



Discover



Develop



Deploy



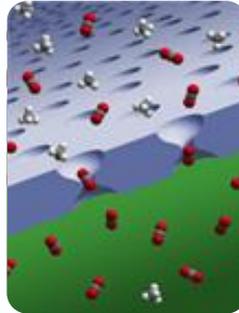
Virtual screening



Chemistry



Tuning porosity



Material scale-up



Commercial design



# Control of Physical Aging in Super Glassy Polymer Membranes Without Permeability Loss

## MOF Mixed Matrix Membranes

Cher Hon (Sam) LAU | Research Scientist

25 March 2015

MANUFACTURING FLAGSHIP/ ADAPTIVE POROUS MATERIALS TEAM

[www.csiro.au](http://www.csiro.au)



Australian National University

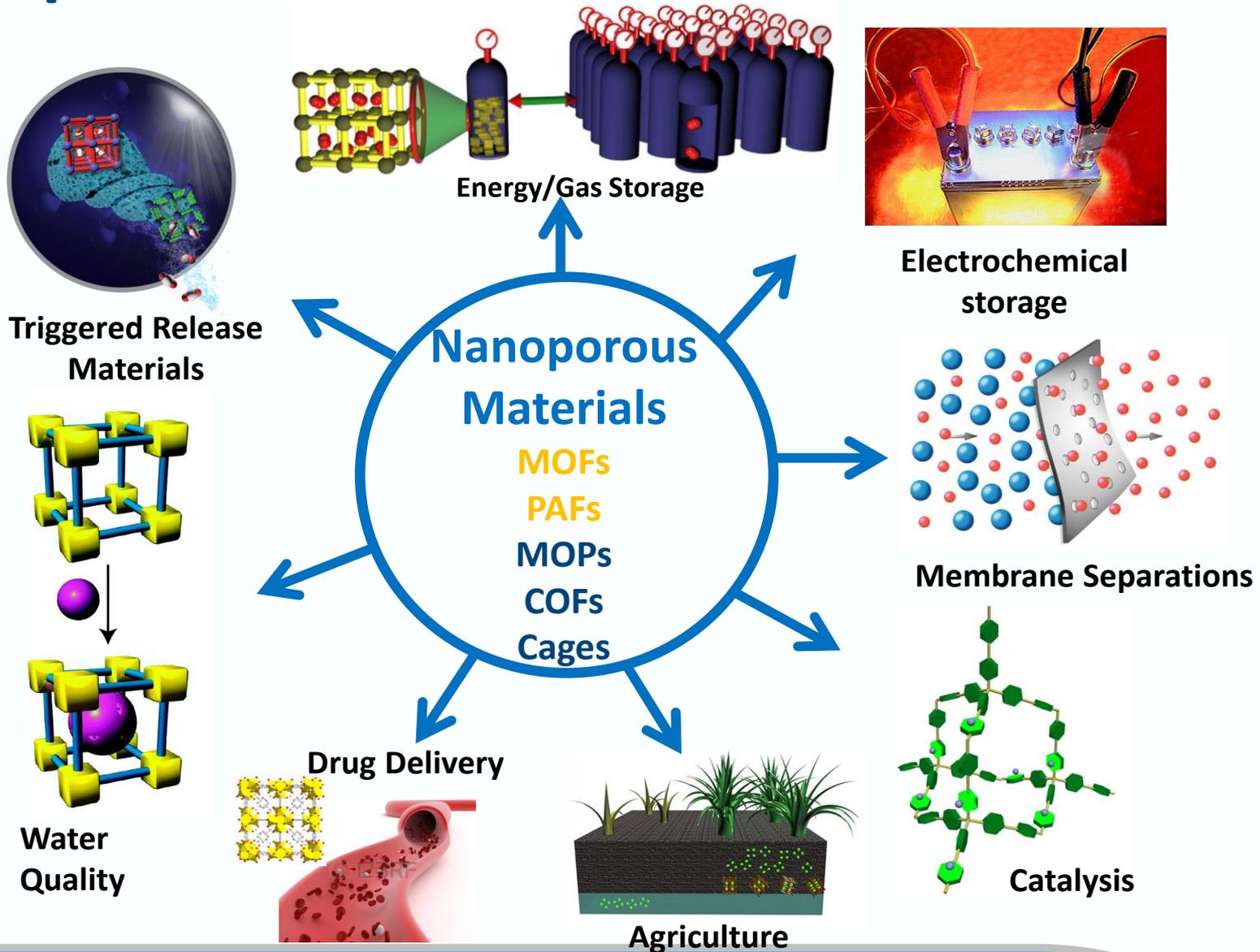


# Presentation Outline

- Adaptive Porous Materials Team
- Porous Frameworks
- CSIRO's Approach
- Conclusion

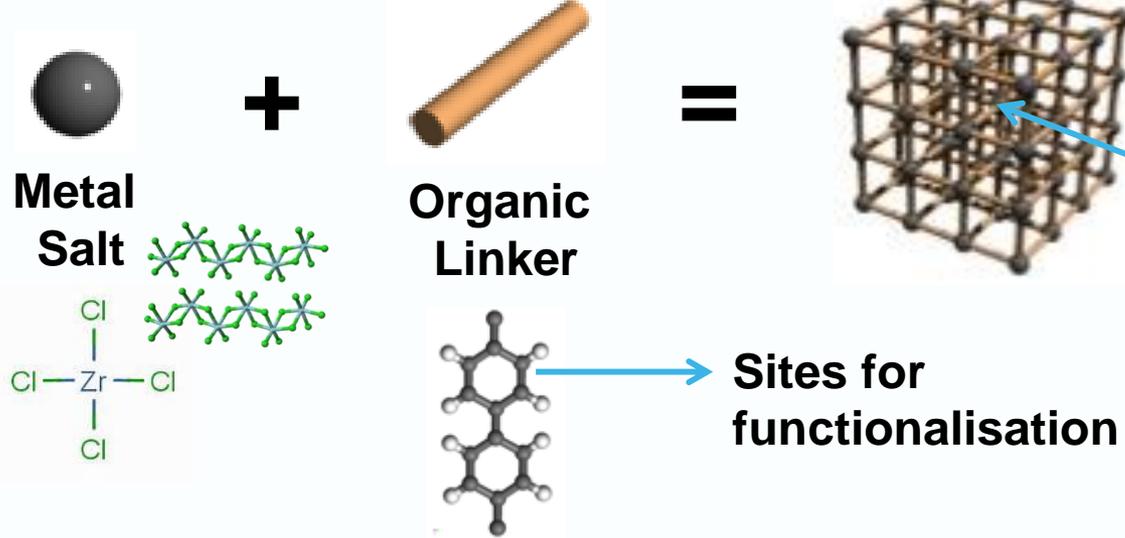


# Adaptive Porous Materials Team in CSIRO



# Porous Frameworks

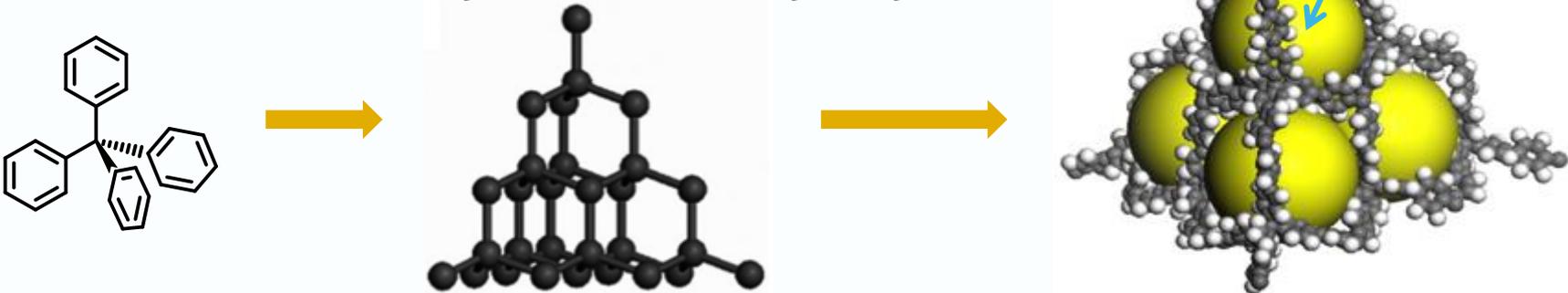
## Metal Organic Frameworks (MOFs)



**Void space for storage**

## Porous Aromatic Frameworks (PAFs)

Thermally and chemically very stable



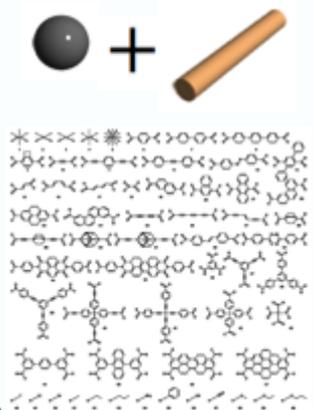
# Virtual screening of MOF candidates

## Elements

Periodic Table of the Elements

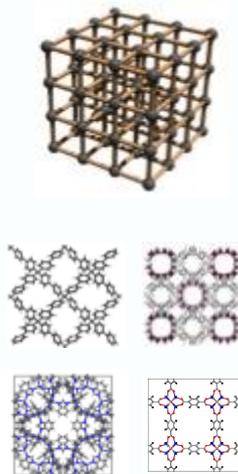
- Carbon
- Zinc
- Oxygen
- Hydroge
- n
- Nitrogen
- +

## Building Blocks



- Zn<sup>+2</sup>
- Cu<sup>+2</sup>
- BTB
- BDC
- DOBDC
- +

## MOF Candidates



- PAFs
- ZIFs
- COFs
- POCs
- SNUs
- +

## Properties



- Surface area
- Porosity
- Gas adsorption
- Gas permeation
- Water permeation
- +

## Applications



- Separation
- Storage
- Catalysis
- Sensors
- Barriers
- +

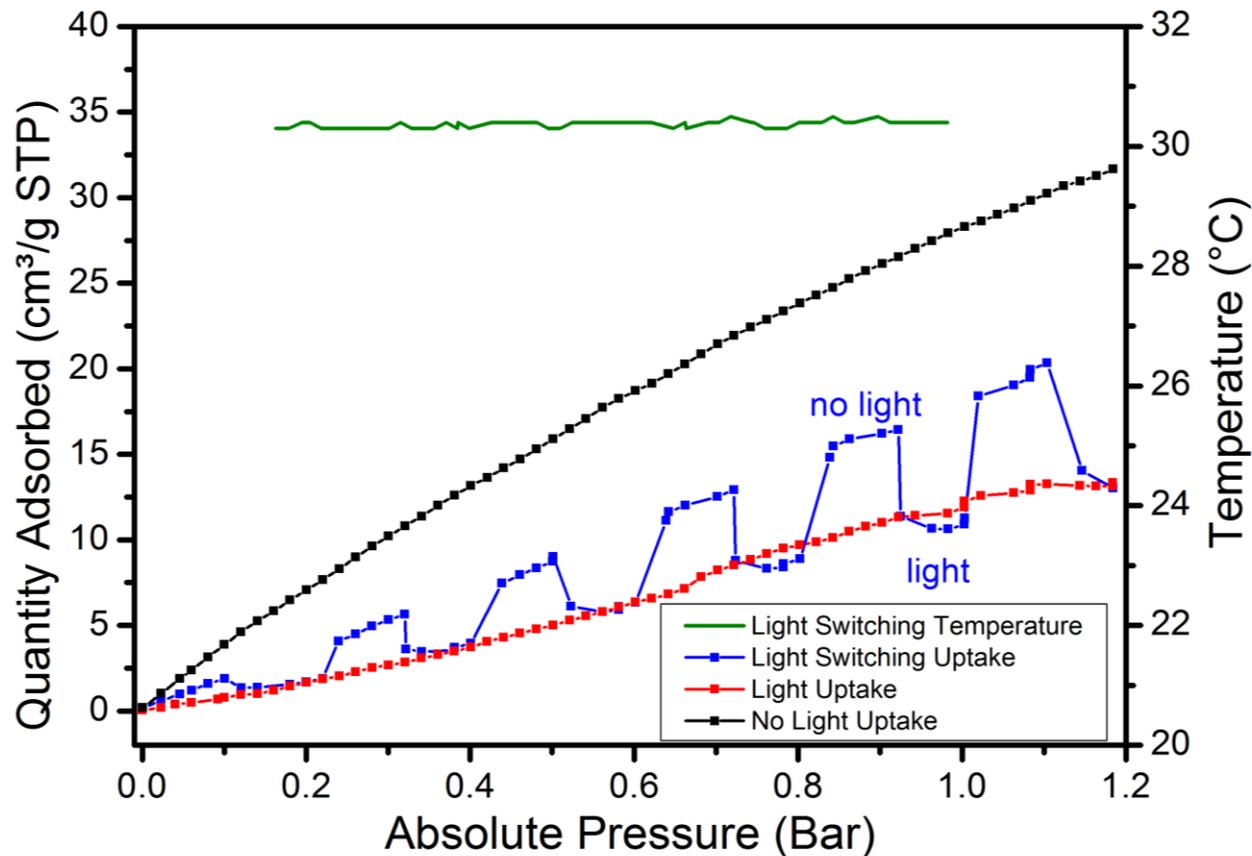
# Triggered Release Materials

## UV-triggered release of CO<sub>2</sub>



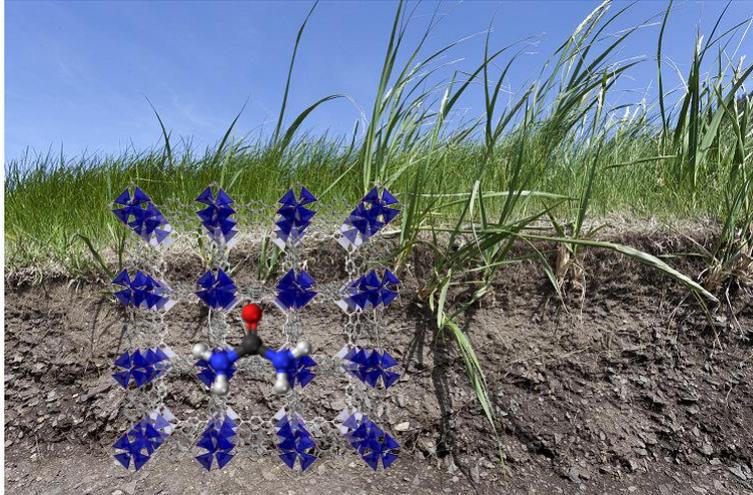
R. Lyndon, K. Konstas, M. R. Hill; *Angew. Chem. Int. Ed.*, **2013**, 52, 3695.

