



CCS IN ACTION - CRANFIELD BIENNIAL
21-22 April 2015

Novel membranes for carbon capture



Peter M. Budd

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School of Chemistry
University of Manchester*

Membrane processes

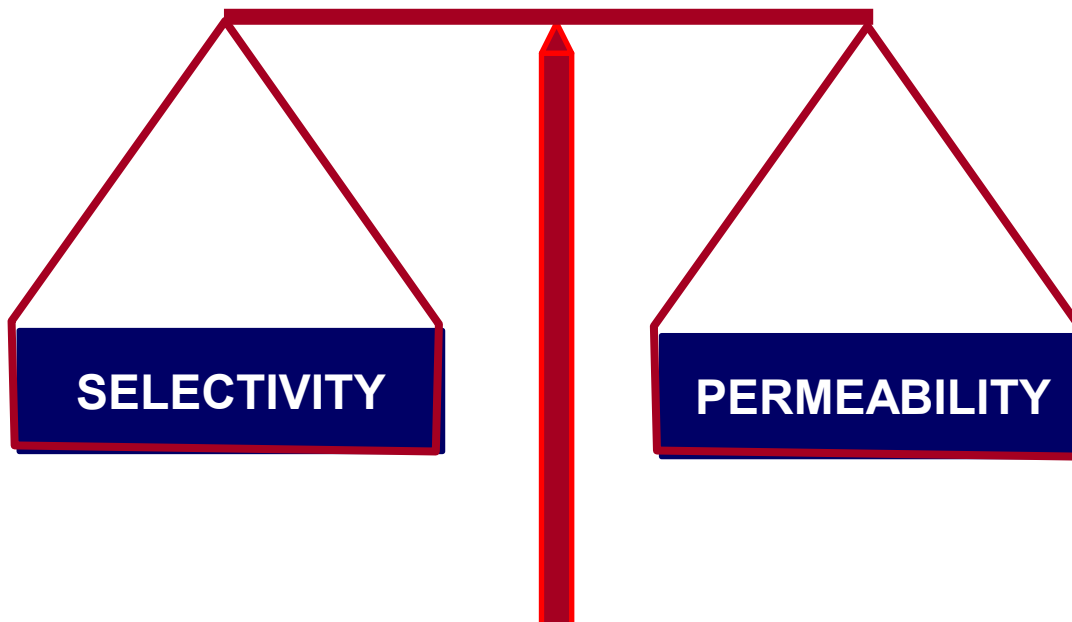
Example	Size/ nm	Membrane process
Suspensions	10,000	Particle filtration
Emulsions	1,000	Microfiltration
Colloids	100	Ultrafiltration
Macromolecules	10	Nanofiltration
Liquid mixtures	1	Pervaporation
Solutions		Reverse osmosis
Vapour/ gas mixtures		Vapour permeation Gas separation

Membrane materials

Requirements

Selectivity

Productivity (permeability, flux)

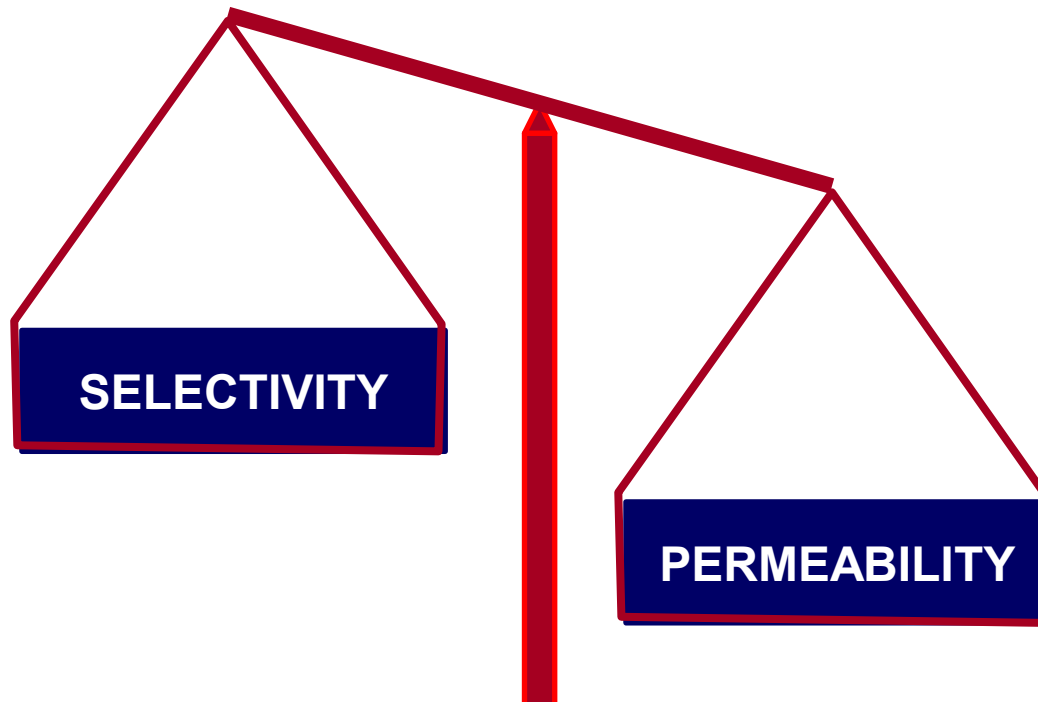


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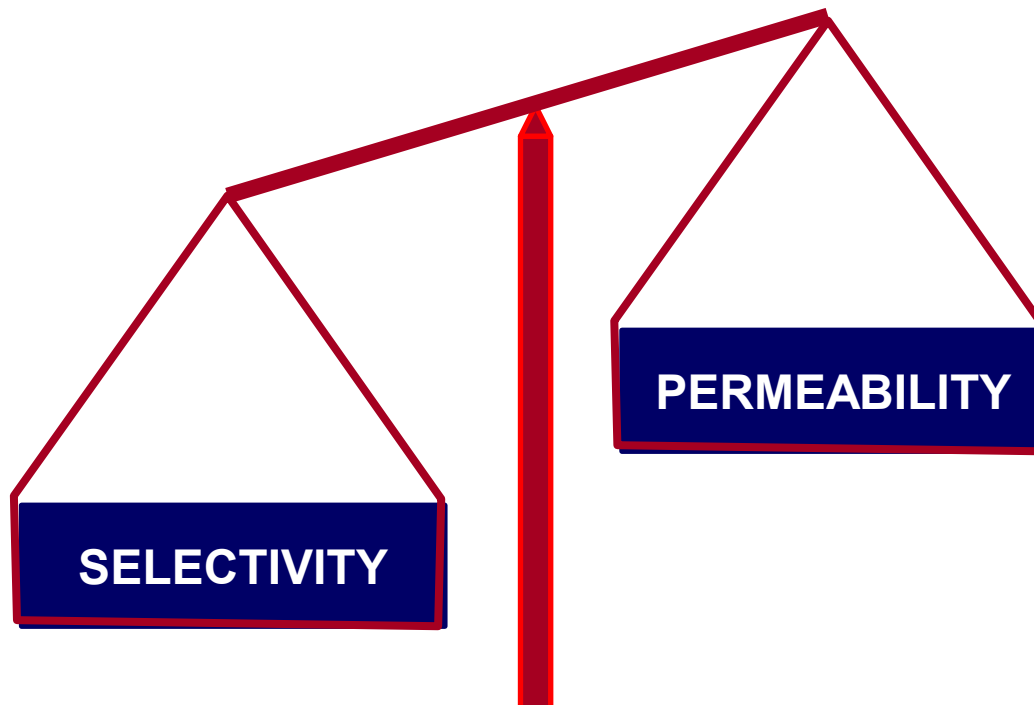


Membrane materials

Requirements

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Productivity (permeability, flux)



Membrane materials

Requirements

Selectivity

Productivity (permeability, flux)

} Trade-off

Membrane materials

Requirements

Selectivity

Productivity (permeability, flux)

Processability

Mechanical properties

Chemical / thermal stability

Long-term performance (resistance to ageing, fouling...)

