (STP)cm/cm^2s cmHg.

[b] 35 °C and 3.5 atm

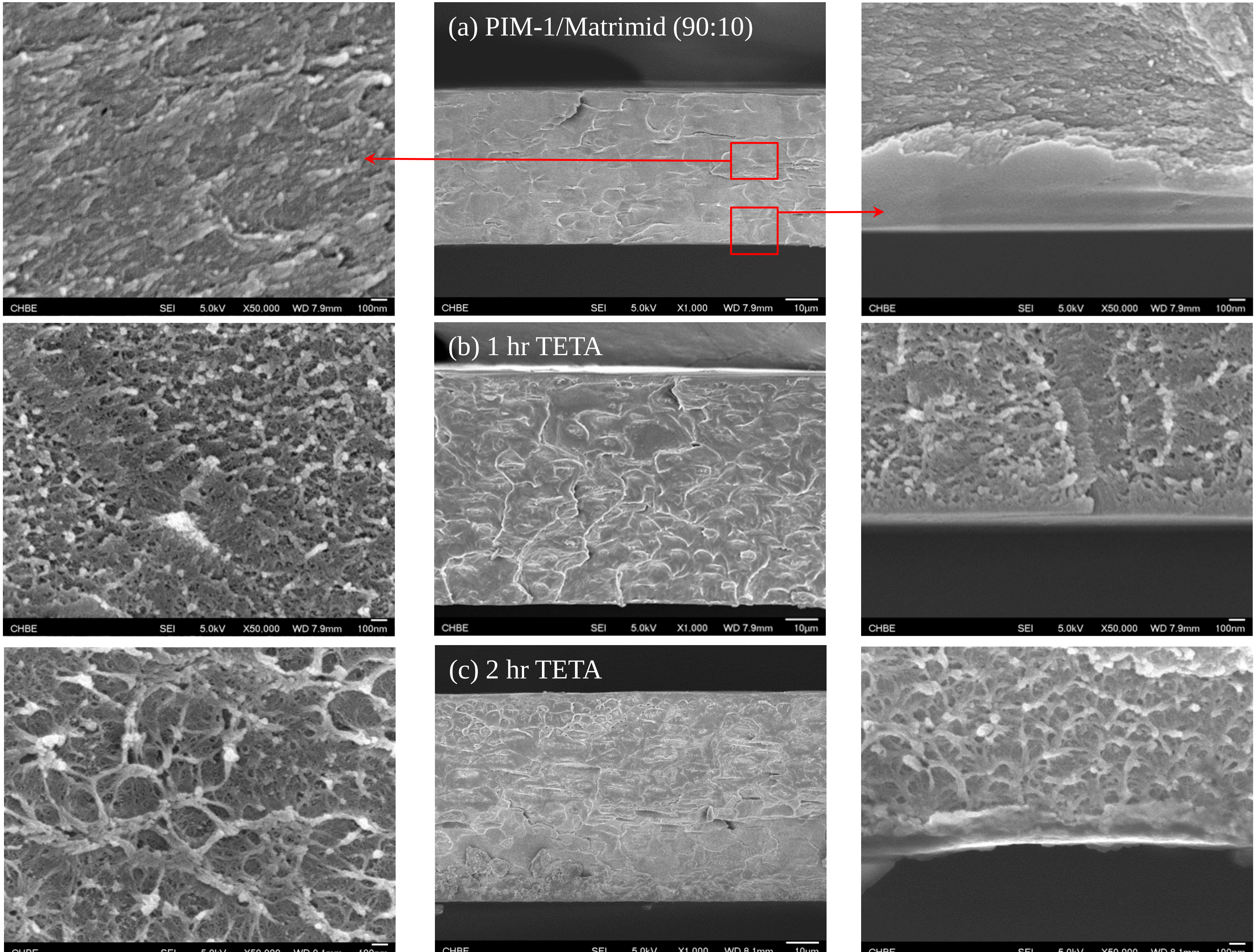
- Highest degree of cross-linking



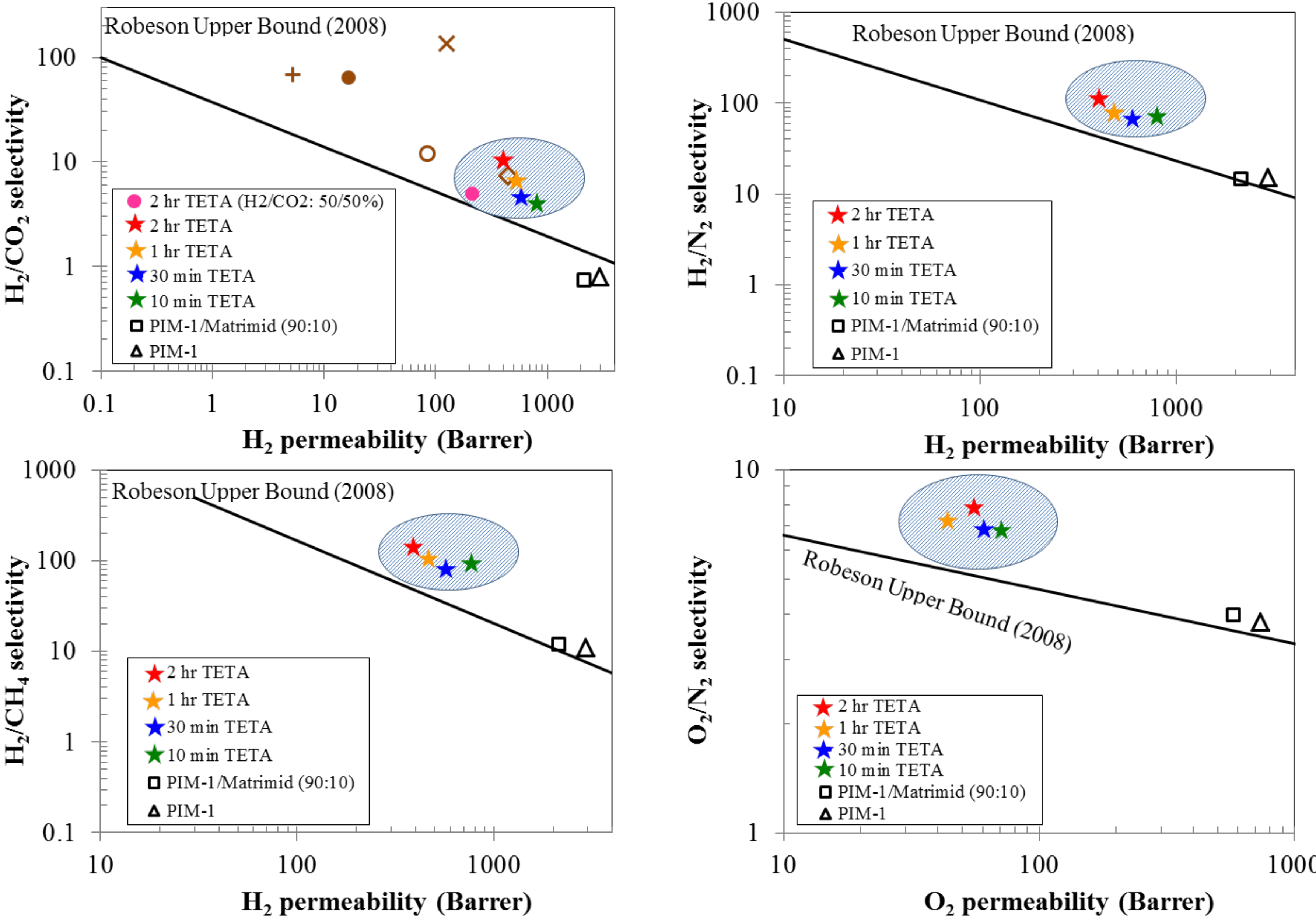
Ethylenediamine (EDA) / Triethylenetetramine (TETA)

Cross-sectional Morphology

RW3: H_2-selective



Benchmarking with Robeson Upper Bound



6FDA-ODA/NDA (PDA 90 min) (●)[16]; 6FDA-durene (DETA 60 ° C 10 min) (x)[20]; (PIM-1-UV4 hr (◊)[30]; PBI/ZIF-8 (70:30) (o)[51]; polysulfone/zeolite 3A (+)[52].

Summary

- 1st work:
  - Incorporation of PIM-1 in Matrimid increases permeability significantly.
  - Matrimid rich membranes suitable for natural gas separation (e.g. 5-10 wt% of PIM-1 in Matrimid).
  - PIM-1 rich membranes competent for air separation (e.g. 5-30 wt% of Matrimid in PIM-1).

- 2nd work:
  - High flux hollow fiber membranes spun from 5-15 wt% PIM-1 in Matrimid.
  - The CO_2 permeance of the fiber containing 15 wt% PIM-1 displays a greater improvement of 2.8 folds to 243.2 GPU with a CO_2/CH_4 selectivity of 34.3 after silicon rubber coating.