# Triggered Release Materials

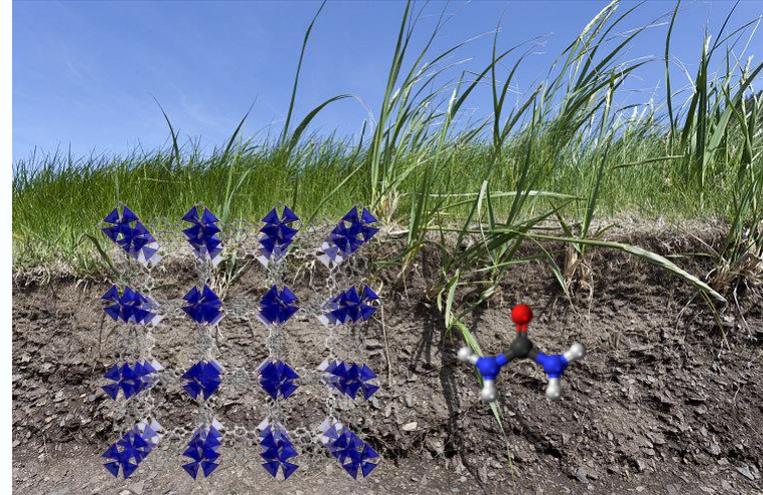


R. Lyndon, K. Konstas, M. R. Hill; *Angew. Chem. Int. Ed.*, **2013**, 52, 3695.

# Intelligent Fertilizers



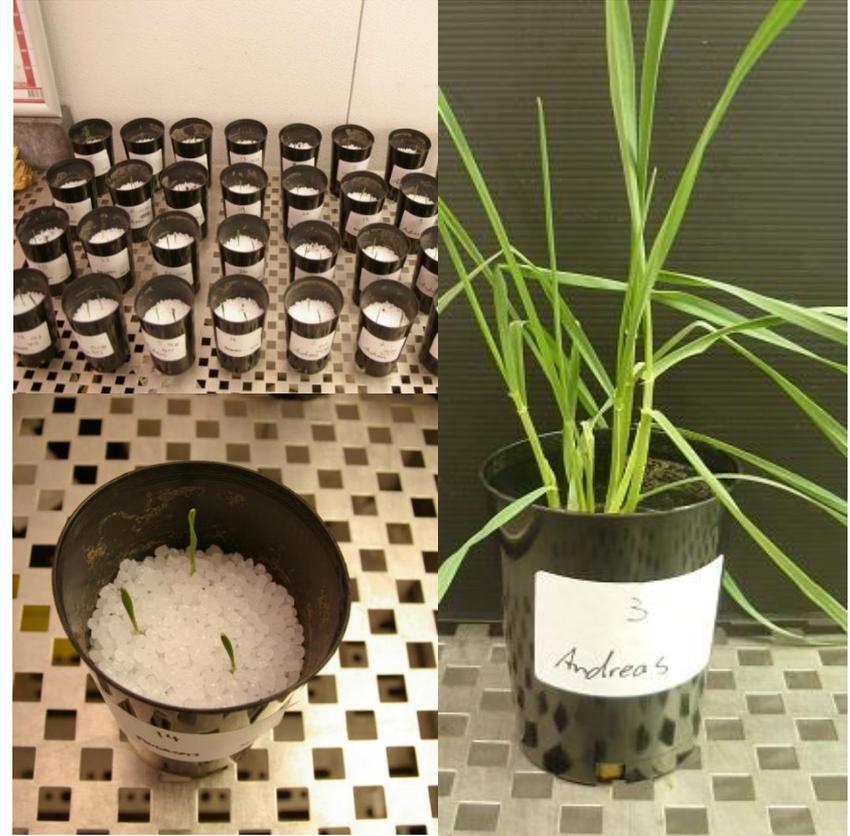
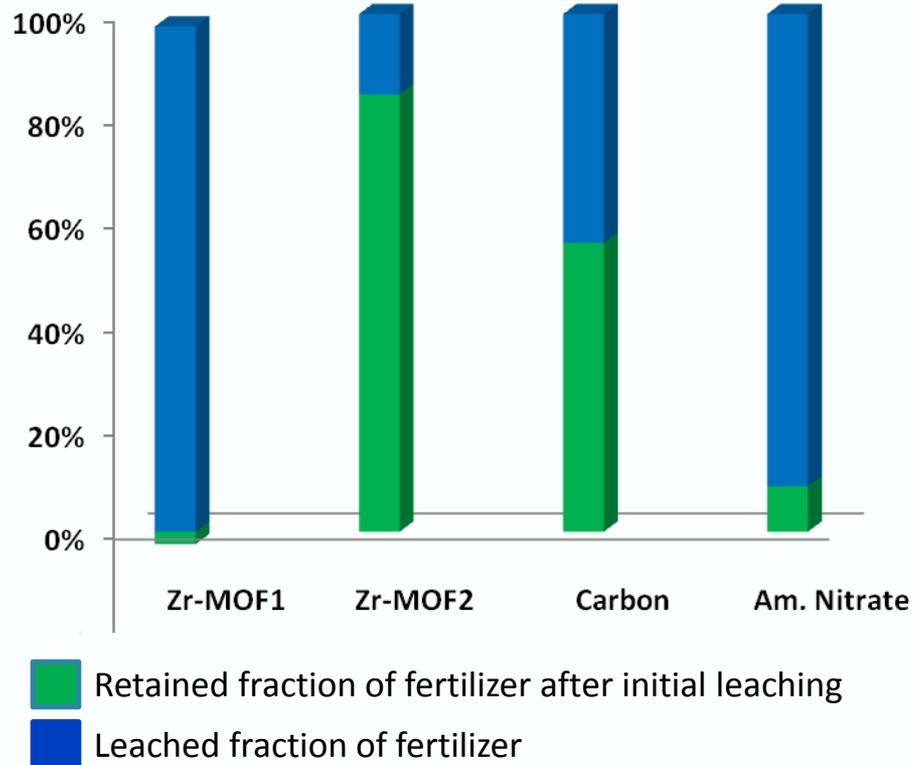
H<sub>2</sub>O  
Plant demand  
→



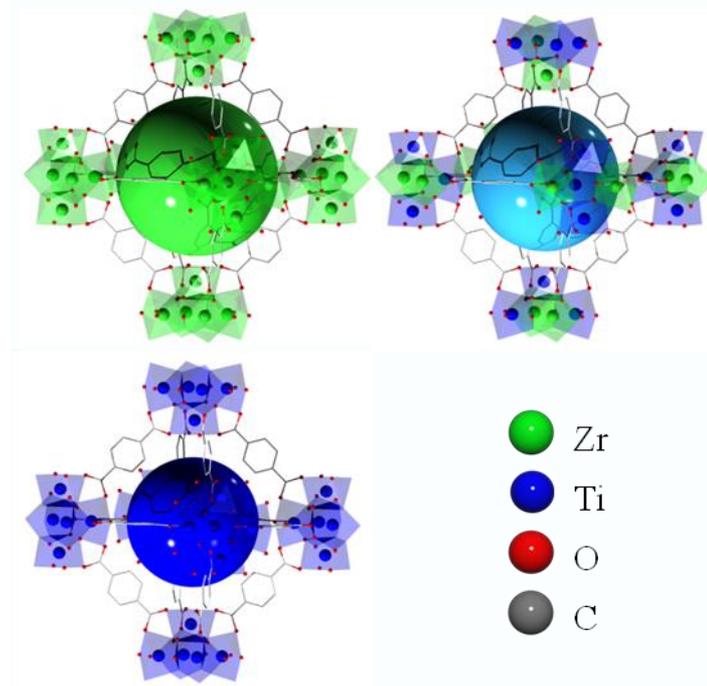
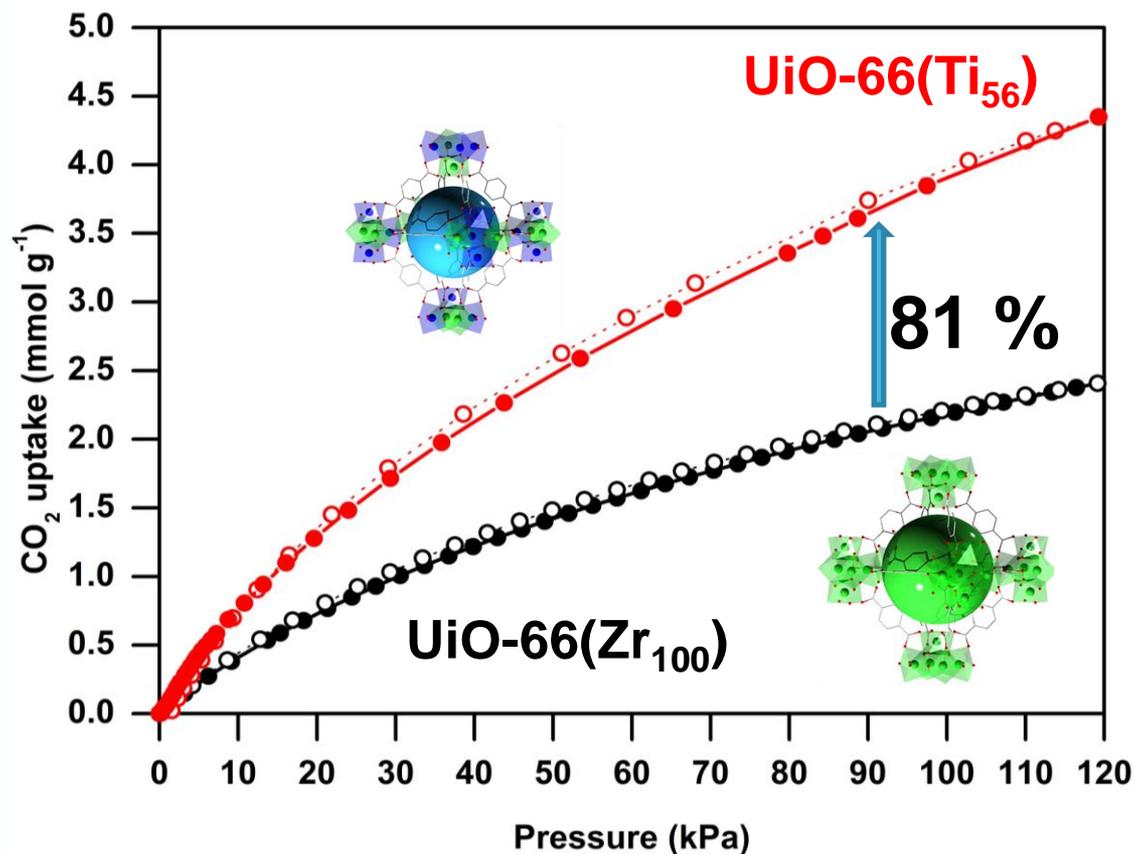
## Requirements:

- High pore volume
- Low cost
- Water stable
- Eco-friendly

# Intelligent Fertilizers

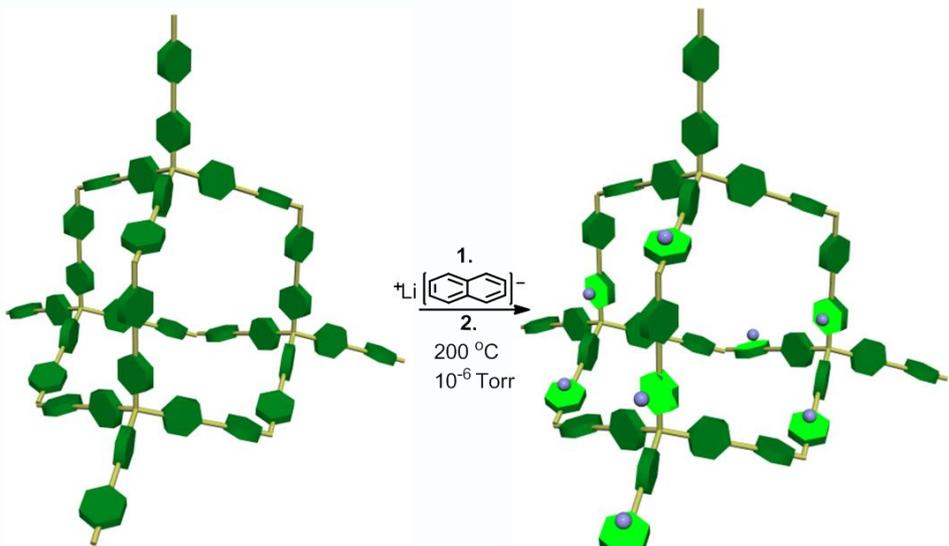


# Carbon Capture

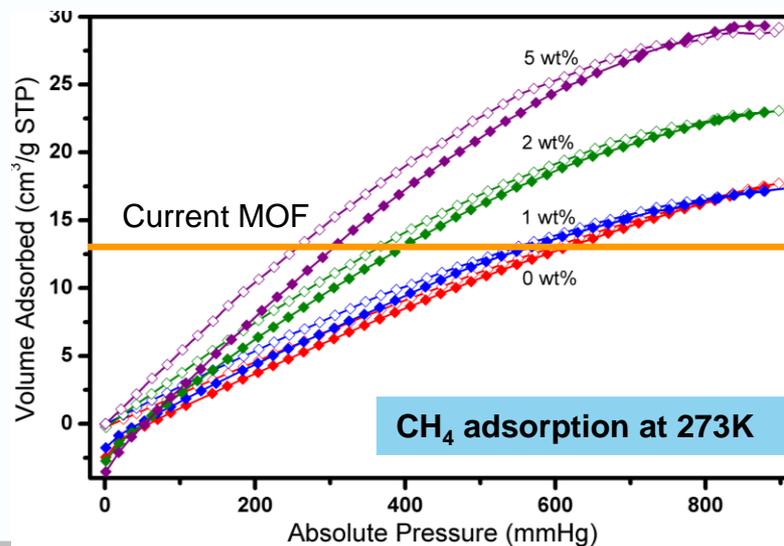
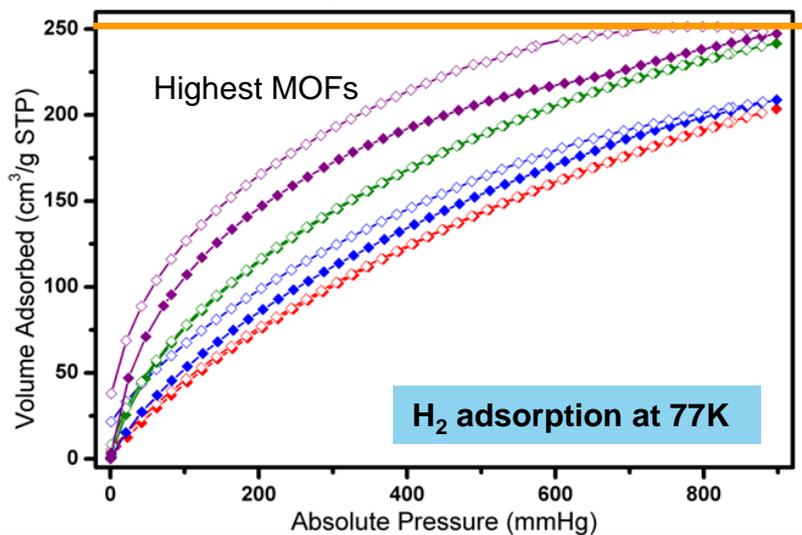
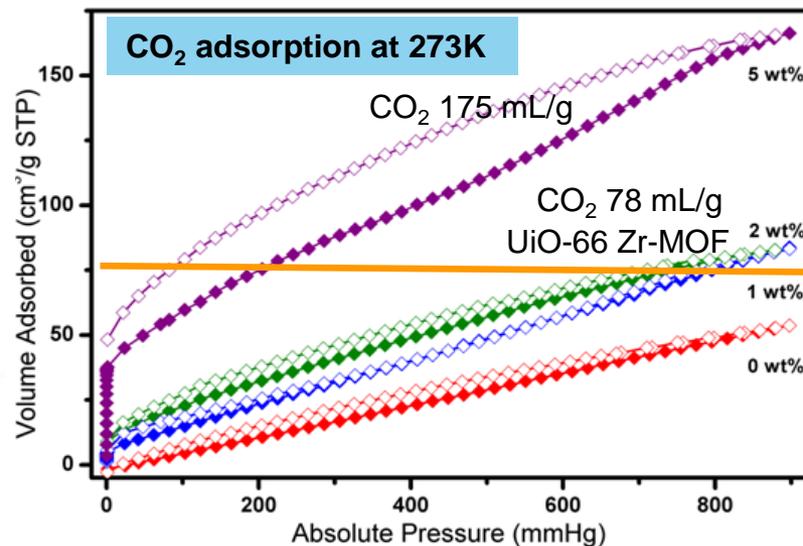