} Trade-off

Post-combustion CO₂ capture

Low concentration

10–15% CO₂ in N₂

Large volume

600 MW coal-fired power station produces
~10,000 tonnes CO₂ per day

Low pressure

Post-combustion CO₂ capture

Low concentration

10–15% CO₂ in N₂

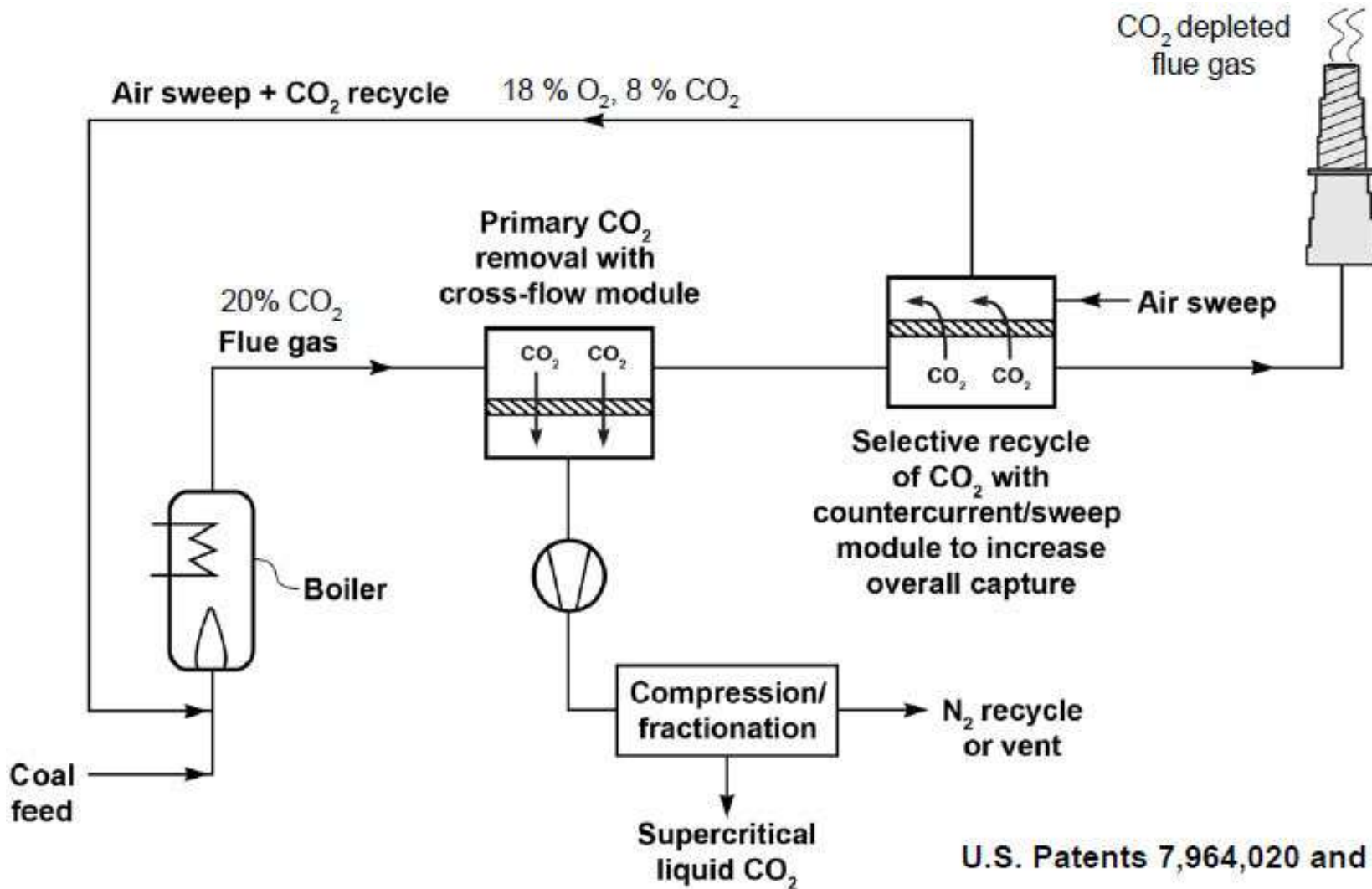
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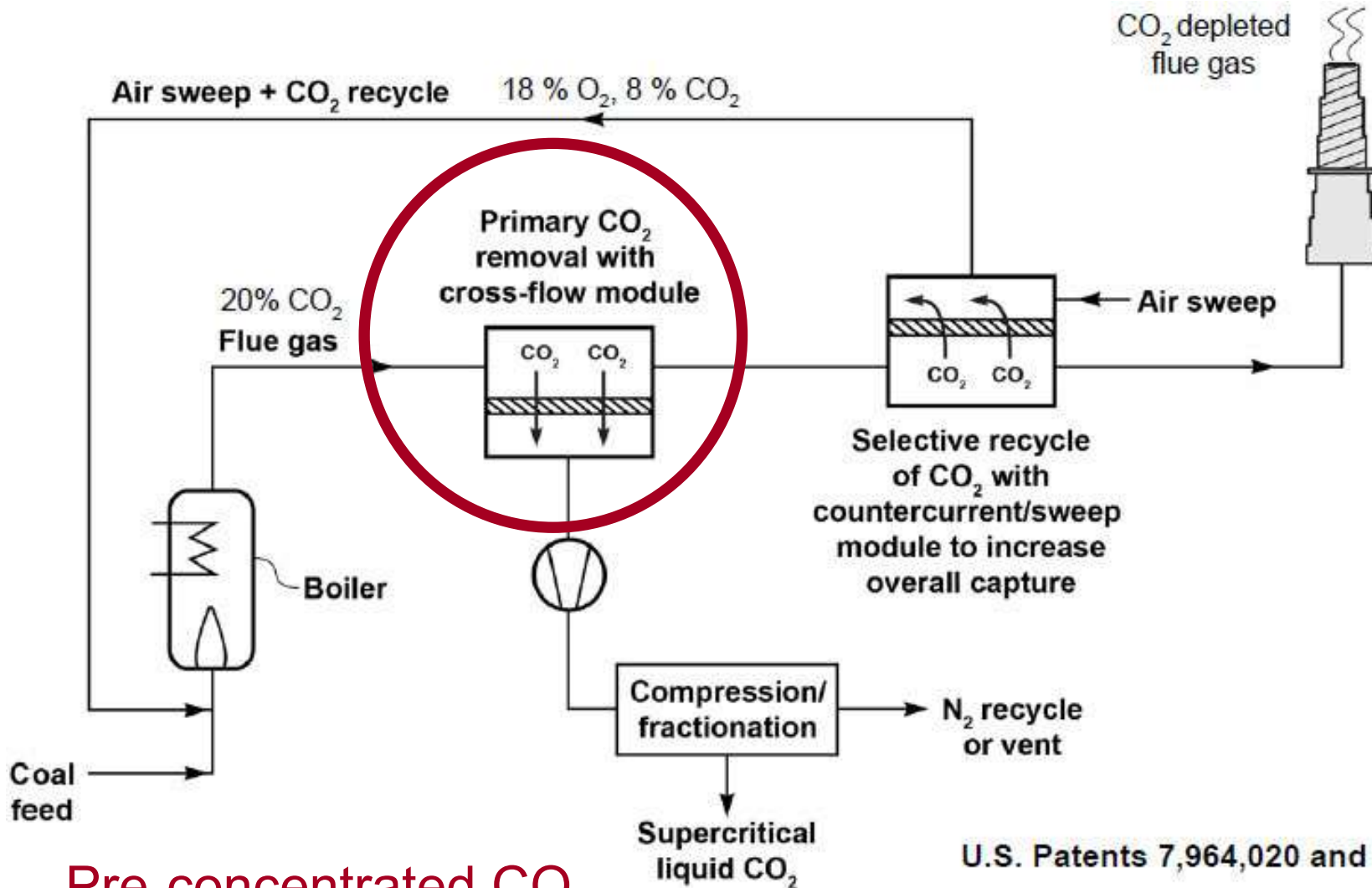
**Cannot get high purity and high recovery
using a single-stage membrane process**

MTR CO₂ capture process



U.S. Patents 7,964,020 and 8,025,715

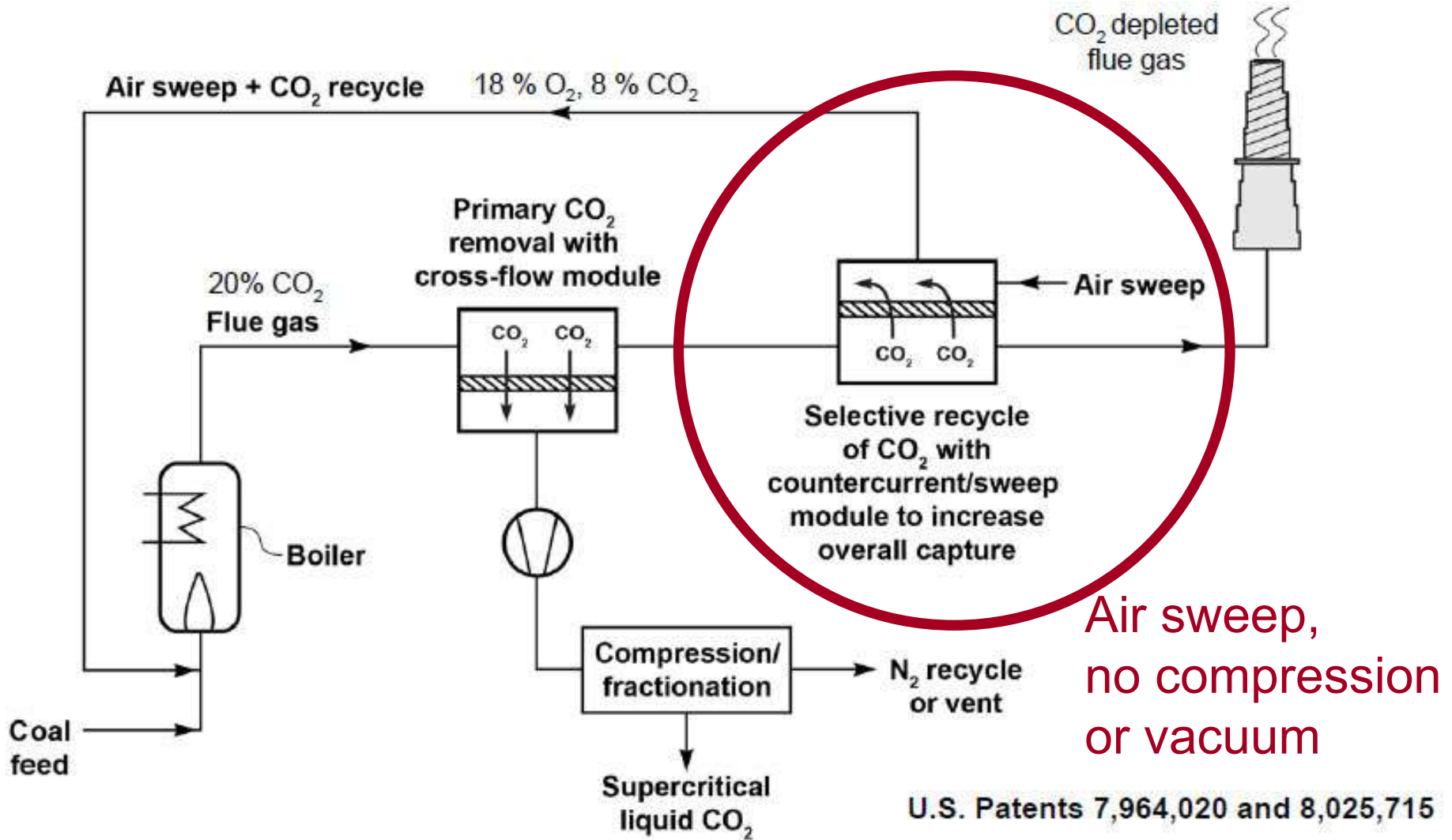
MTR CO₂ capture process



U.S. Patents 7,964,020 and 8,025,715

Pre-concentrated CO₂,
reduces membrane area and power

MTR CO₂ capture process

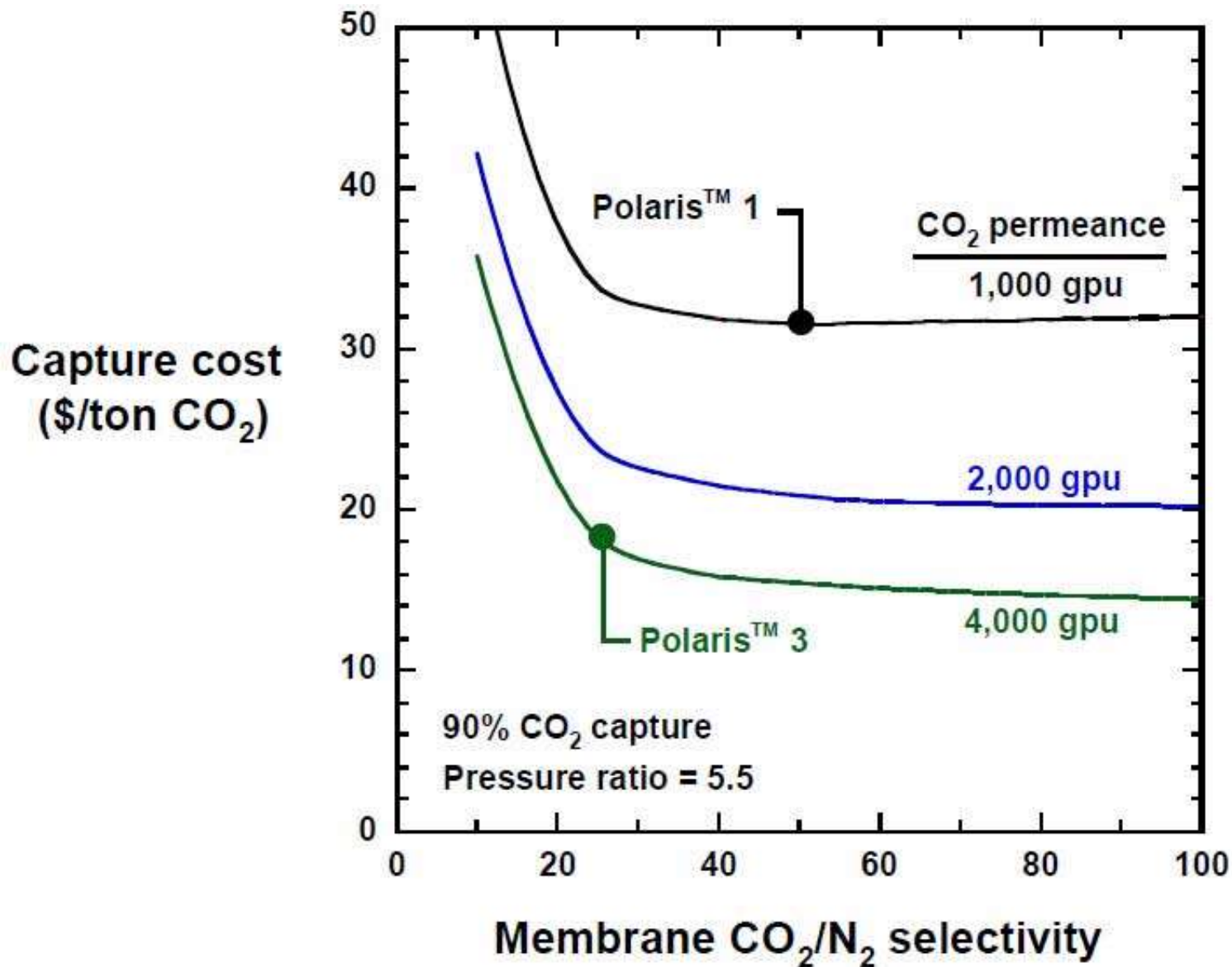


Air sweep,
no compression
or vacuum

U.S. Patents 7,964,020 and 8,025,715



Test system at
National Carbon Capture Centre (NCCC)