  - Fiber containing 15 wt% PIM-1 has a CO_2/CH_4 selectivity of 28.8 in binary gas test.

- W.F. Yong et al., J. Membr. Sci., 407–408 (2012) 47–57.
- W.F. Yong et al., J. Membr. Sci. 443 (2013) 156–169.
- W.F. Yong et al., J. Mater. Chem. A, 1 (2013) 13914-13925.

Summary (cont')

- 3rd work:
  - The intrinsic properties of PIM-1 membranes tuned from CO_2-selective to H_2-selective via blending with Matrimid and cross-linking with diamine.
  - The ideal H_2/CO_2 selectivity of the membrane after modification by 2 hr TETA improved from 0.7 to 9.6 with a H_2 permeability of 395 Barrer.
  - The developed membranes show exceptional separation performance surpassing the present upper bound for H_2/CO_2, H_2/N_2, H_2/CH_4 and O_2/N_2 separations.

- W.F. Yong et al., J. Membr. Sci., 407–408 (2012) 47–57.
- W.F. Yong et al., J. Membr. Sci. 443 (2013) 156–169.
- W.F. Yong et al., J. Mater. Chem. A, 1 (2013) 13914-13925.

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- NUS membrane research lab mates
- http://www.chbe.nus.edu.sg/membrane/

- cheywf@nus.edu.sg