Lau, C. H.; Babarao, R.; Hill, M. R., *Chem. Commun.* 2013, 49 (35), 3634

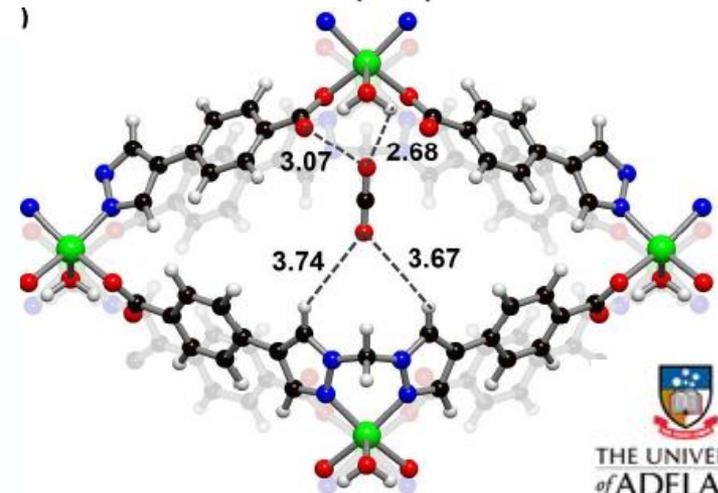
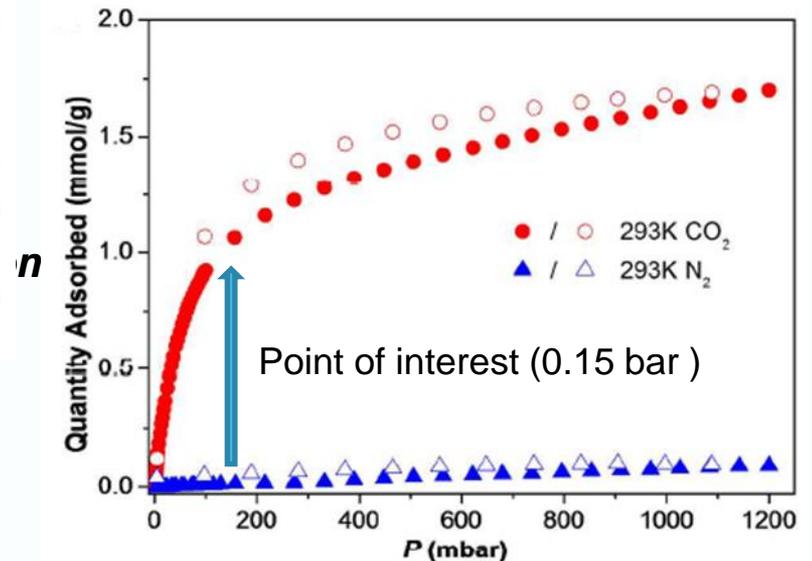
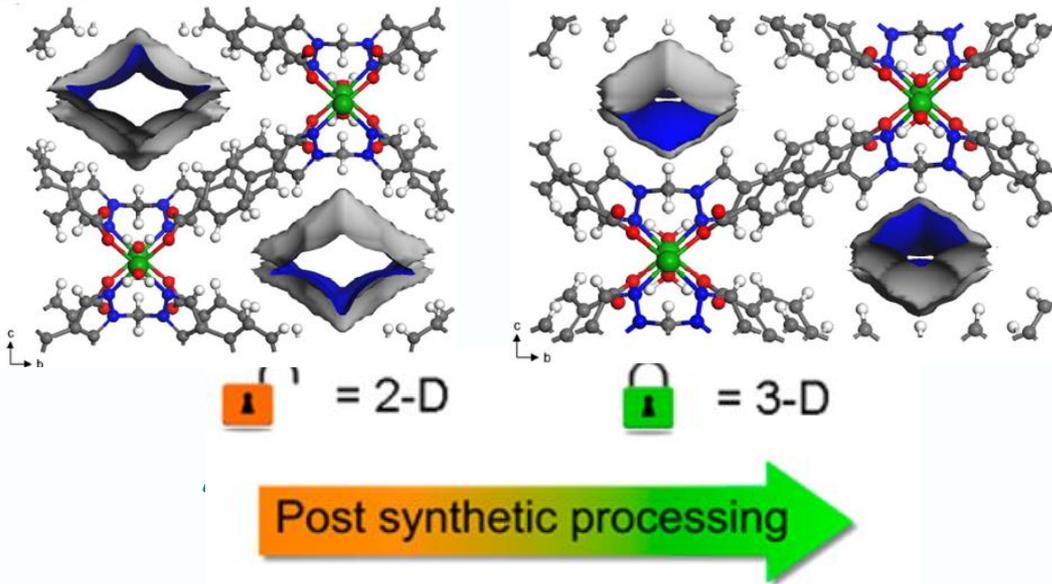
# Energy & Gas Storage



K. Konstas, M. R. Hill; *Angew. Chem. Int. Ed.*, **2012**, *51*, 6639-6642.



# Energy & Gas Storage



- ❑ Predicted selectivity for  $\text{CO}_2/\text{N}_2$  (15/85 wt % mixture) of 590 at 293 K and 1 atm
- ❑ Flue gas composition  $\text{CO}_2$  (15%),  $\text{N}_2$  (75%),  $\text{O}_2$  (4 - 5 %),  $\text{H}_2\text{O}$  (5 - 8 %) and  $\text{SO}_x$  and  $\text{No}_x$
- ❑ Predict mixed gas isotherms (difficult to obtain experimentally)

# Porous Frameworks

As adsorbents for CO<sub>2</sub> capture



**600 MW coal-fired power plant  
Flue gas 13 % CO<sub>2</sub> (460 tonnes/hr)<sup>a</sup>**

MOF CO<sub>2</sub> Capacity <sup>b</sup>

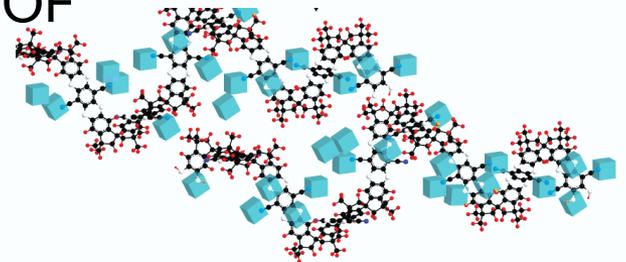
146 tonne MOF = **\$2.9 billion** (based on BASF prices)

MOF Mixed Matrix Membrane

a, b

0.17 million m<sup>2</sup> – 2.46 million m<sup>2</sup>

0.15 - 2.1 tonne MOF

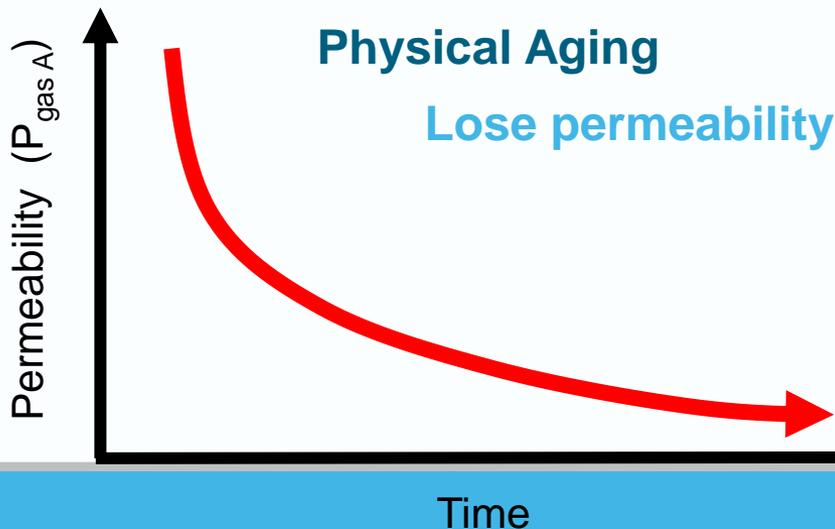
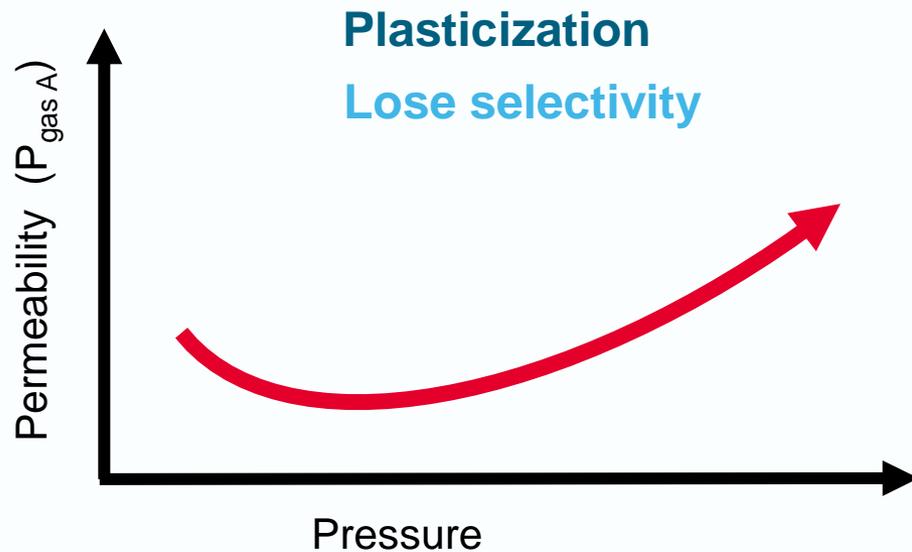
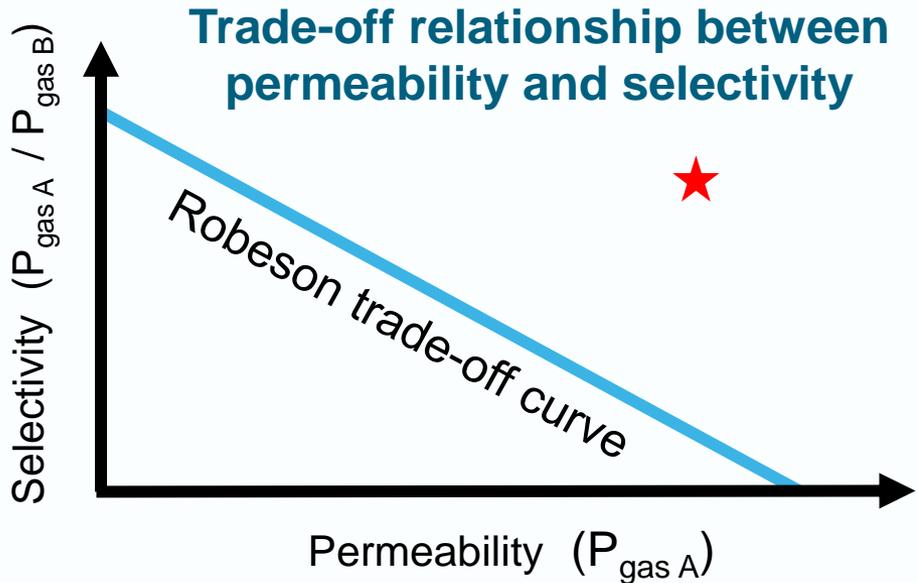


a) T. C. Merkel\*, H. Lin, X. Wei, R. Baker; J. Membr. Sci., 359 (2010) 126–139

b) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu; Chem. Soc. Rev, 2012,41, 2308–2322

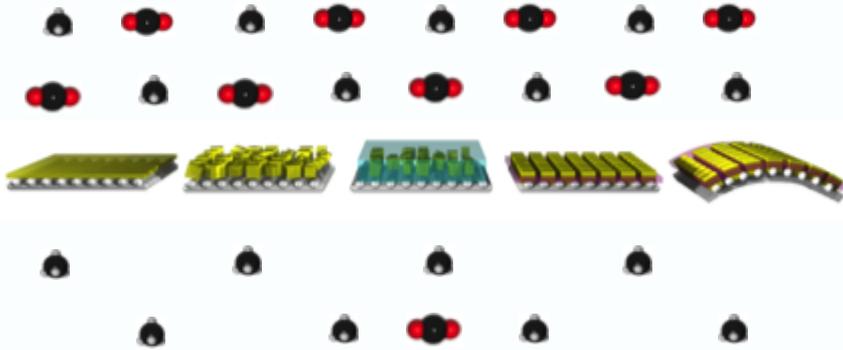
c) L. M. Robeson, J. Membr. Sci., 2008, 320, 390-400