High CO₂ permeance is necessary to reduce cost

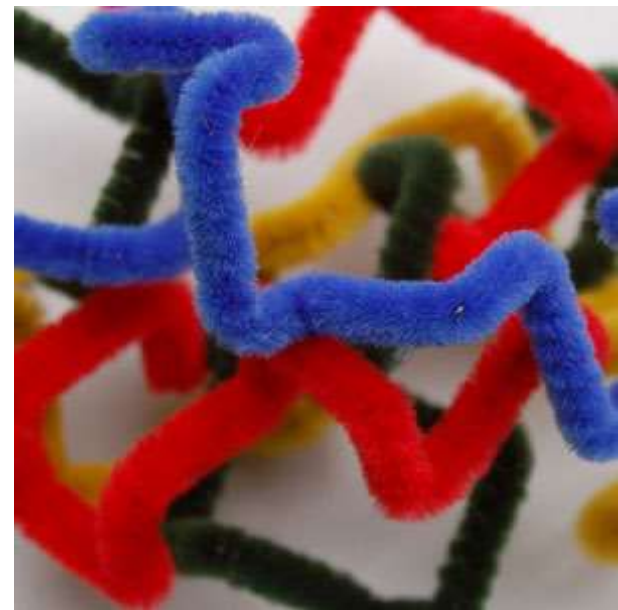
Polymers of Intrinsic Microporosity



Flexible polymer chains can rearrange

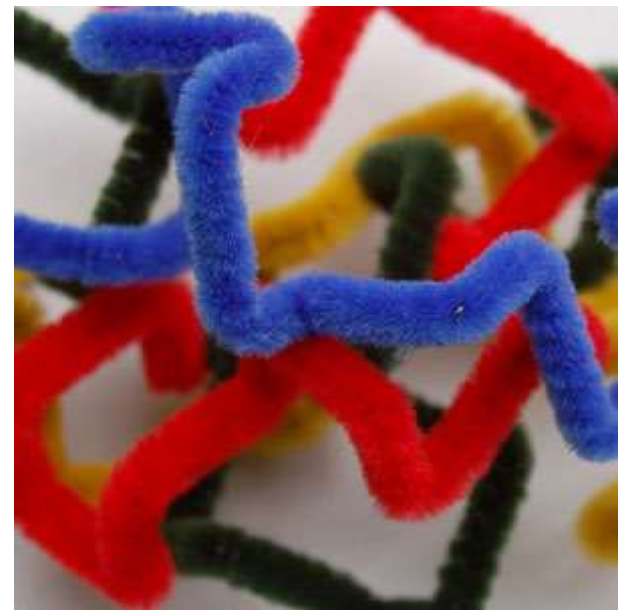


Rigid polymer chains pack together



Rigid, contorted polymer chains cannot fill space

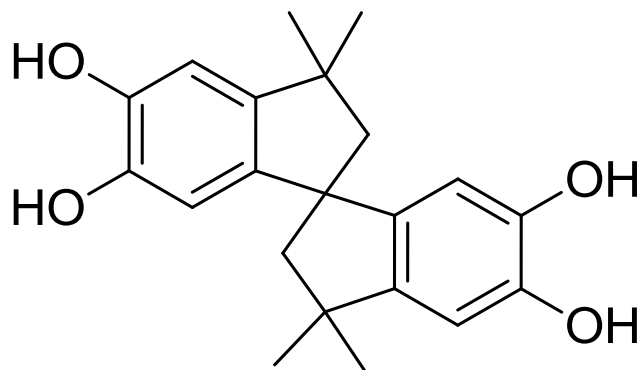
Polymers of Intrinsic Microporosity



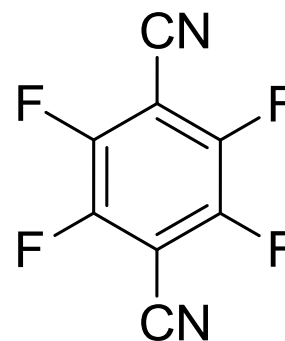
Molecular
sieve

PIM-1

5,5',6,6'-tetrahydroxy-
3,3,3',3'-tetramethyl-
1,1'-spirobisindane

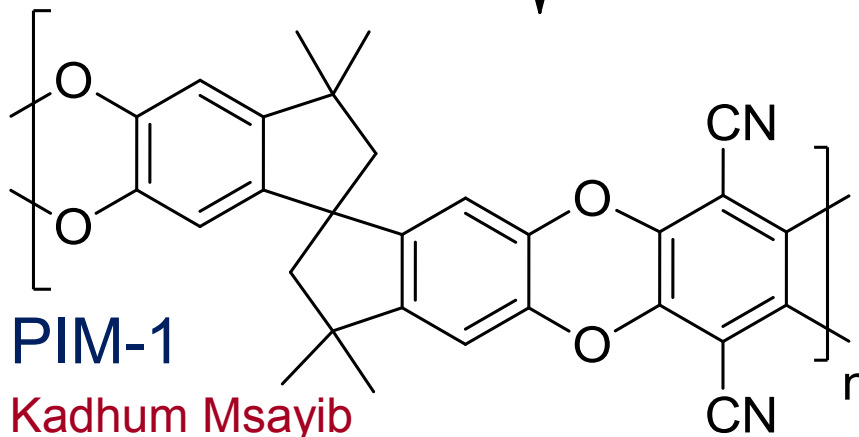
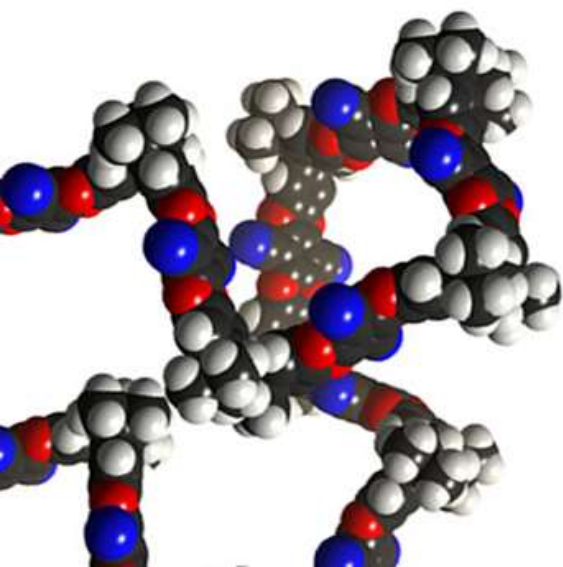