# What we aim to achieve with CSIRO's MOF Membranes?

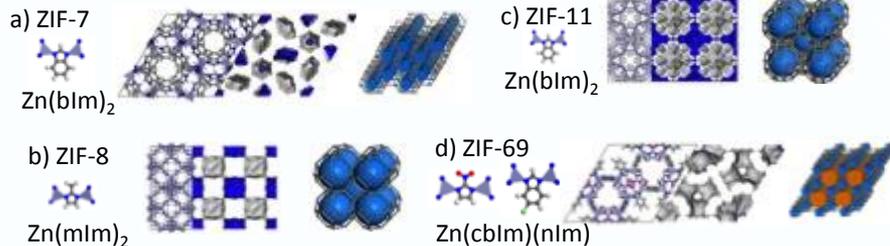


# Example: Screening for membrane materials

Application: CO<sub>2</sub> capture and H<sub>2</sub> generation

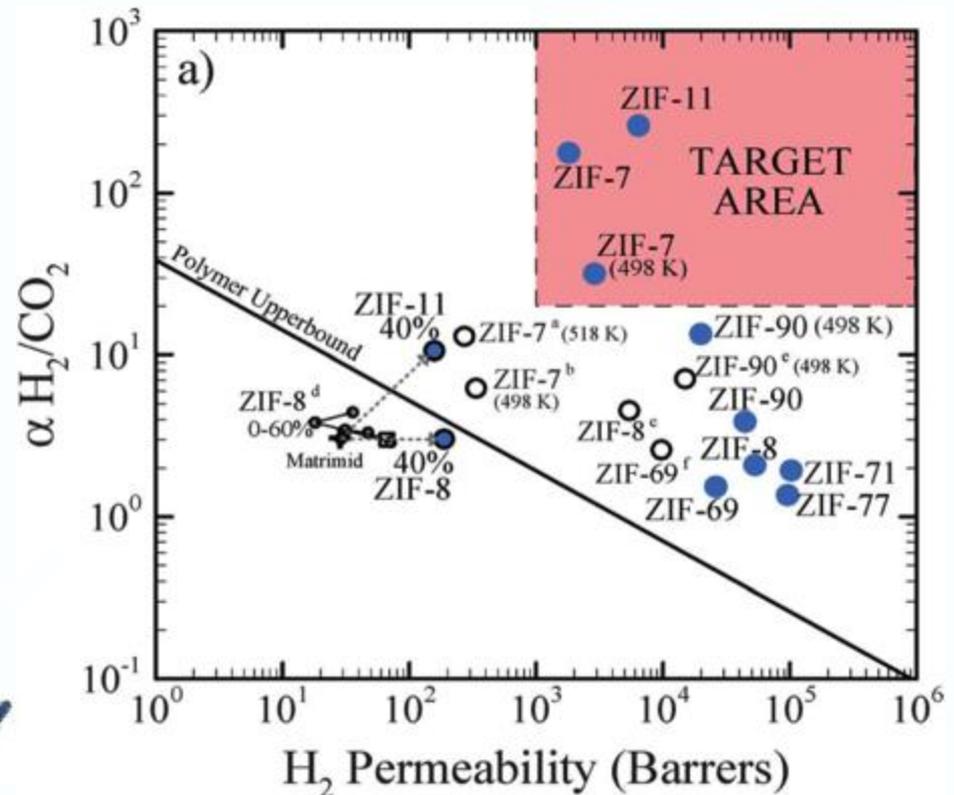


Candidate Materials: Zeolitic Imidazolate Frameworks



## Industrial Feasibility Criteria

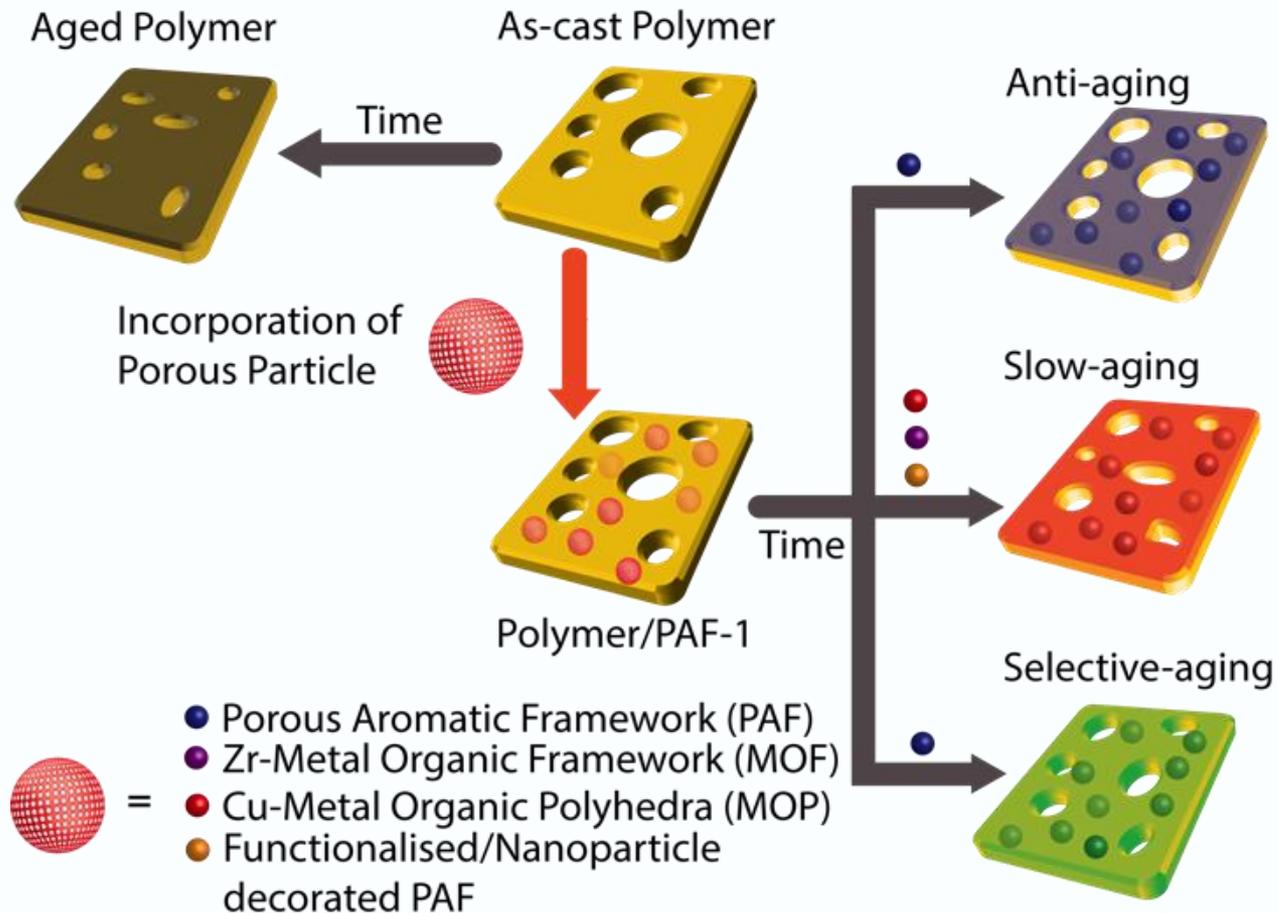
Intergovernmental Panel on Climate Change (IPCC)



Thornton et al. "Feasibility of Zeolitic Imidazolate Framework membranes for clean energy applications" Energy & Environmental Science 2012

# CSIRO's Approach

## Mixed Matrix Membranes with Porous Frameworks

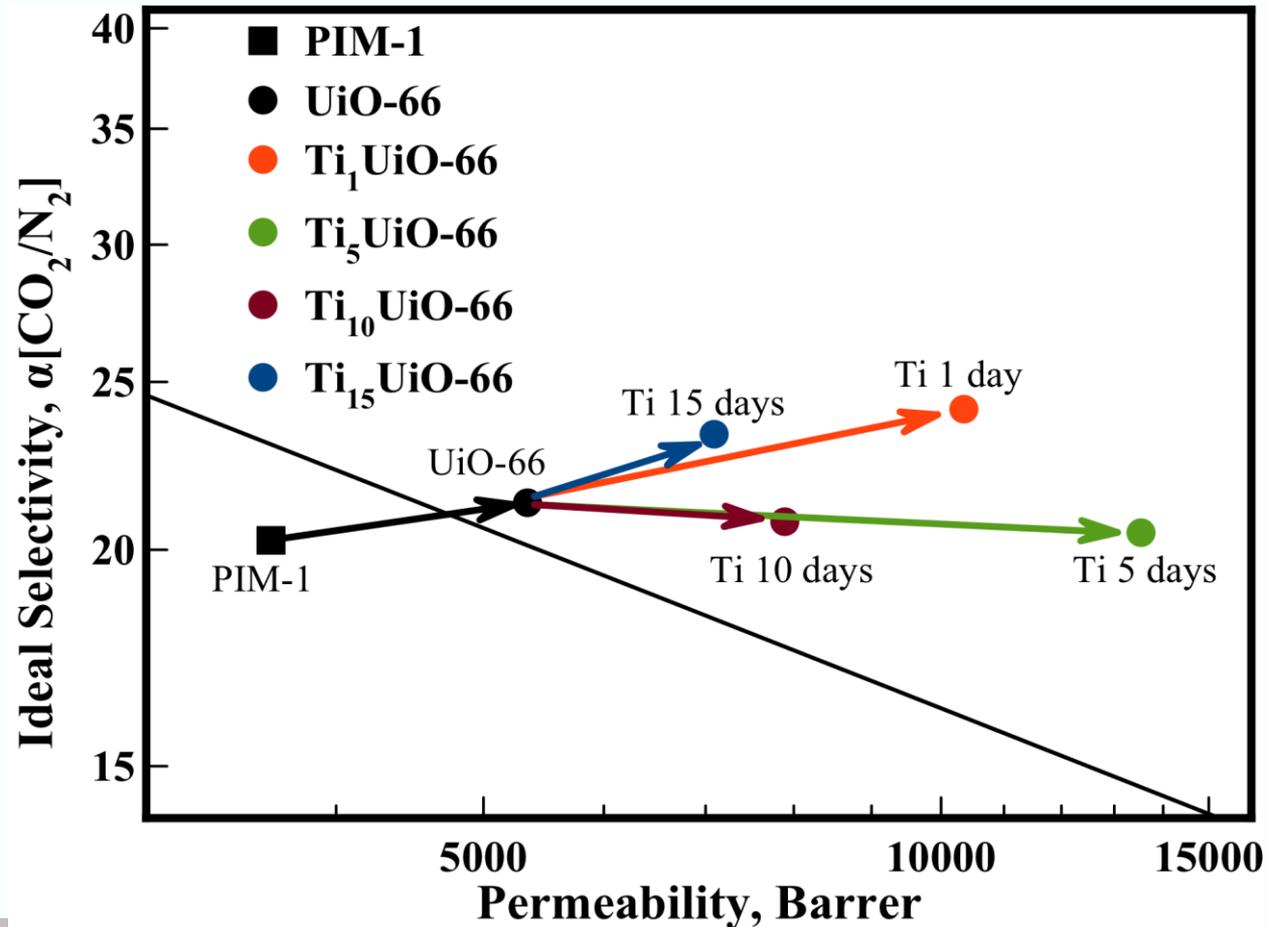
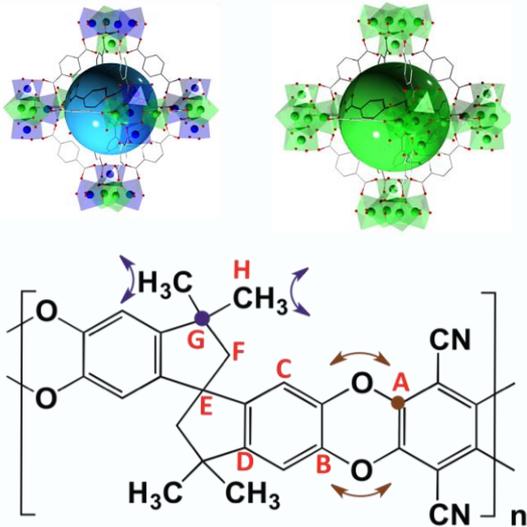


# CSIRO's Membranes

## Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF, Ti-UiO-66

Polymer: PIM-1

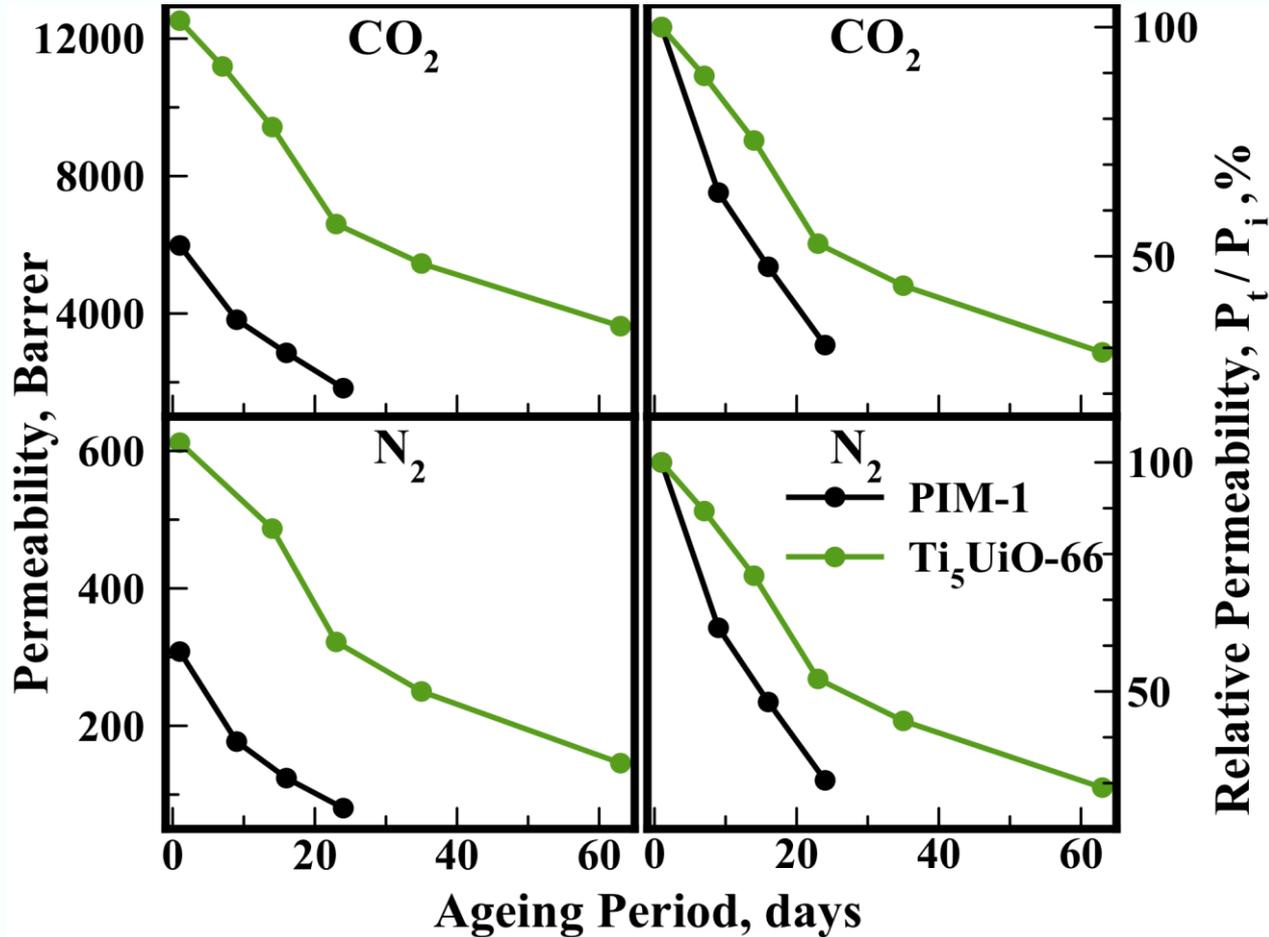


Smith, S. J. D.; Ladewig, B. P.; Hill, A. J.; Lau, C. H.; Hill, M. R., *Sci. Rep.* 2015, 5, 7823

# CSIRO's Membranes

## Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF



Smith, S. J. D.; Ladewig, B. P.; Hill, A. J.; Lau, C. H.; Hill, M. R., *Sci. Rep.* 2015, 5, 7823

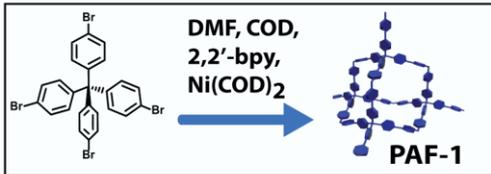
# CSIRO's Membranes

## Slow Aging Membranes – Organic Solvent Nanofiltration

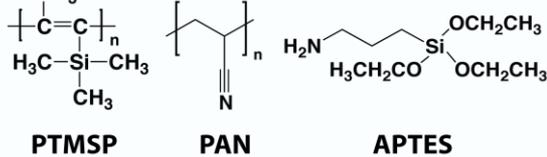
Additive: PAF-1

Water-Hydrocarbon Separations

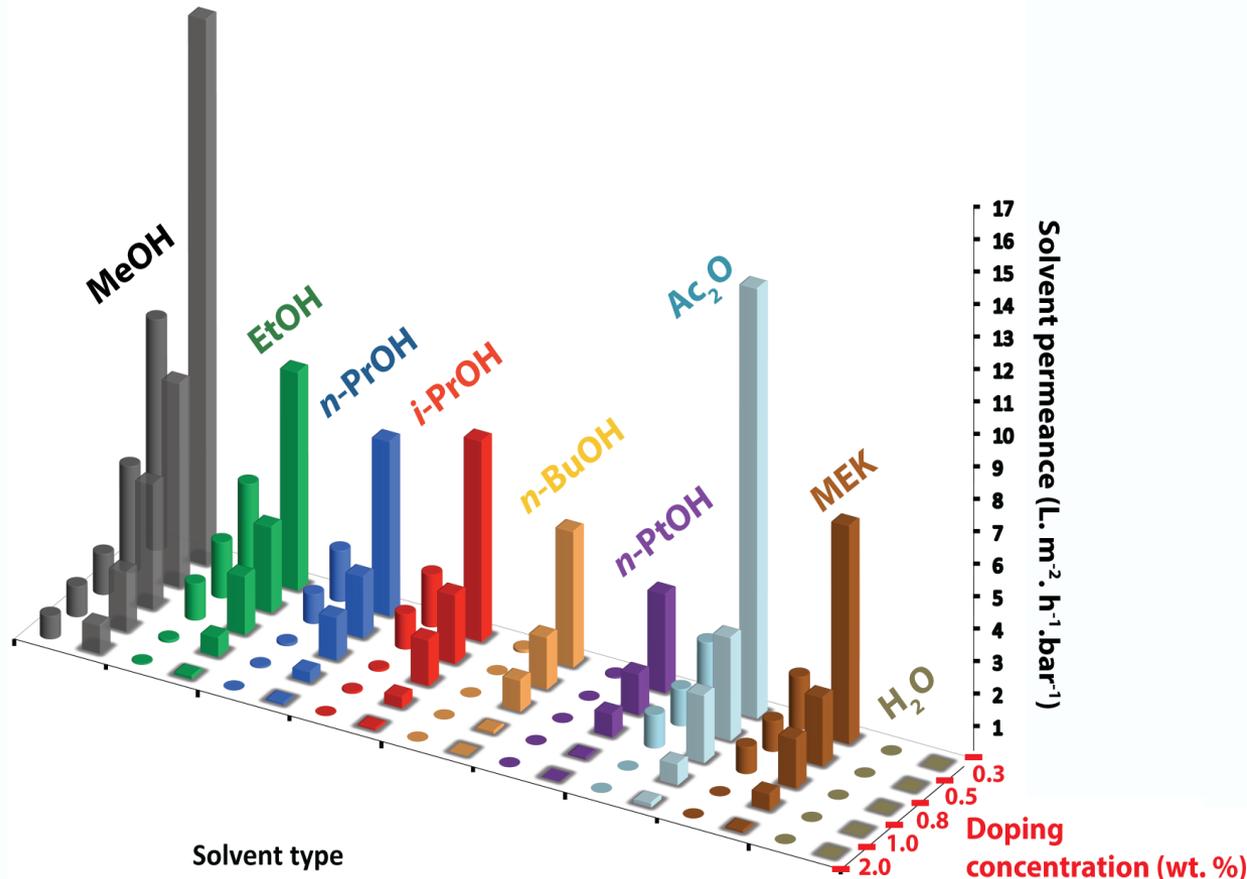
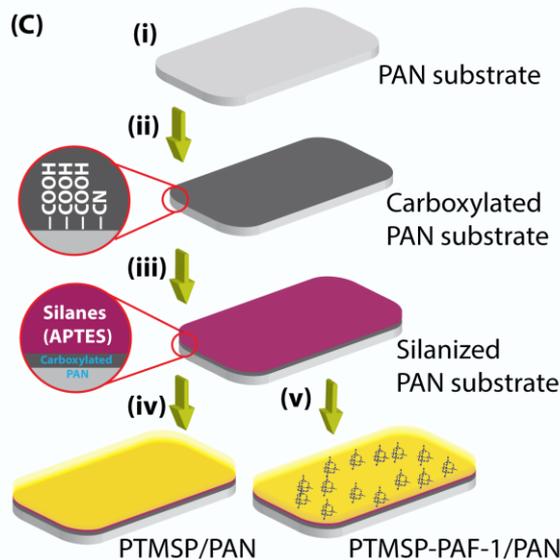
(A)