tetrafluoro-
terephthalonitrile



K_2CO_3
dimethylformamide
65 °C

+

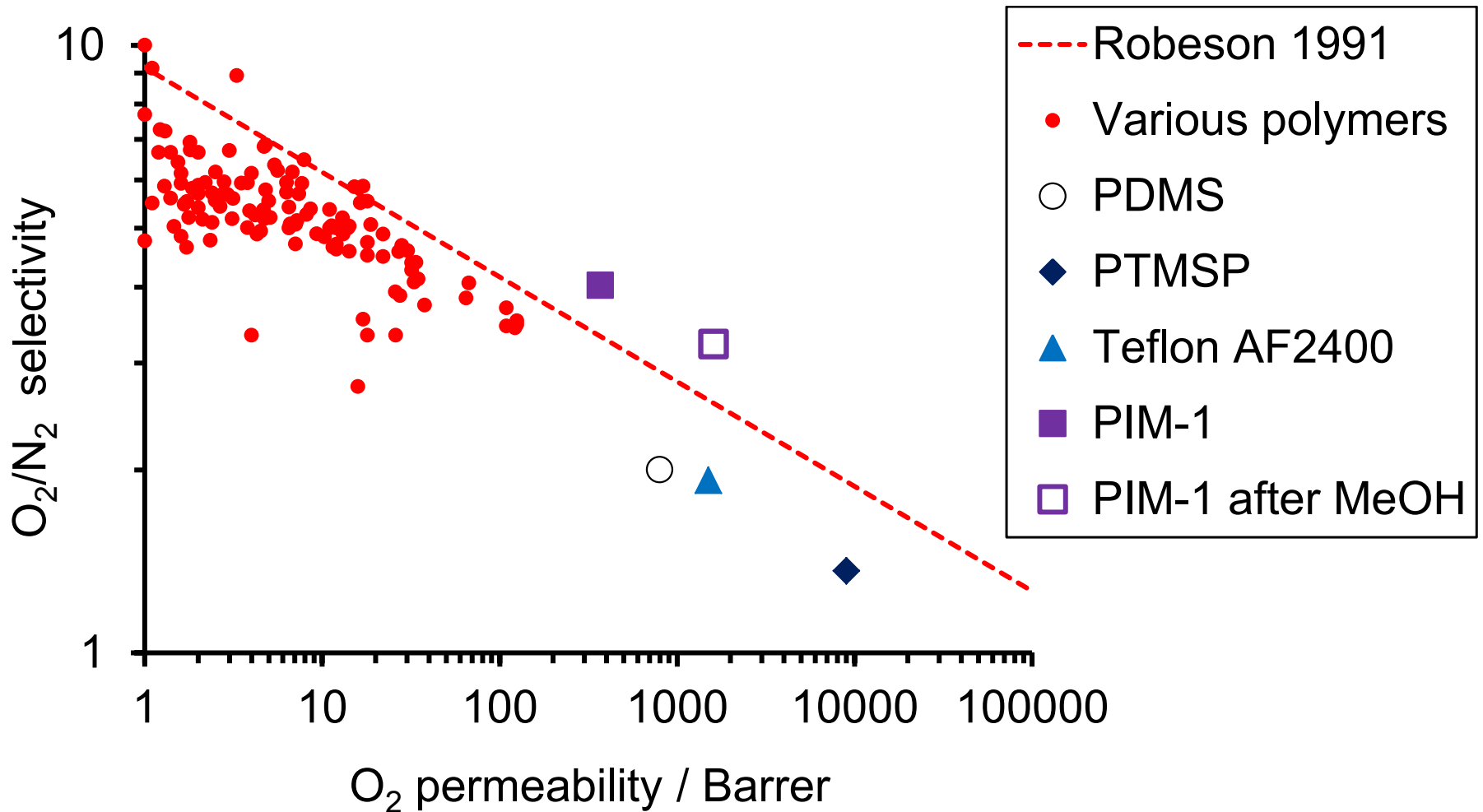


PIM-1

Kadhun Msayib

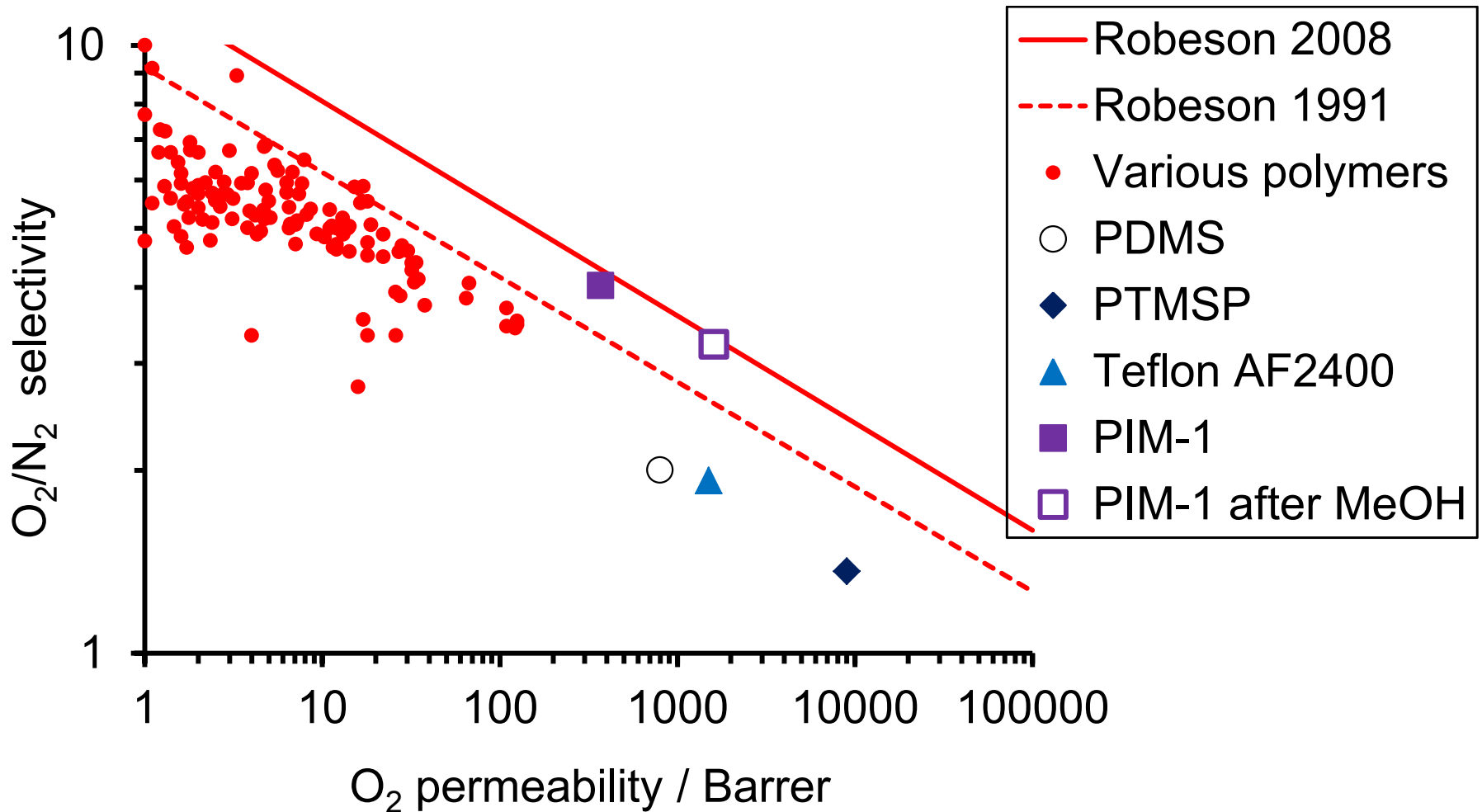
P.M. Budd *et al.*,
Chem. Commun.,
2004, 230.

Gas separation



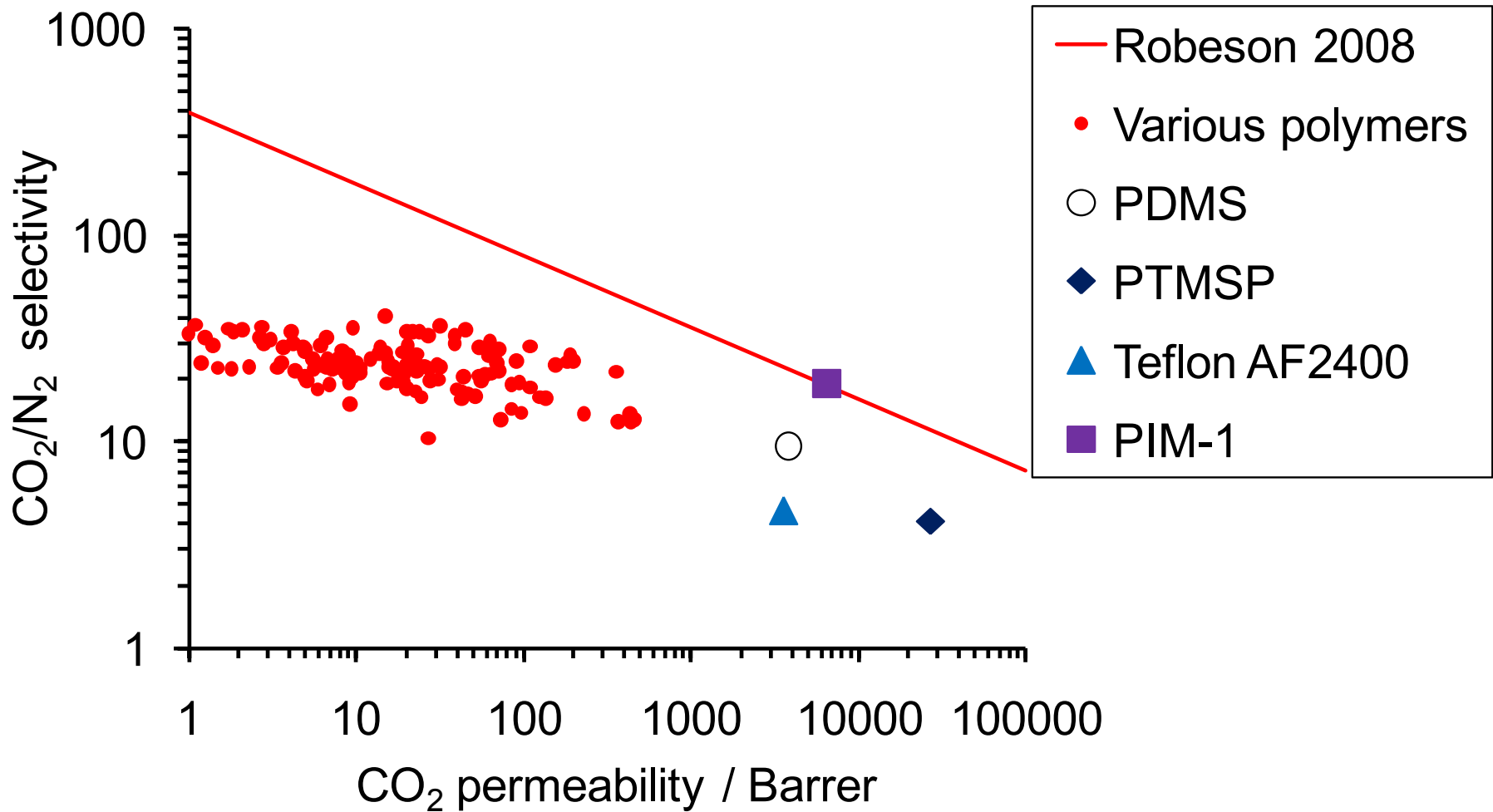
P.M. Budd *et al.*,
J. Membr Sci., 2005, **252**, 263; 2008, **325**, 851.

Gas separation



P.M. Budd *et al.*,
J. Membr Sci., 2005, **252**, 263; 2008, **325**, 851.

Gas separation



P.M. Budd *et al.*,
J. Membr Sci., 2005, **252**, 263; 2008, **325**, 851.

Mixed matrix membranes

PIM-1

+

Inorganic porous materials

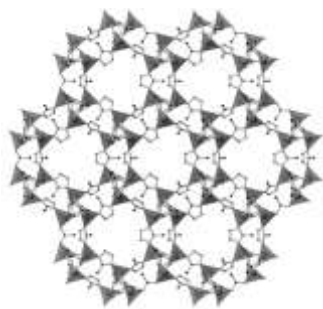


Silicalite

C.R. Mason *et al.*,
Polymer,
2013, **54**, 2222.

Uni. Manchester
Uni. Calabria
ITM-CNR
ICT Prague

Metal-organic frameworks

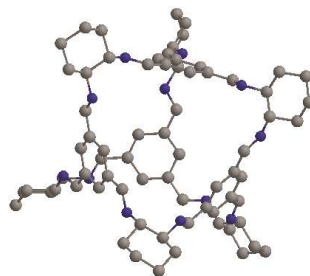


ZIF-8

A.F. Bushell *et al.*,
J. Membr. Sci.,
2013, **427**, 48.

Uni. Manchester
TIPS-RAS
ITM-CNR
ICT Prague

Organic cage molecules

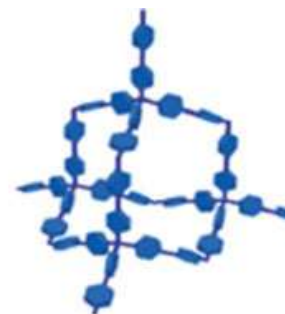


Cage-3

A.F. Bushell *et al.*,
Angew. Chem. Int. Edn.,
2013, **52**, 1253.

Uni. Manchester
Uni. Liverpool
ITM-CNR

Organic polymer frameworks

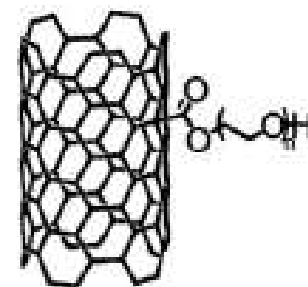


PAF-1

C.H. Lau *et al.*,
Angew. Chem. Int. Edn.,
2014, **53**, 5322.

CSIRO
Uni. Colorado
Monash Uni.

Carbons



Nanotubes

M.M.Khan *et al.*,
J. Membr. Sci.
2013, **436**, 109.

HZG

MANCHESTER
1824

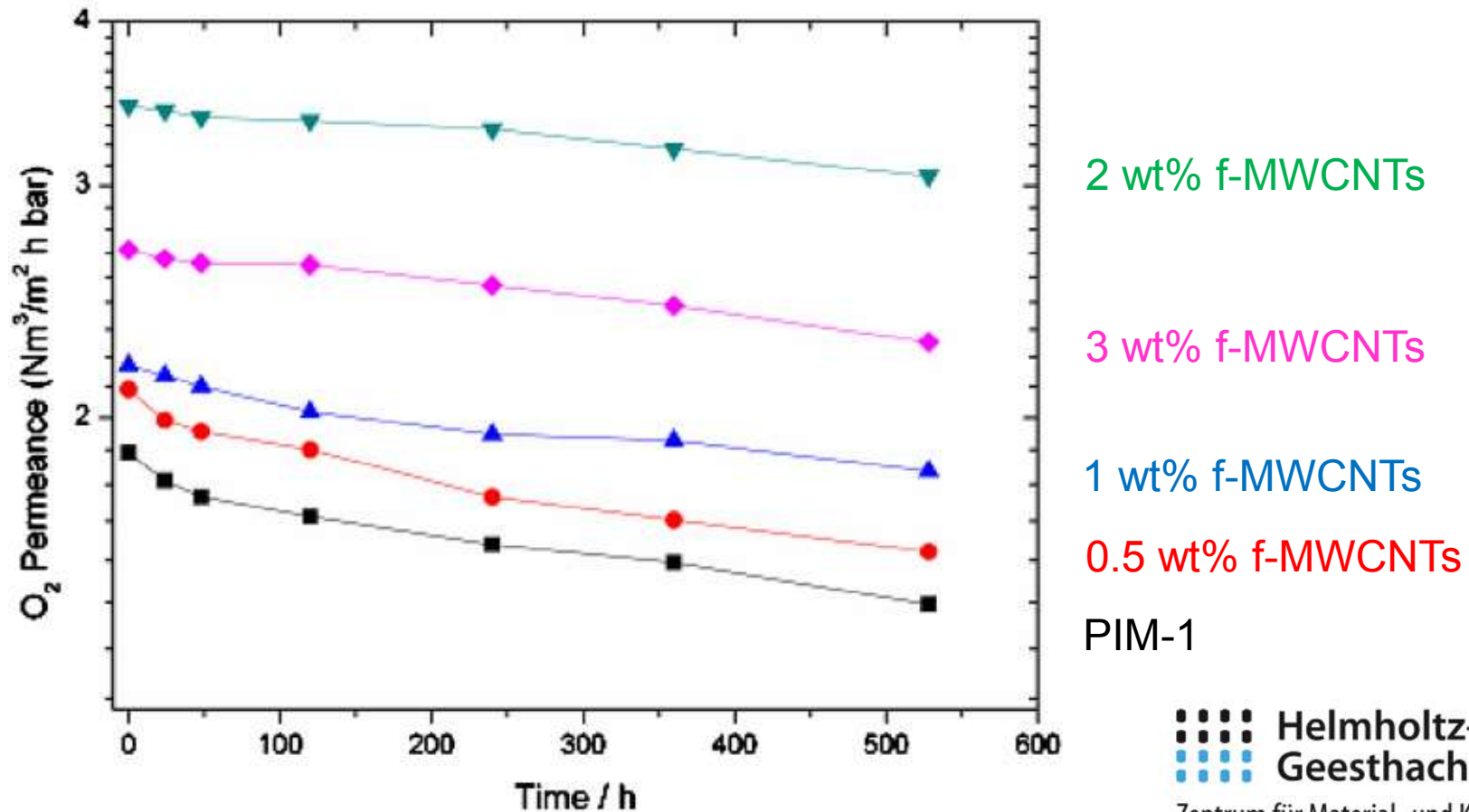
The University of Manchester

PIM-1 / carbon nanotubes

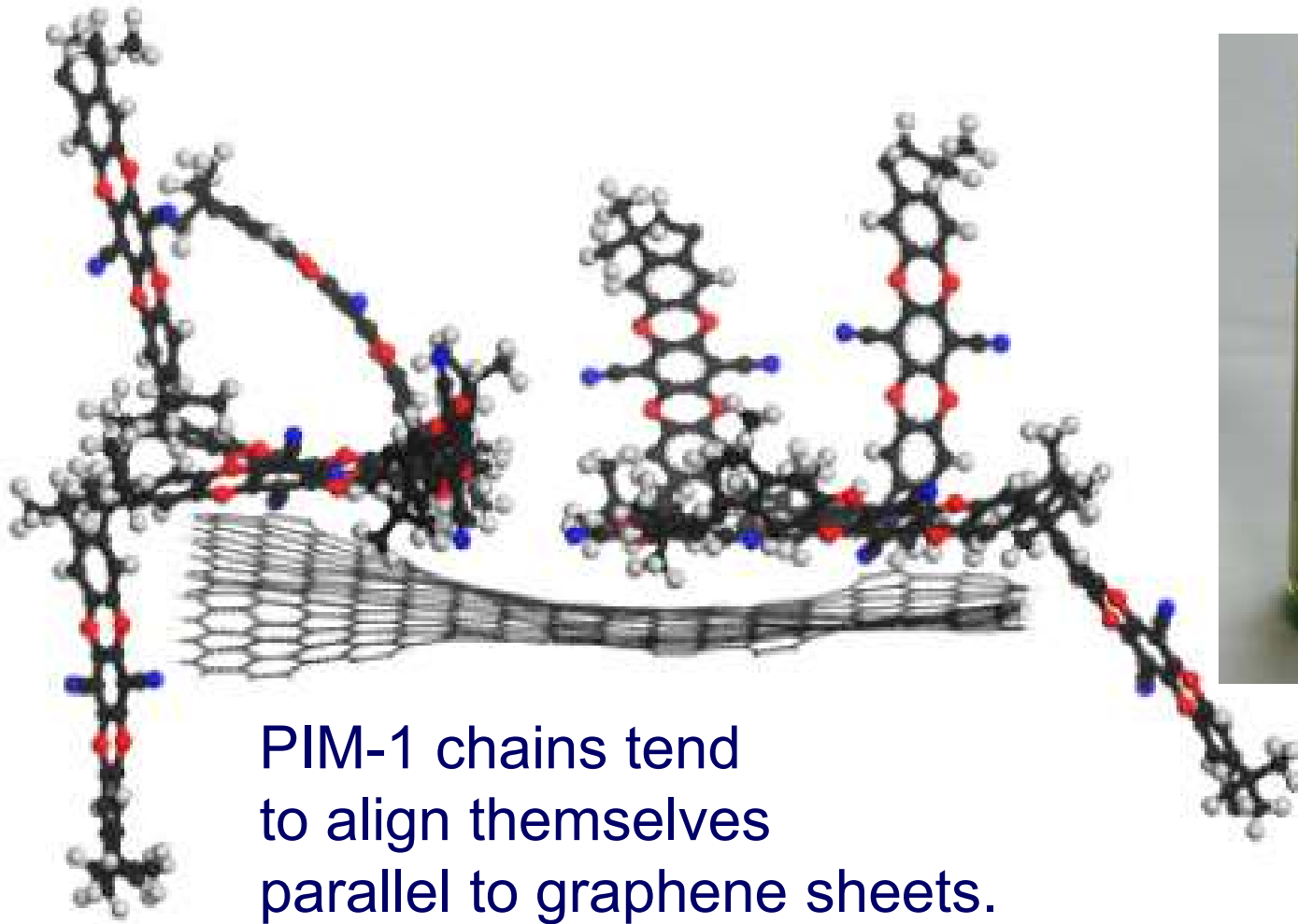
Helmholtz-Zentrum Geesthacht

M. Khan *et al.*, *Nanoscale Res. Lett.*, 2012, 7, 504.

MWCNTs functionalised with PEG



PIM-1 / graphene

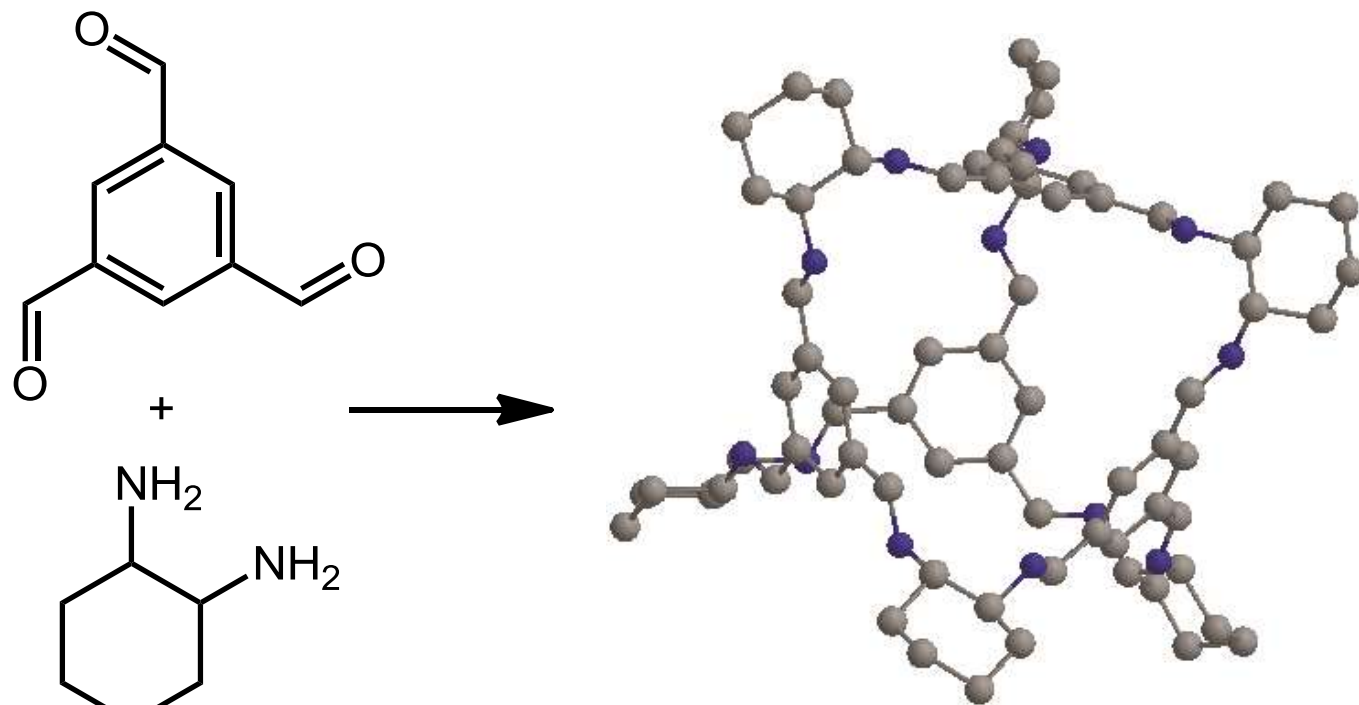


PIM-1 chains tend to align themselves parallel to graphene sheets.