(B)



(C)

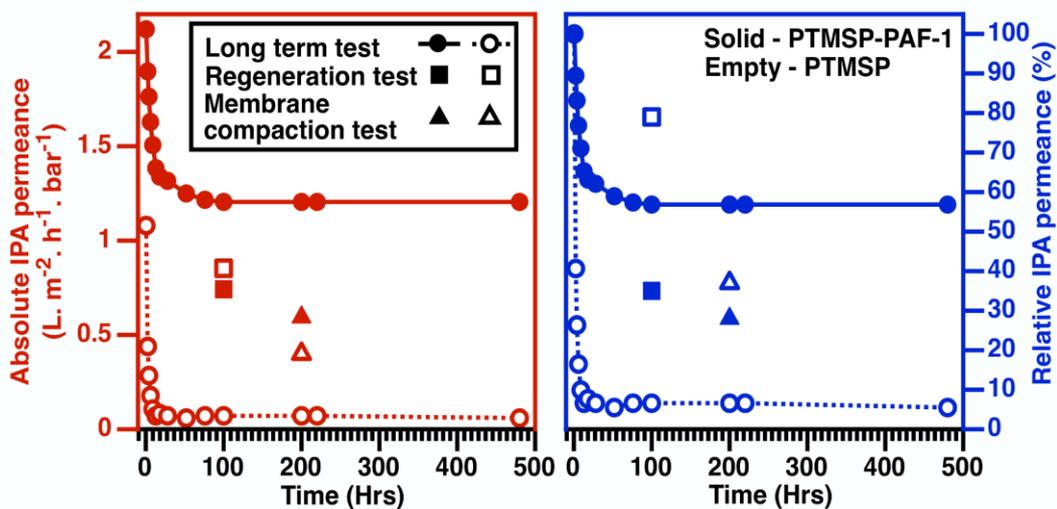


# CSIRO's Membranes

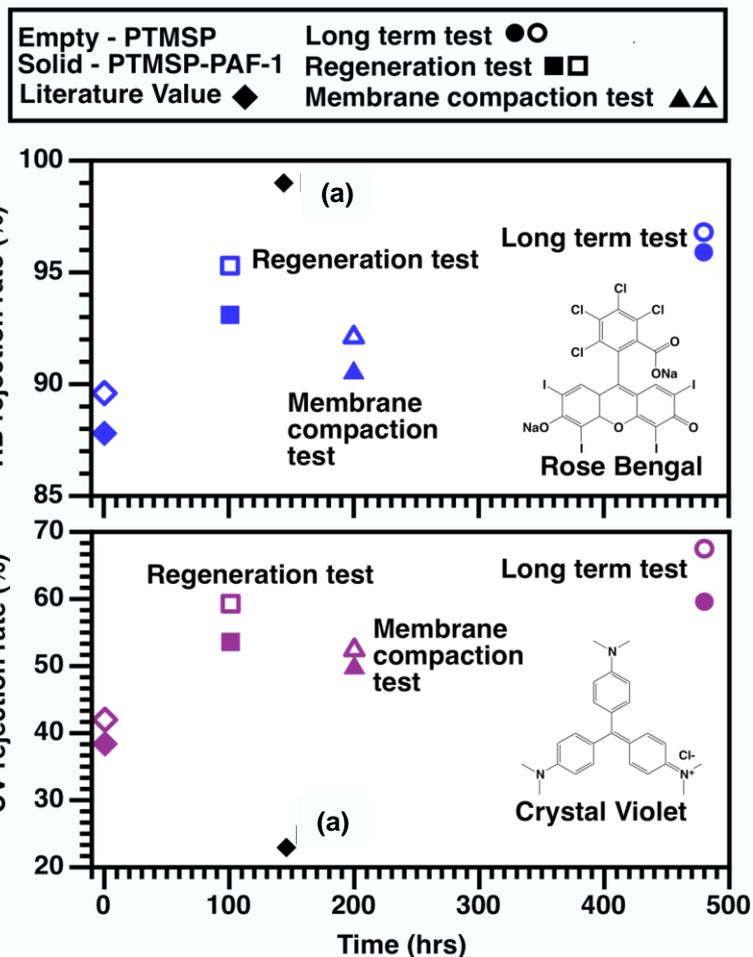
## Slow Aging Membranes – Organic Solvent Nanofiltration

Additive: PAF-1

### Hydrocarbon-Dye Separations

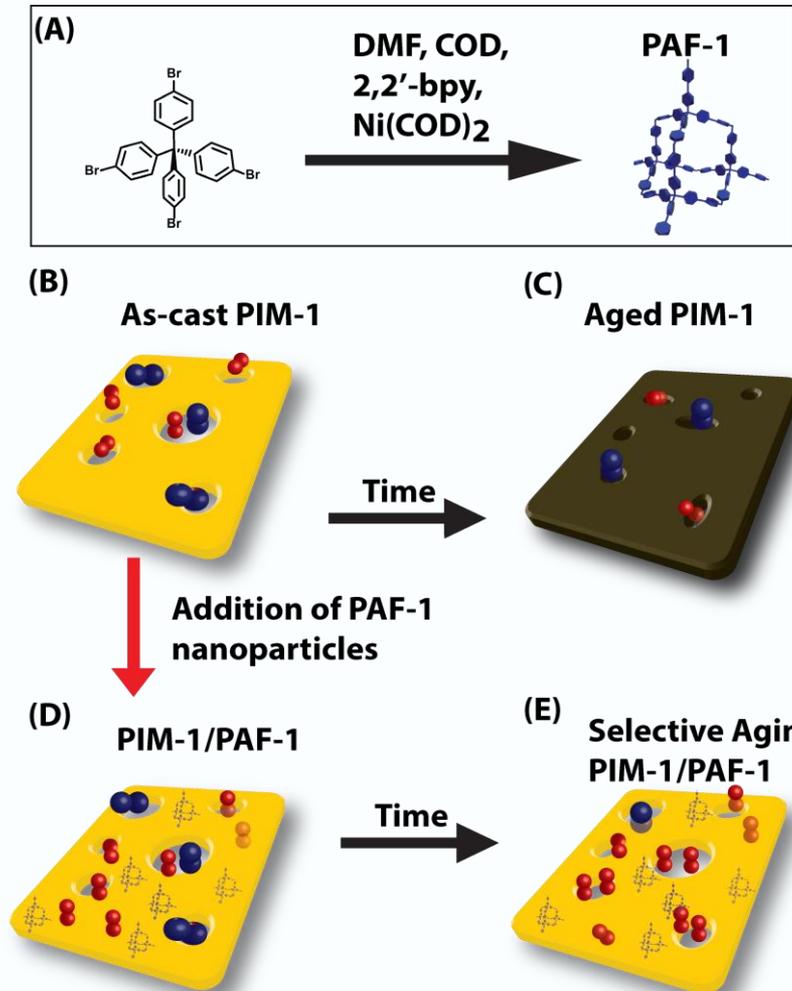


(a) Li, X.; De Feyter, S.; Chen, D.; Aldea, S.; Vandezande, P.; Du Prez, F.; Vankelecom, I. F. J. *Chem. Mater.* **2008**, 20, 3876 – 3883.



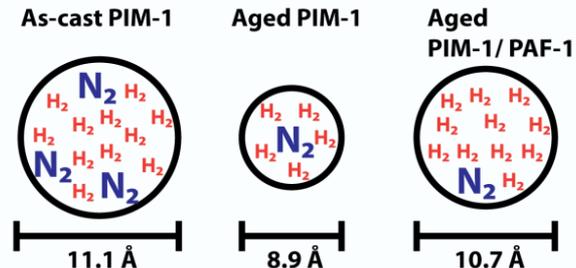
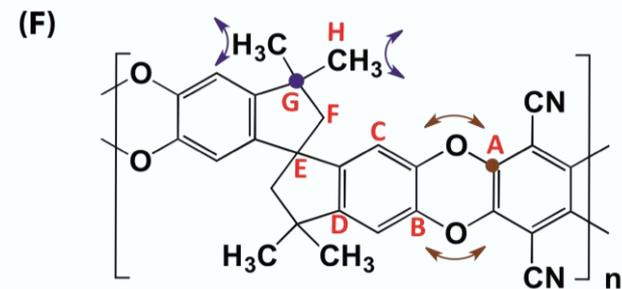
# CSIRO's Membranes

## Selective Aging Membranes – Hydrogen Purification



Additive: PAF-1

Polymer: PIM-1

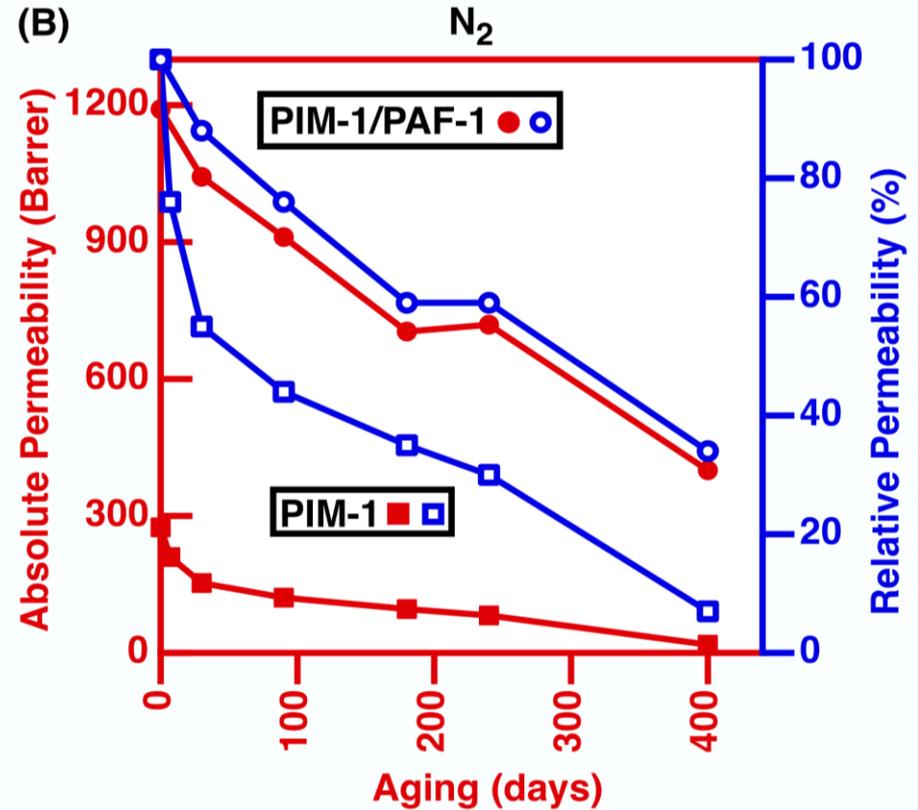
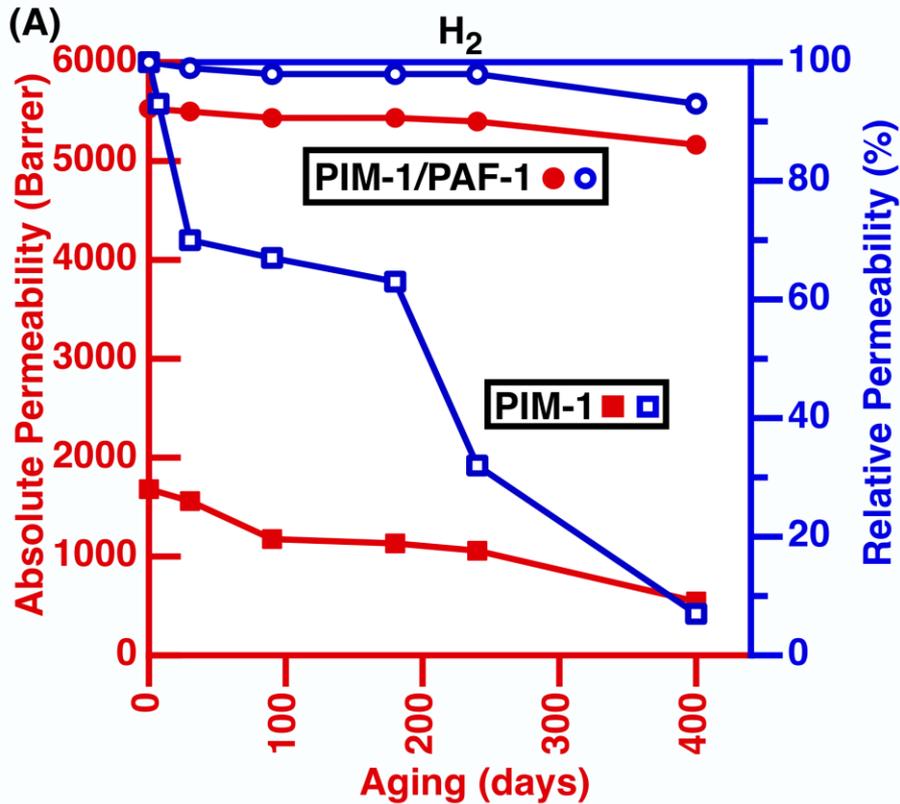
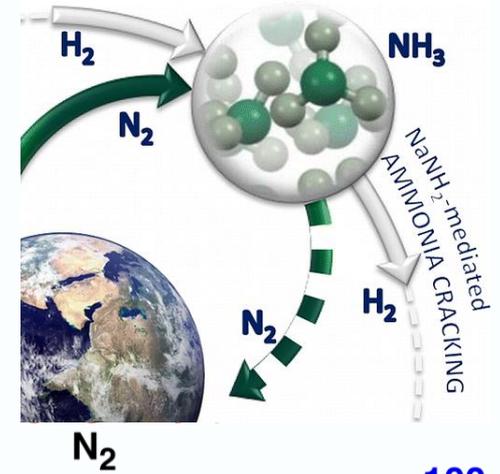