A. Gonciaruk *et al.*,
Micropor. Mesopor. Mater., 2015, **209**, 126.

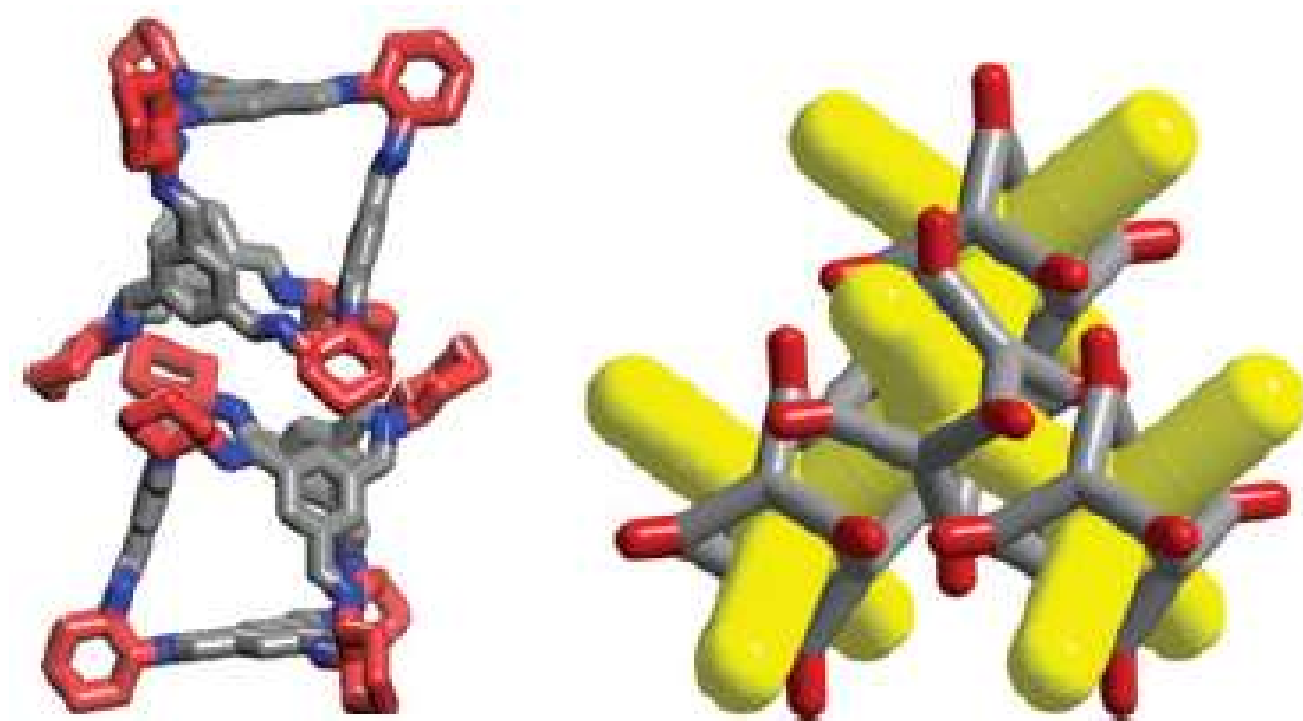
PIM-1 / cage CC3



CC3 windows *ca.* 0.6 nm

T. Tozawa *et al.*, *Nat. Mater.*, 2009, **8**, 973.
J.T.A. Jones *et al.*, *Nature*, 2011, **474**, 367.

PIM-1 / cage CC3

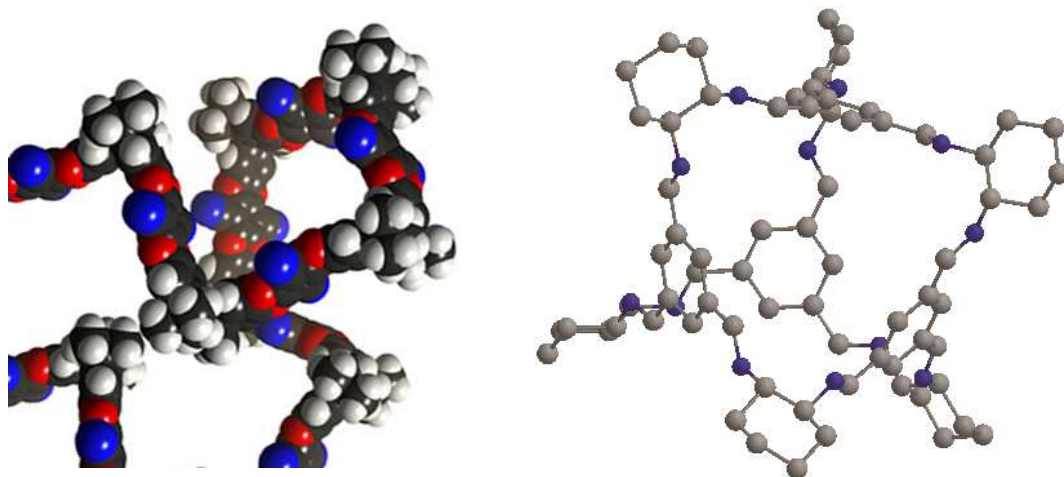


CC3 packs window to window in crystal structure, generating an interconnected pore network.

T. Tozawa *et al.*, *Nat. Mater.*, 2009, **8**, 973.
J.T.A. Jones *et al.*, *Nature*, 2011, **474**, 367.

PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



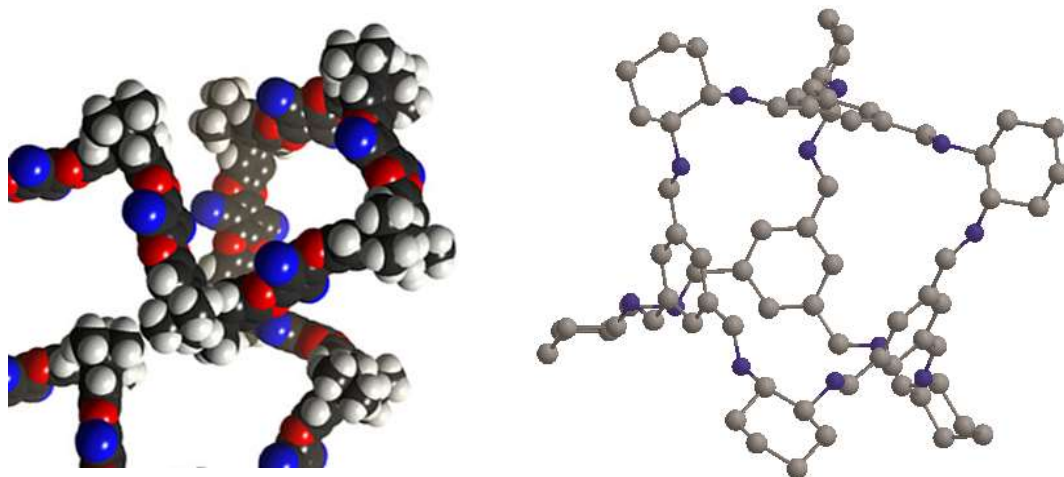
(1) In-situ crystallization of porous imine cage-3R (CC3) from molecular solution.



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PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



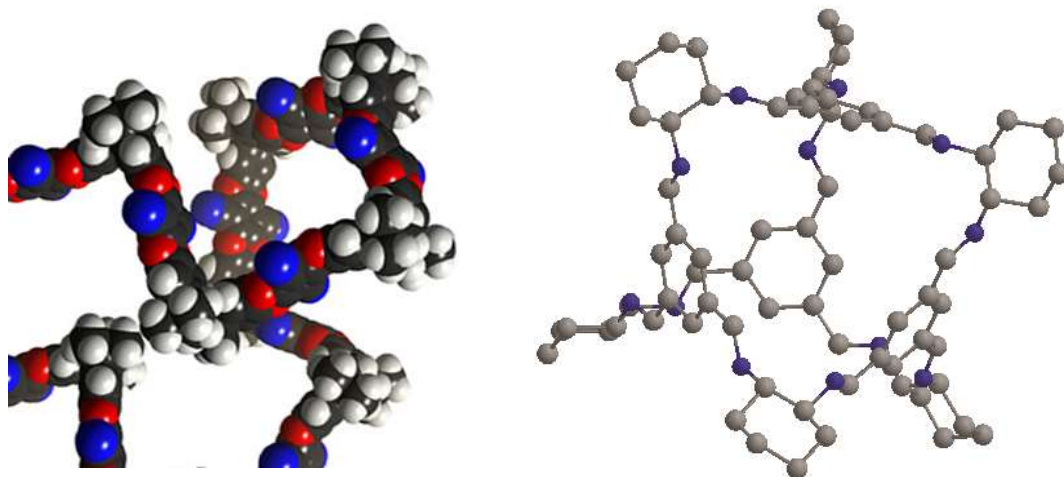
- (1) In-situ crystallization of porous imine cage-3R (CC3) from molecular solution.
- (2) Dispersion of preformed racemic CC3 nanocrystals (nanoCC3).



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PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



- (1) In-situ crystallization of porous imine cage-3R (CC3) from molecular solution.
- (2) Dispersion of preformed racemic CC3 nanocrystals (nanoCC3).
- (3) Reduced, non-porous amine form of CC3 (redCC3).



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PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



PIM-1/CC3



PIM-1/nanoCC3



PIM-1/redCC3

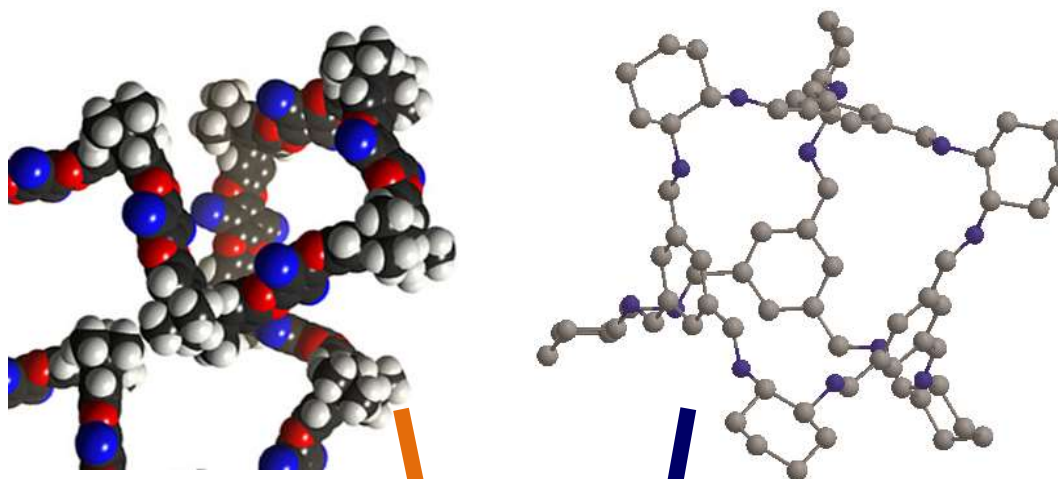
wt. ratio 10:2
wt. fraction 0.17



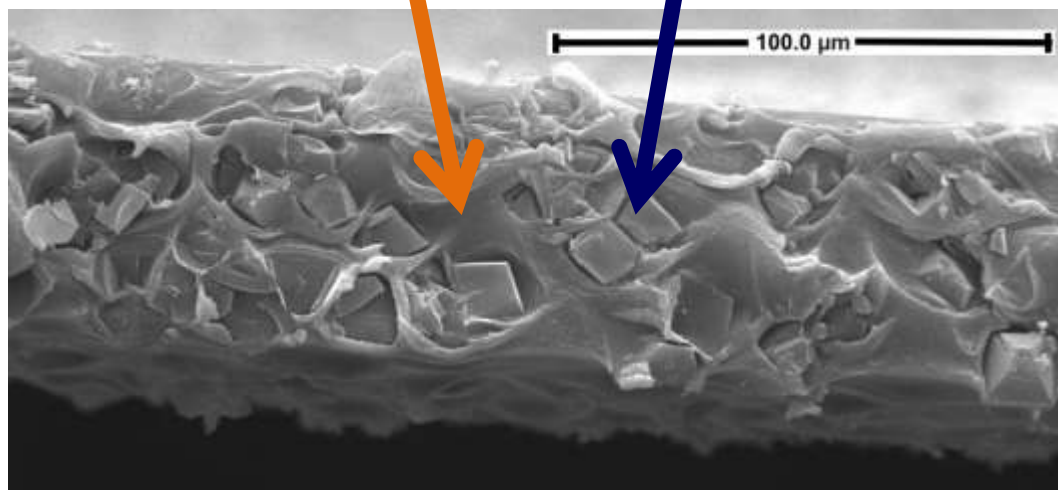
The University of Manchester

PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



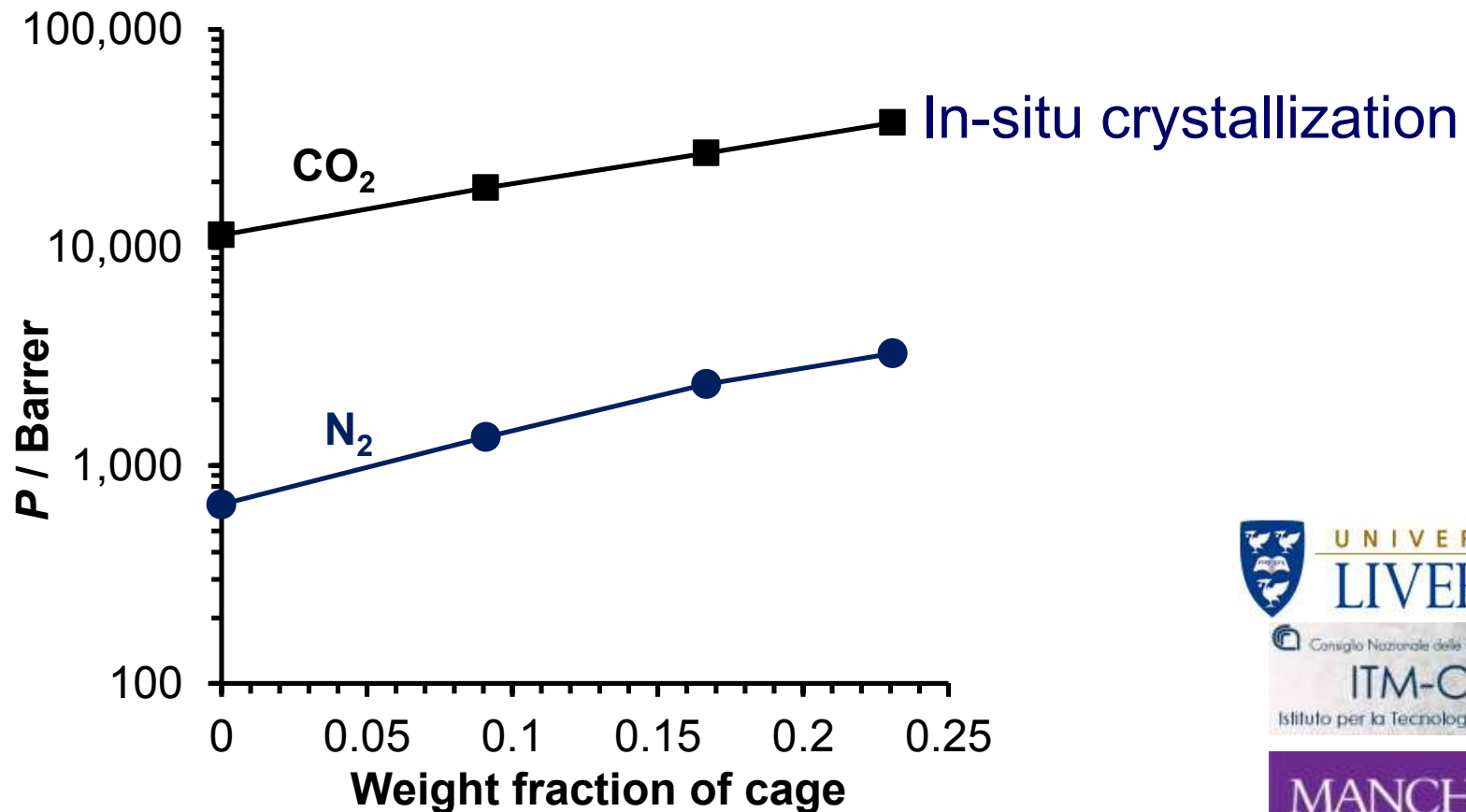
In-situ
crystallization



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PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