C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

# CSIRO's Membranes

## Selective Aging Membranes – Hydrogen Purification

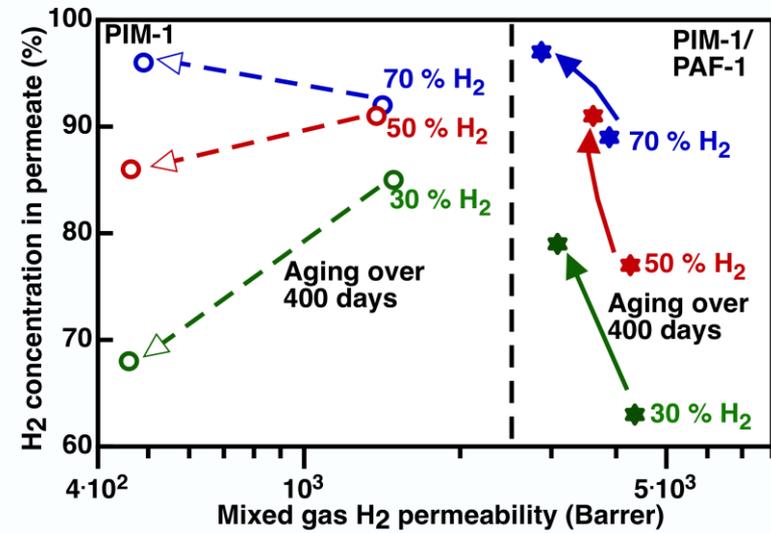
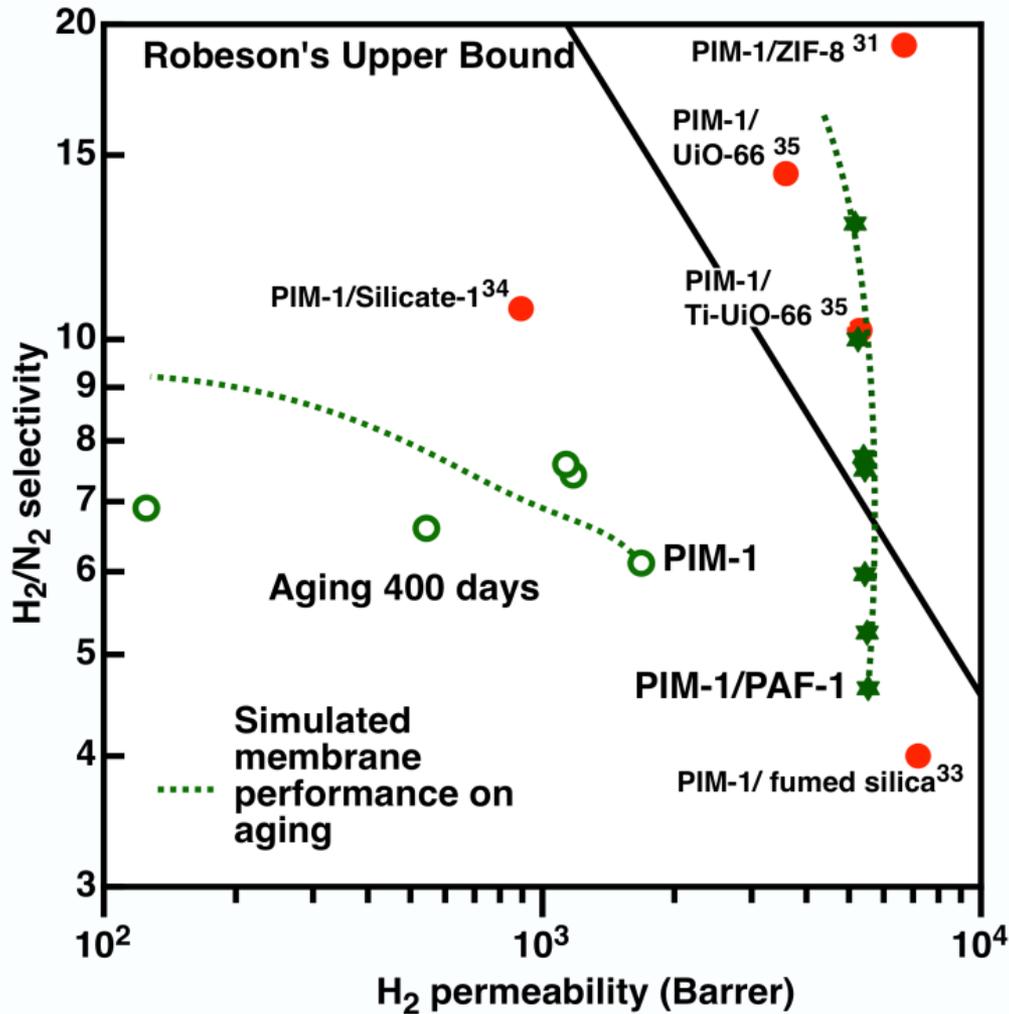
David et al.; *J. Am. Chem. Soc.* 2014, 136, 13082.



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

# CSIRO's Membranes

## Selective Aging Membranes – Hydrogen Purification



**Simulated membrane performance on aging**

- PIM-1
- ★ PIM-1/PAF-1



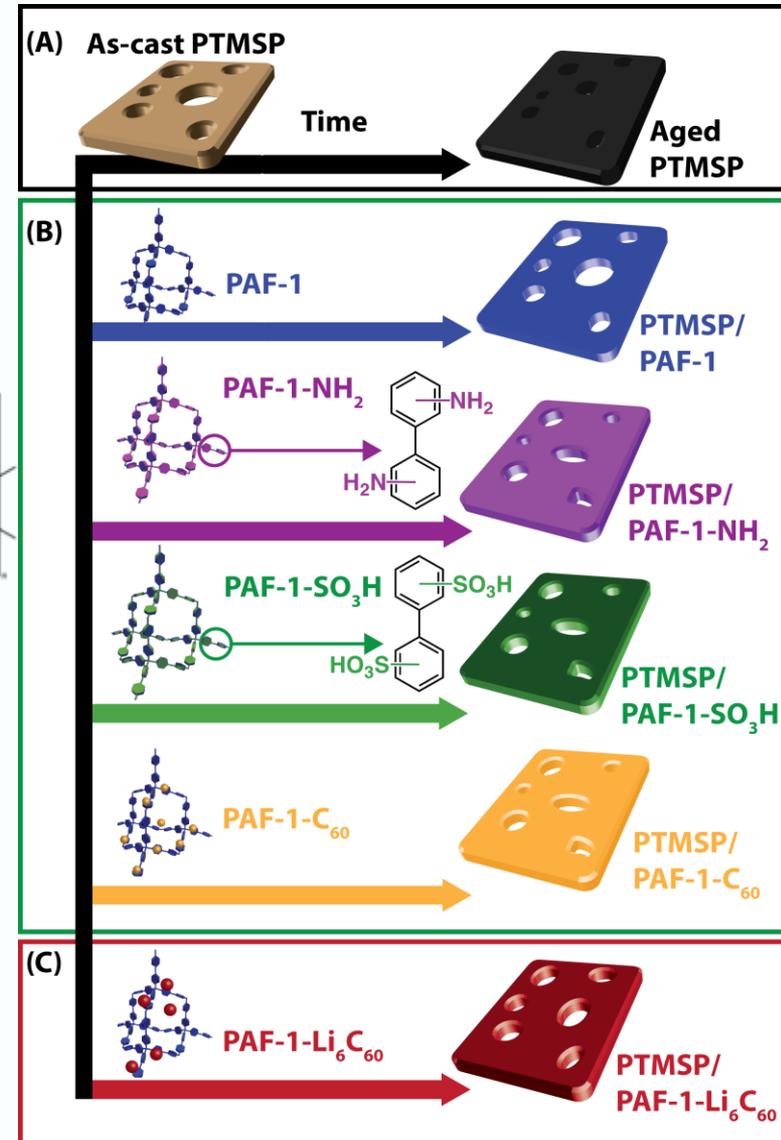
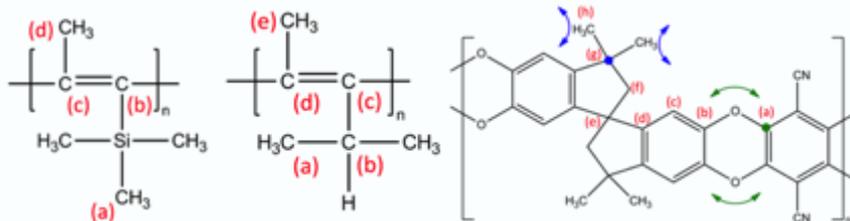
C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

# CSIRO's Membranes

## Anti-Aging Membranes – Carbon Capture

Additive: PAF-1

Polymer: PTMSP, PMP, PIM-1



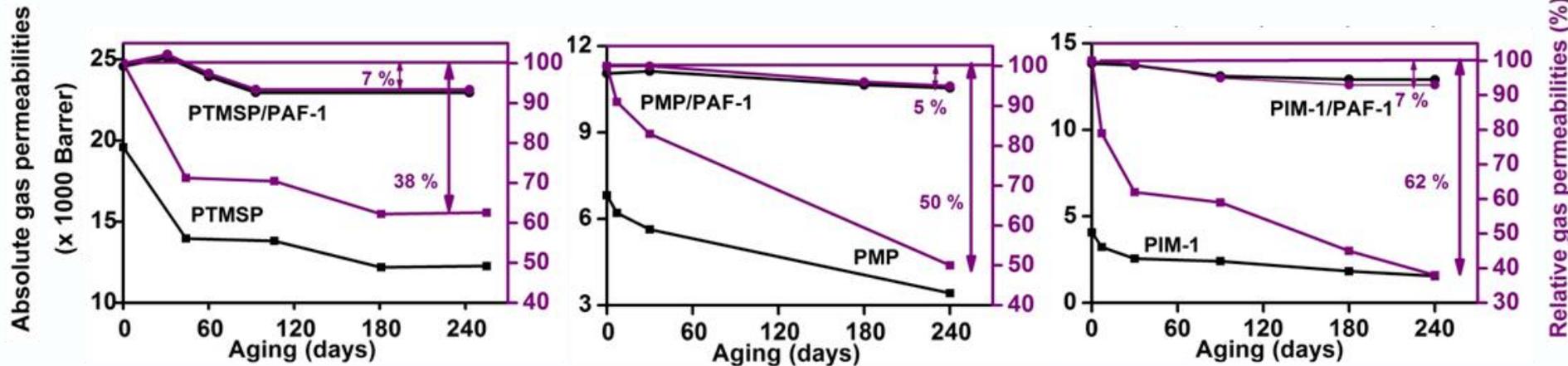
C. H. Lau, M. R. Hill *et al.* *Angew. Chem.* 2014, 53, 5322 - 5326

# CSIRO's Membranes

## Anti-Aging Membranes – Carbon Capture

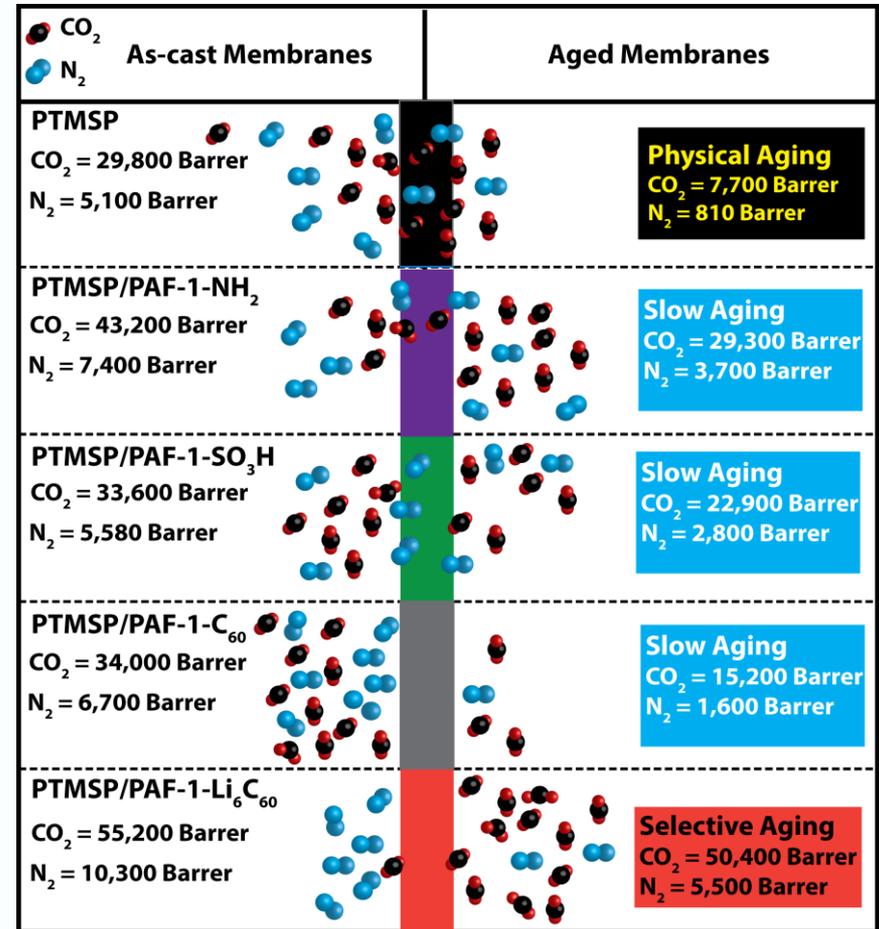
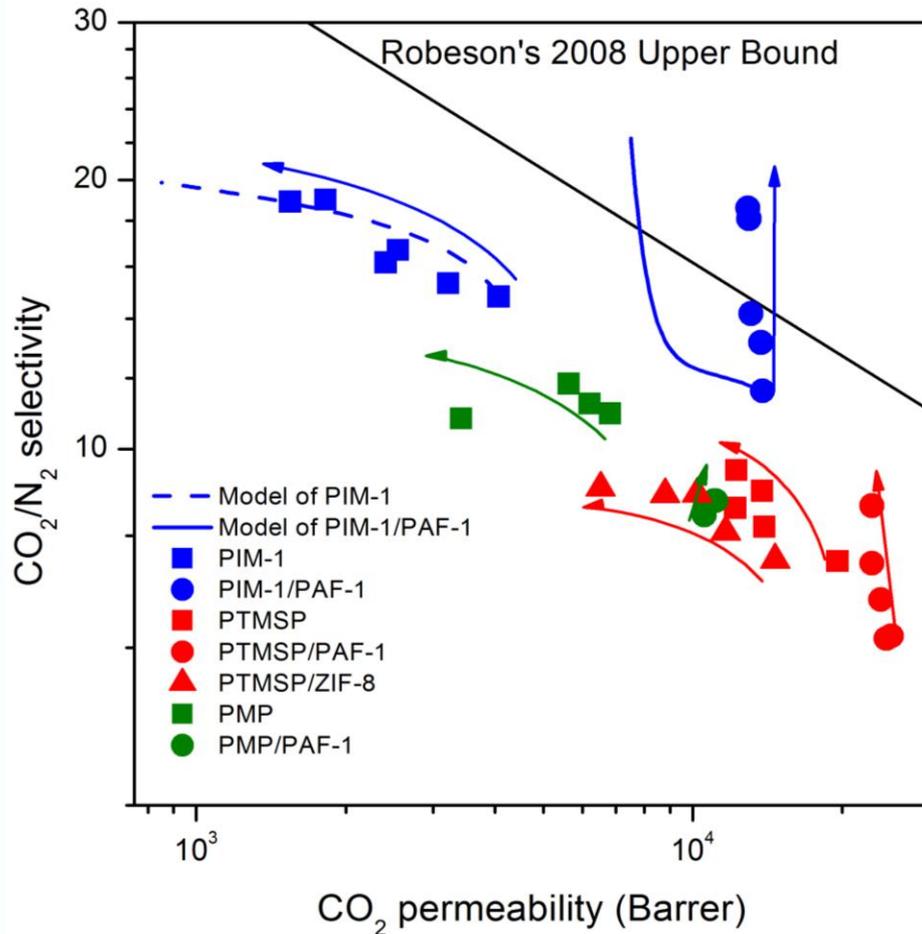
Additive: PAF-1

Polymer: PTMSP, PMP, PIM-1



# CSIRO's Membranes

## Anti-Aging Membranes – Carbon Capture



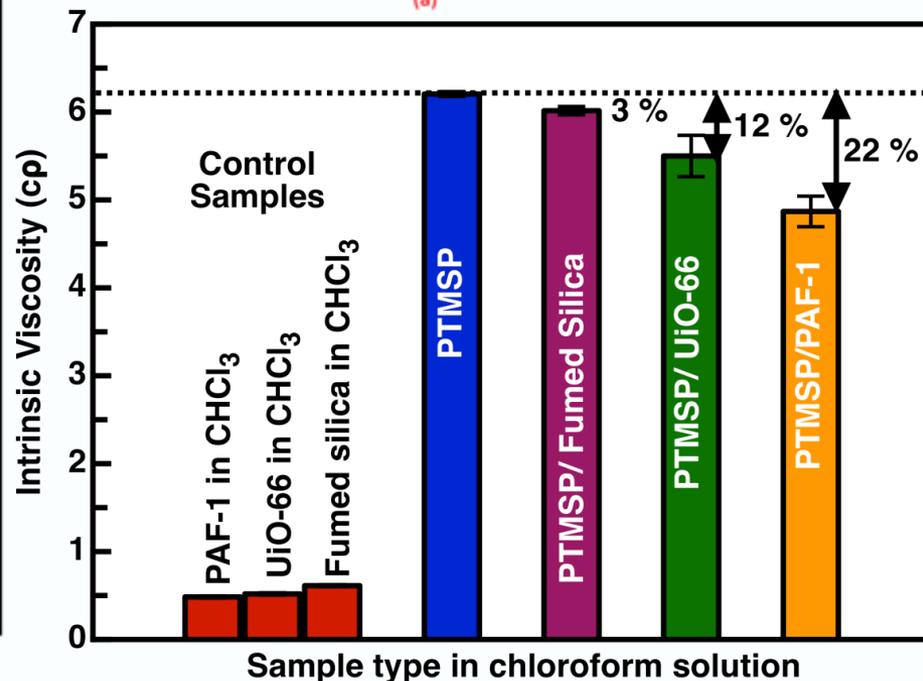
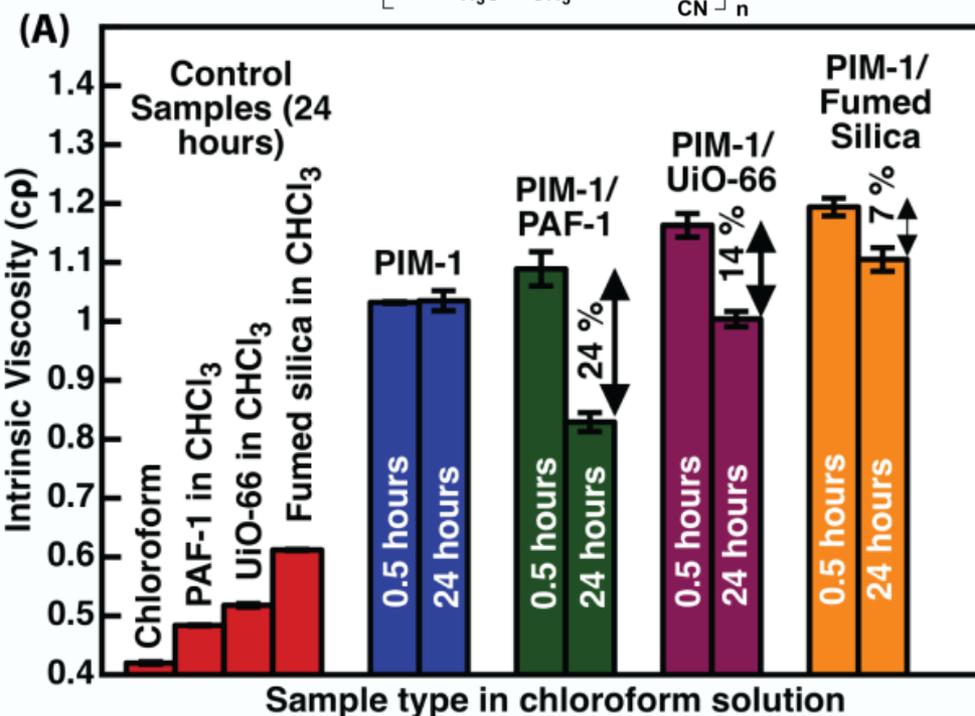
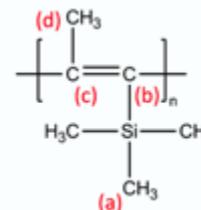
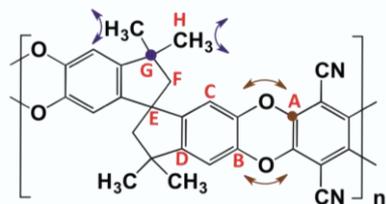
C. H. Lau, M. R. Hill *et al.* *Angew. Chem.* 2014, 53, 5322 - 5326



# CSIRO's Membranes

## How does it work?

### 1. Intimate interaction between porous additives and polymers

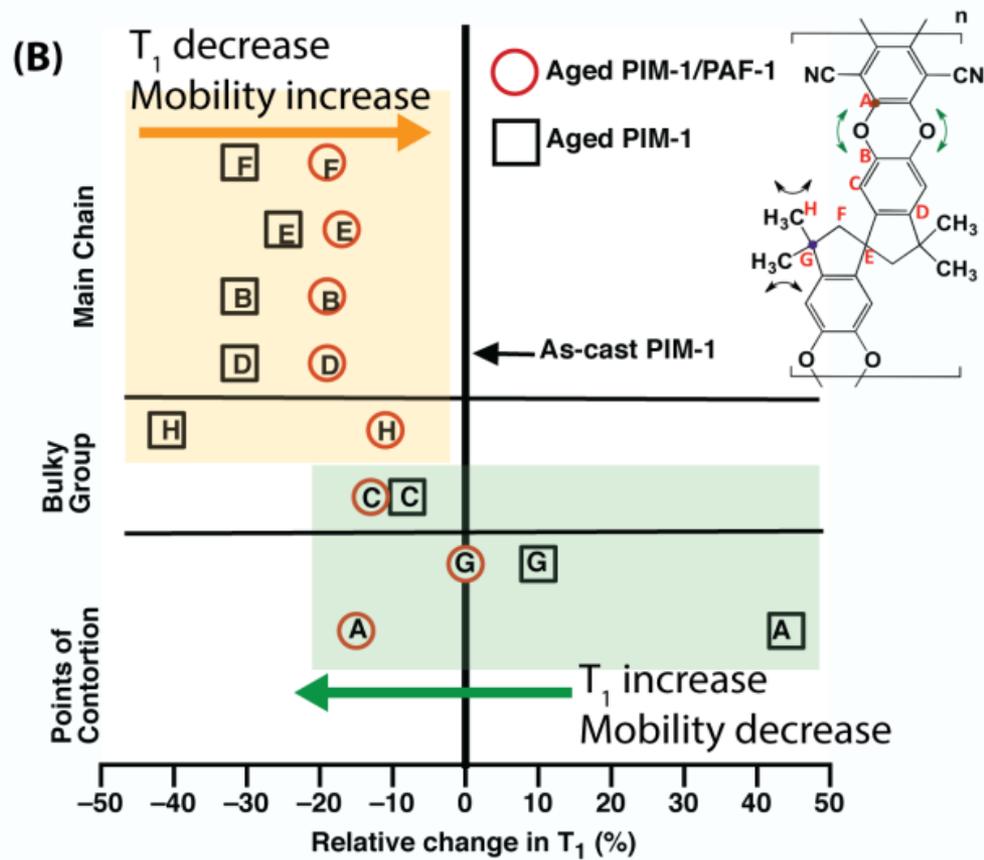


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# CSIRO's Membranes

## How does it work?

### 2. Freezing mobility in carbon atoms of bulky groups in polymer

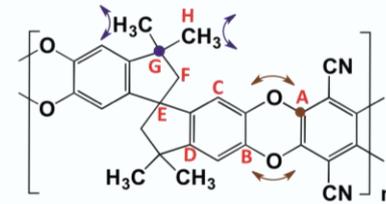
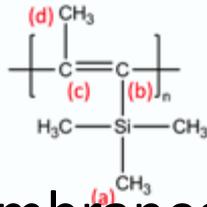


C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

# CSIRO's Membranes

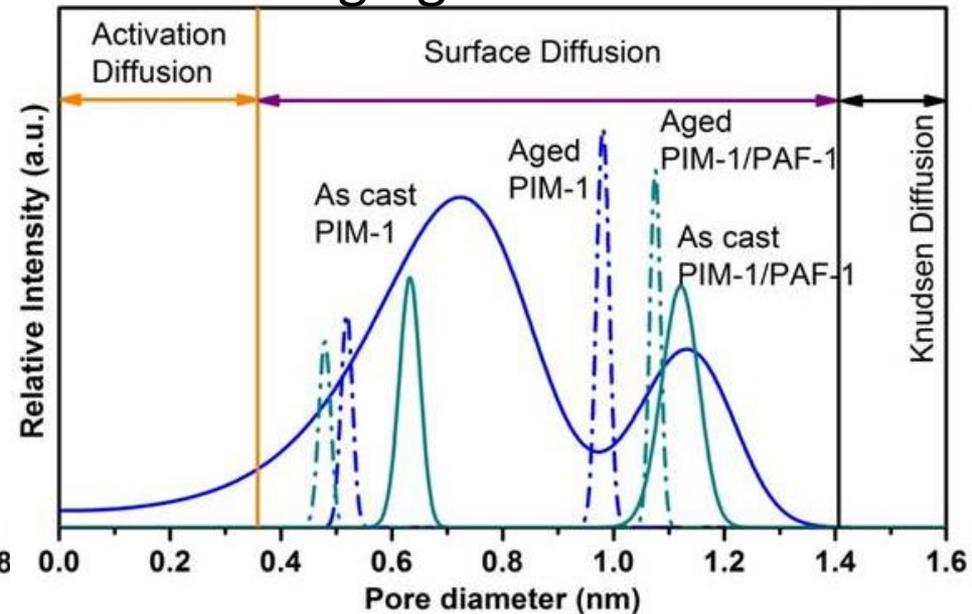
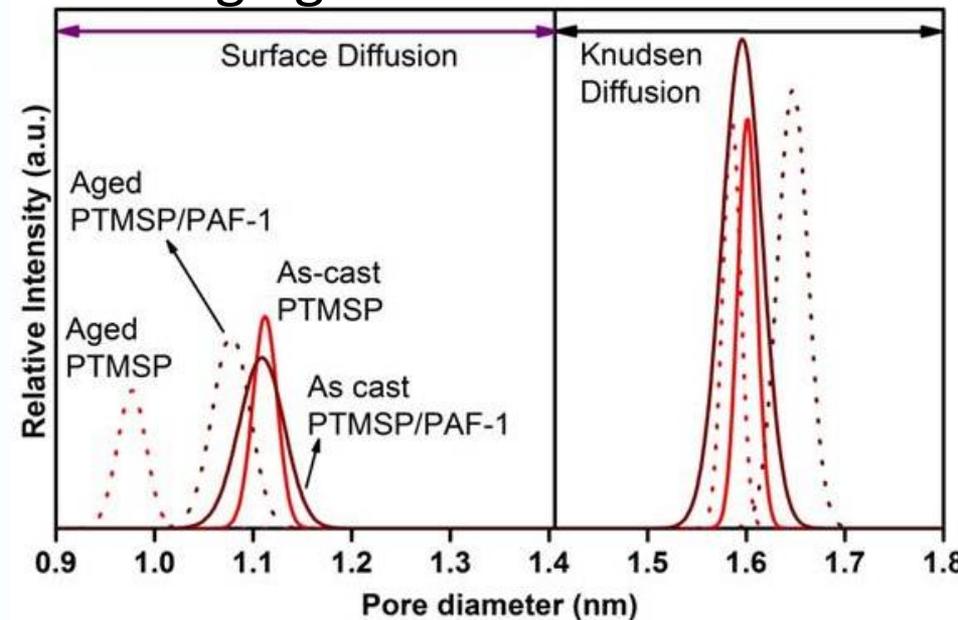
## How does it work?

### 3. Unchanged pore sizes over time



#### Anti-aging membranes

#### Selective-aging membranes



C. H. Lau, M. R. Hill *et al.* *Angew. Chem.* 2014, 53, 5322 - 5326

# Scale-Up Production

## Membranes & MOFs

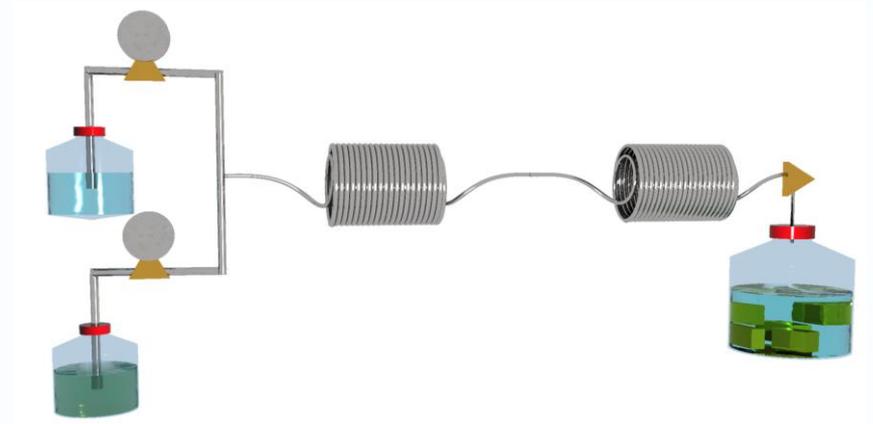
### Membranes

Hollow Fiber Spinning Line



### MOFs

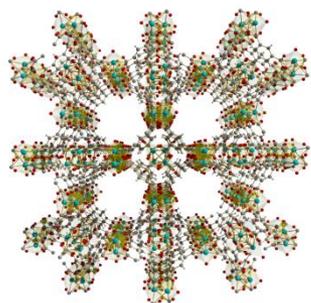
Flow Chemistry



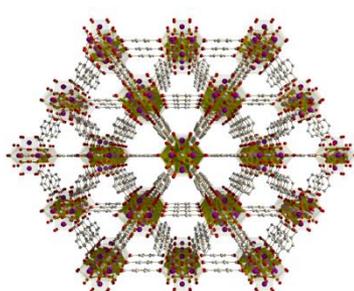
M. Rubio-Martinez, M. P. Batten, A. Polyzos, K.-C. Carey, J. I. Mardel, K.-S. Lim, M. R. Hill, *Sci. Rep.* 2014, 4: 5443

# Scale Up Production MOFs

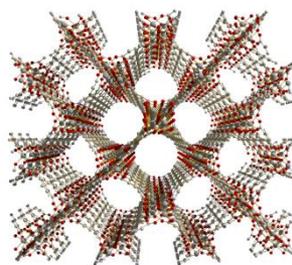
## Proof-of-concept



HKUST-1



UiO-66



NOTT-400

Table 1 | Comparisons of the reaction time between MOFs synthesized by convectional batch and by flow chemistry. BET surface areas, grams of MOF produced per 1 hour using flow chemistry and STY. Full adsorption isotherms are provided in the supplement

MOF	Reaction time	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	$\text{g}\cdot\text{h}^{-1}$	STY ( $\text{Kg m}^{-3} \text{d}^{-1}$ )
HKUST-1 <sup>a</sup>	10 min	1852	1.48	592
HKUST-1 <sup>b</sup>	1.2 min	1805	61.2	4533
HKUST-1 <sup>c</sup>	5 min	1673	2.04	n/a
Basolite C300 <sup>d</sup>	150 min	1820	n/a	225
UiO-66 <sup>a</sup>	10 min	1186	1.68	672
UiO-66 <sup>e</sup>	24 h	1147	n/a	n/a
NOTT-400 <sup>a</sup>	15 min	1078	2.78	741
NOTT-400 <sup>f</sup>	72 h	1350	n/a	n/a

<sup>a</sup>Vapourtec Flow chemistry reactor (Mesoscale).

<sup>b</sup>Salamander flow chemistry results (Macroscale).

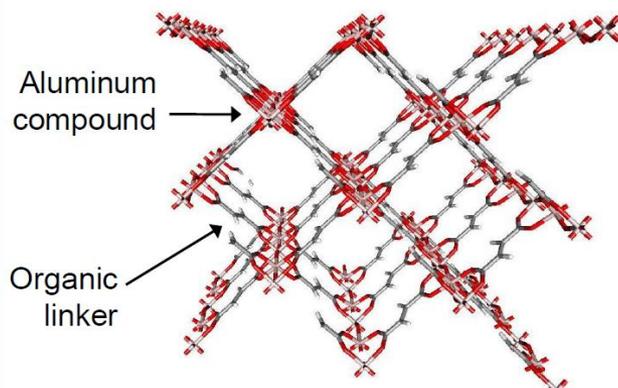
<sup>c</sup>Data from ref. 16.

<sup>d</sup>Data from ref. 24.

<sup>e</sup>Data from ref. 20.

<sup>f</sup>Data from ref. 21. Space-time yields given in this table based on the volume of the reaction mixture in 8 hours. Calculation based on ref. 25.

## Proof-of-scalability

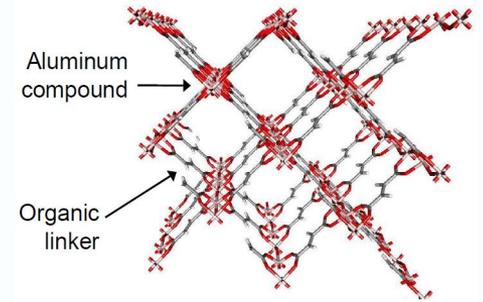


Al fumarate

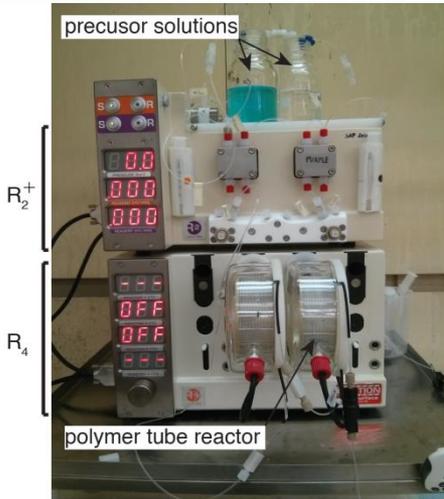
# Scale-Up Production

## MOFs

Al fumarate



### Proof-of-concept: 40 g/h



Reactor: 2,5,10mL  
T: 0-150C  
Diameter tube: 1mm  
Flow rate: 0.10-10 mL/min  
(up to 10 bar)

### Proof-of-scalability: 400 g/h



Reactor: 100mL  
T: 0-150C  
Diameter tube: 6mm  
Flow rate: 1-45mL/min

### Scale-up: 10 kg/h

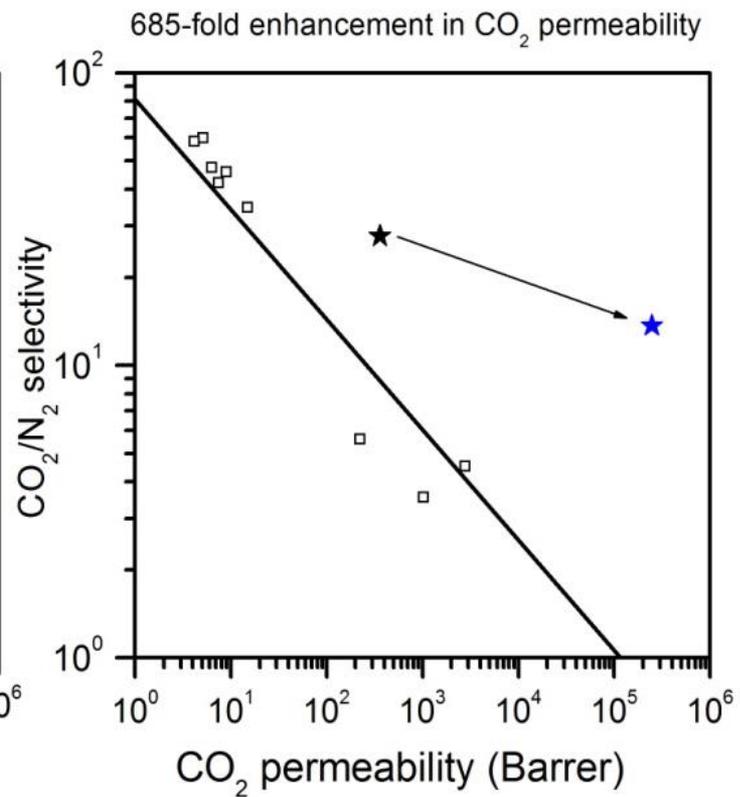
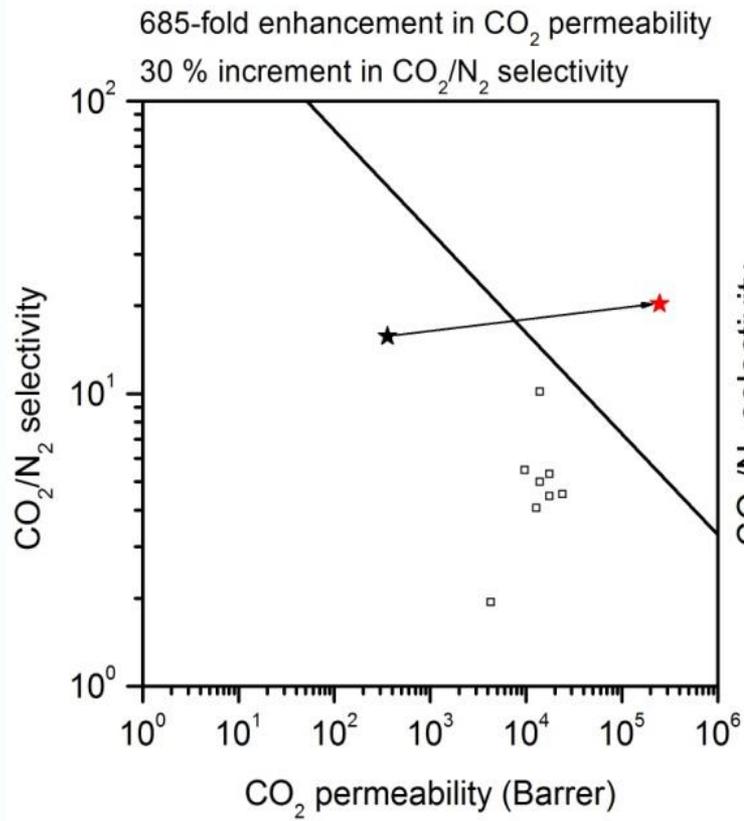


Reactor: 2000mL  
T: 0-150C  
Diameter tube: 12mm  
Flow rate: 1000mL/min

# Conclusions

Capable of scale up productions of porous additives required to:

- 1) **Enhance** gas permeability by up to 300 %
- 2) **Maintain** enhanced gas permeability beyond 1 year
- 3) **Tailor** aging mechanism in membranes according to application
- 4) Fabricate **multi-functional** membranes for carbon capture, solvent purification, and dye sequestration.



# Thank you

**Manufacturing  
Flagship/Adaptive Porous  
Materials Team**

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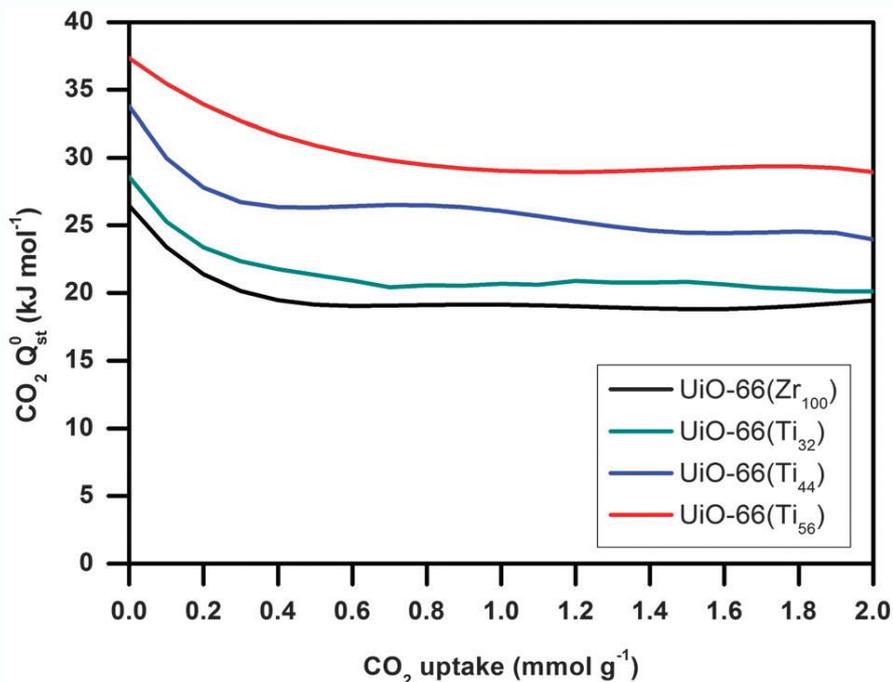


# CSIRO's Membranes

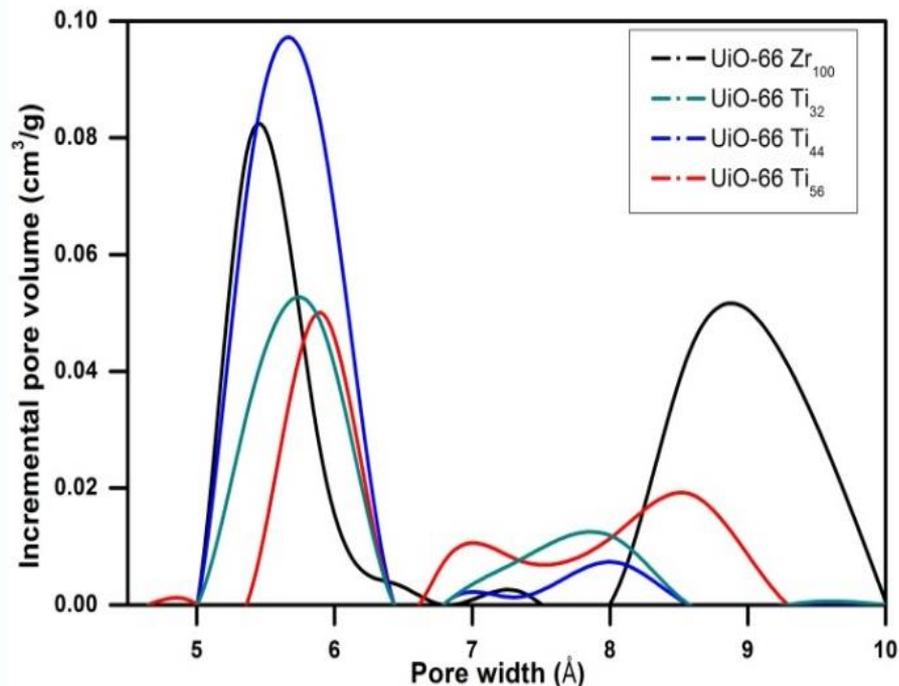
## Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF

### Enthalpy of Adsorption



### Pore Size

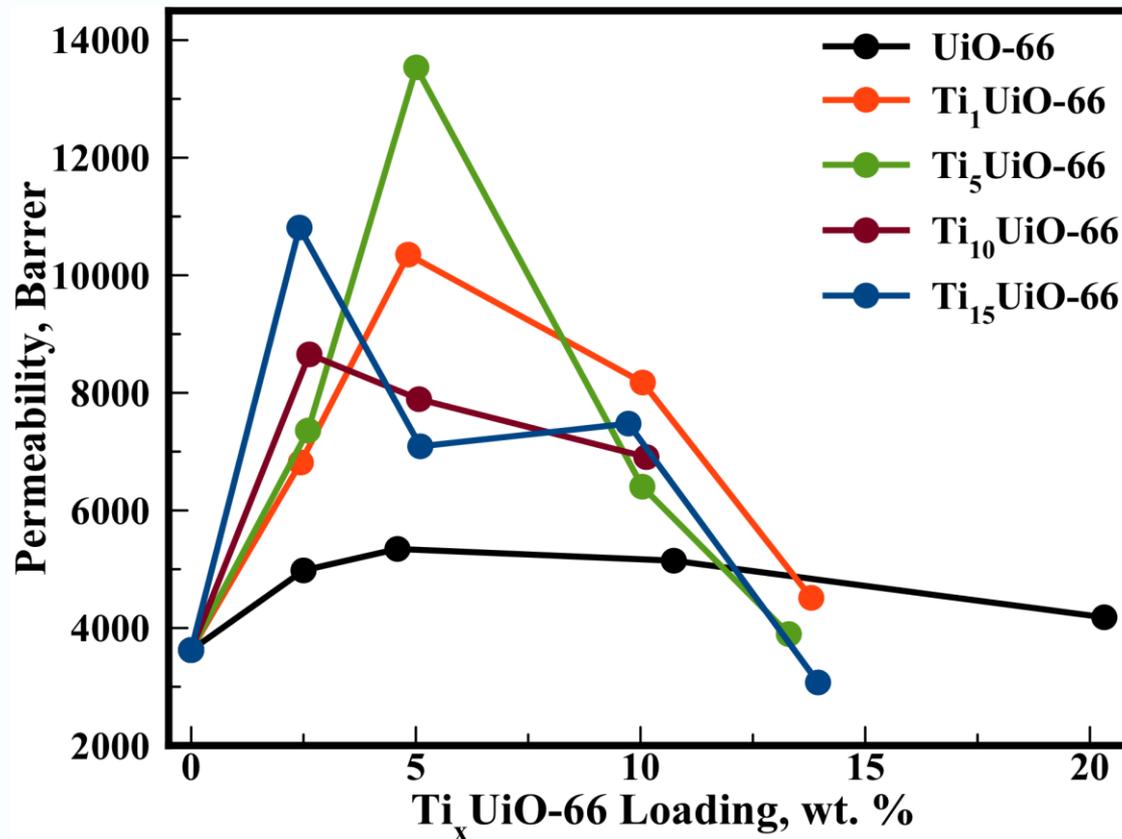


Lau, C. H.; Babarao, R.; Hill, M. R., *Chem. Commun.* 2013, 49 (35), 3634

# CSIRO's Membranes

## Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF



Smith, S. J. D.; Ladewig, B. P.; Hill, A. J.; Lau, C. H.; Hill, M. R., *Sci. Rep.* 2015, 5, 7823