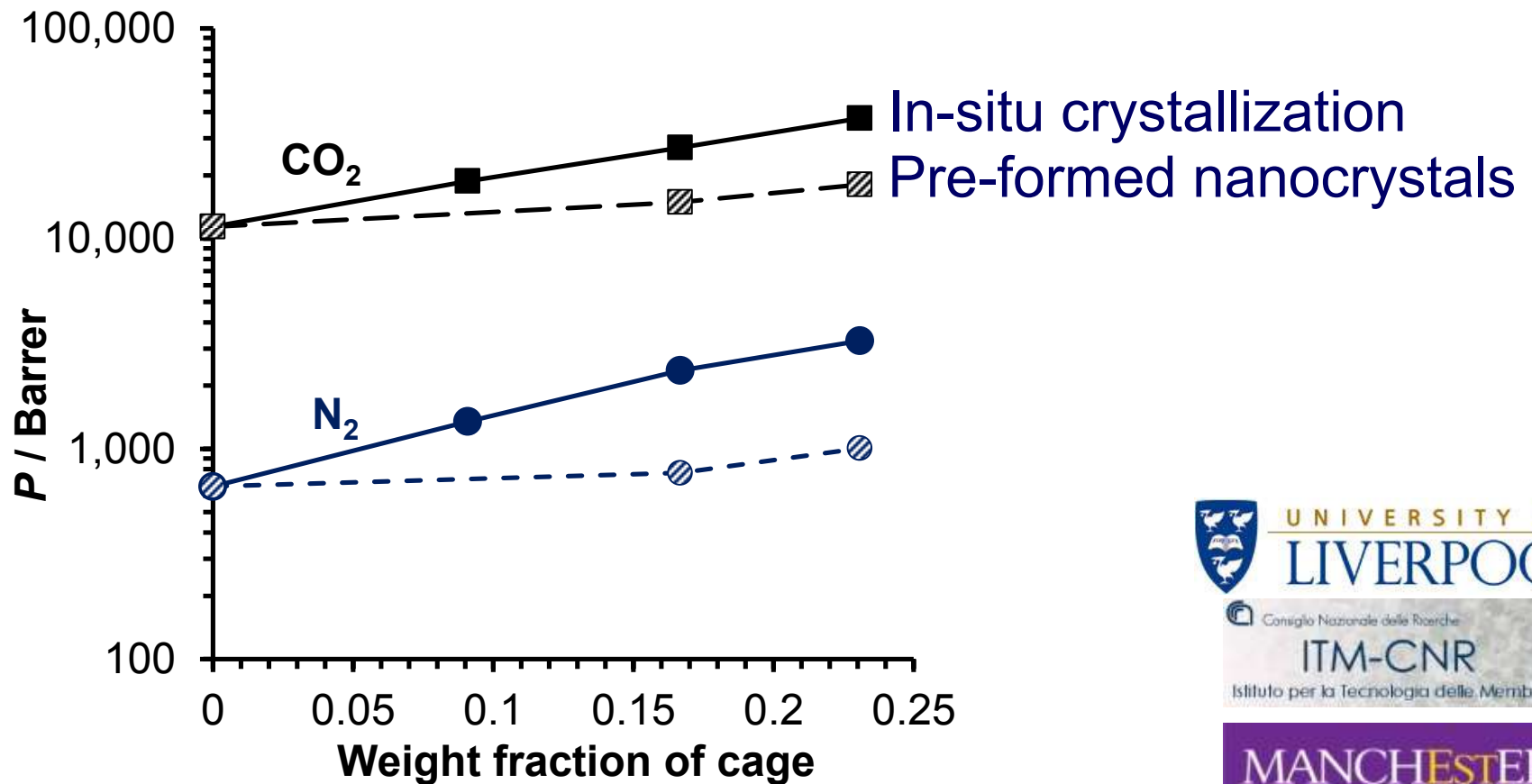
Ethanol-treated membranes



The University of Manchester

PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



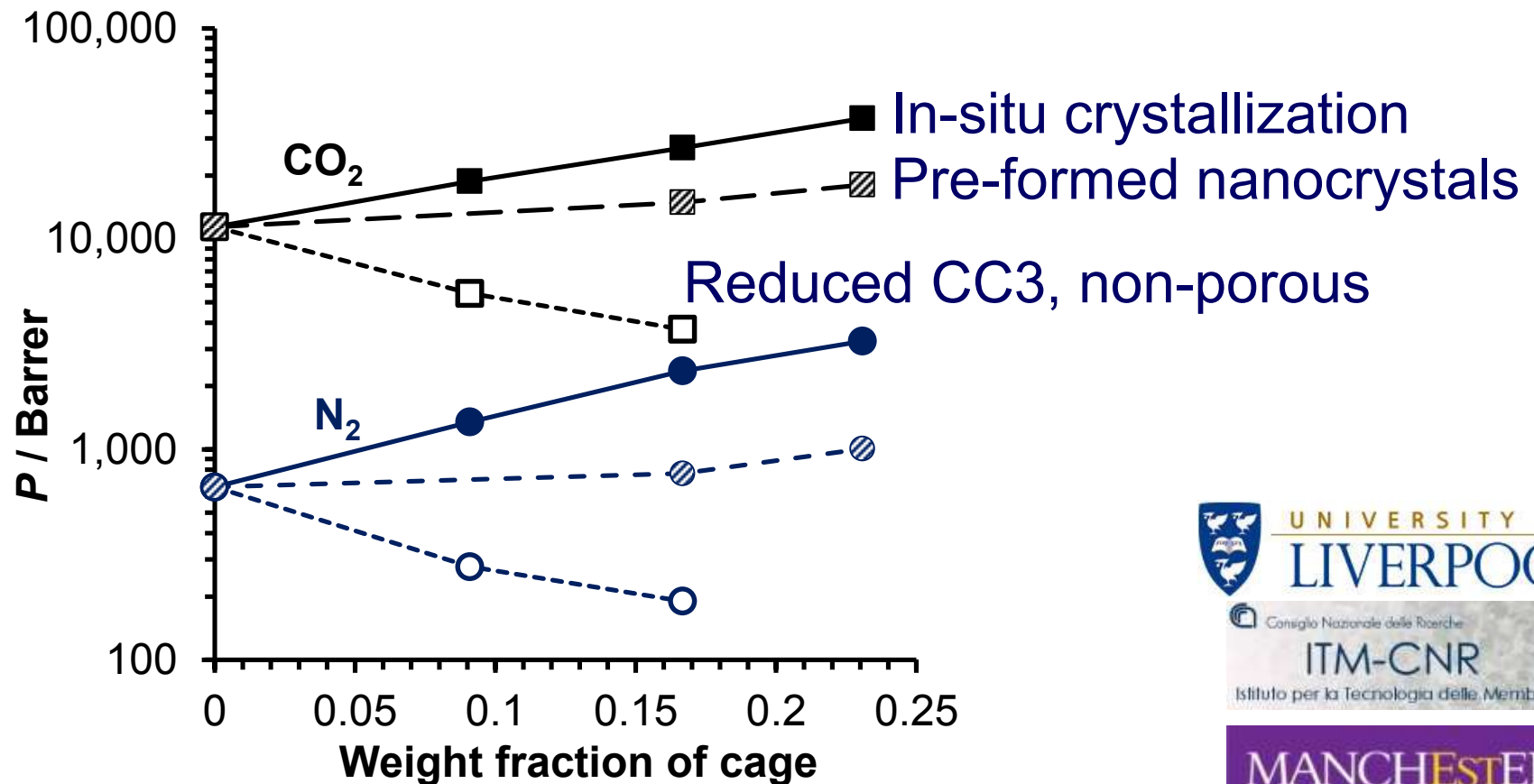
Ethanol-treated membranes



The University of Manchester

PIM-1 / cage CC3

A. Bushell *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 1253.



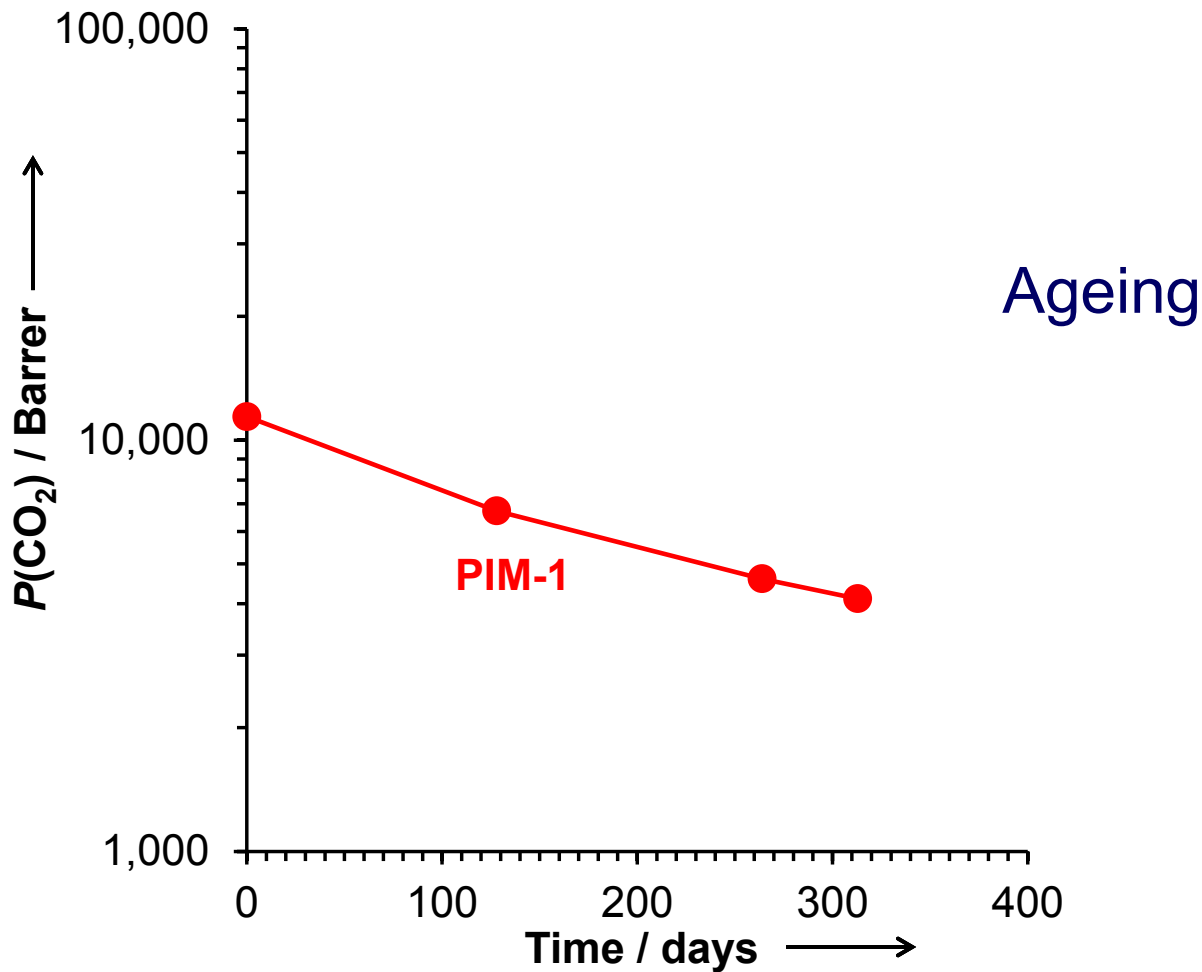
Ethanol-treated membranes



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PIM-1 / cage CC3

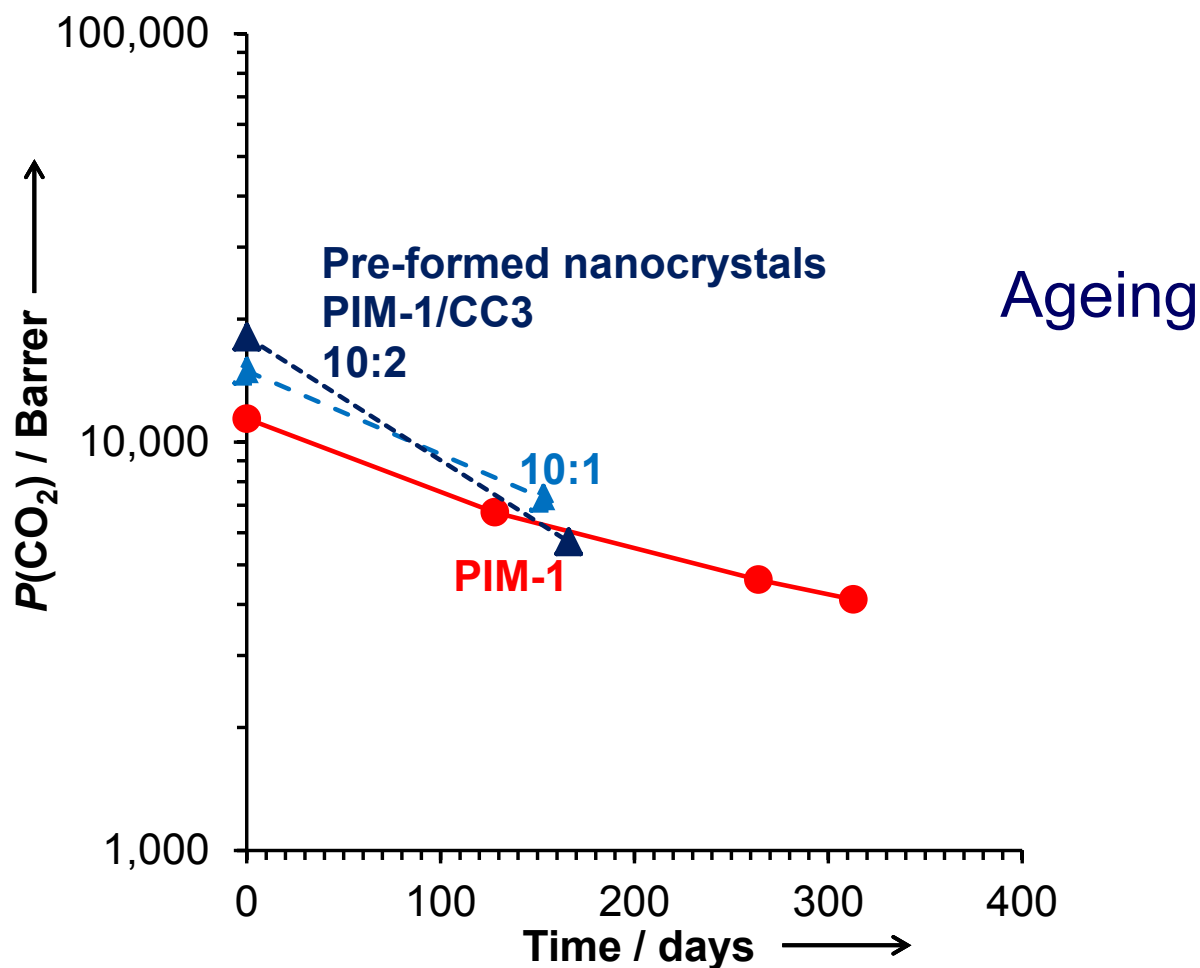
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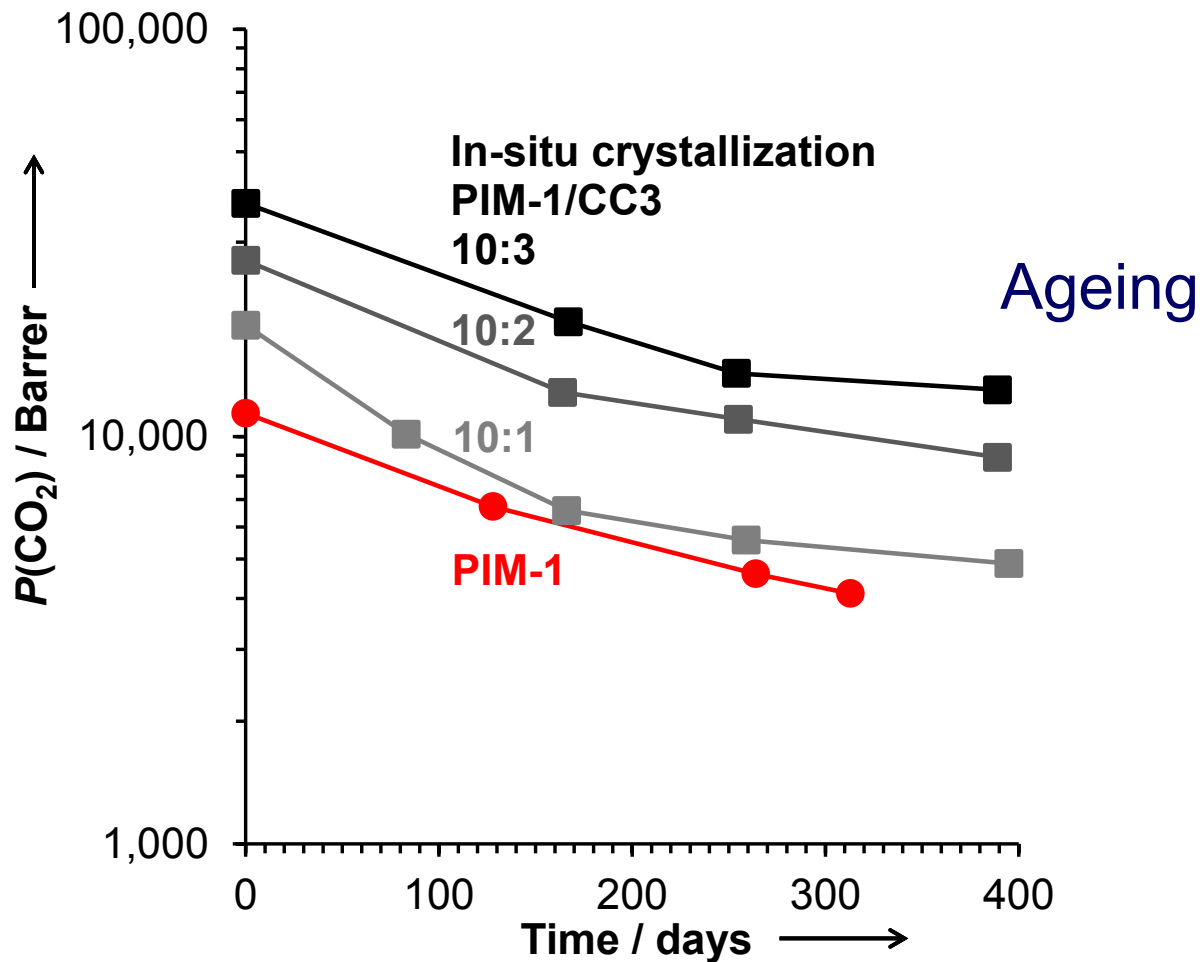
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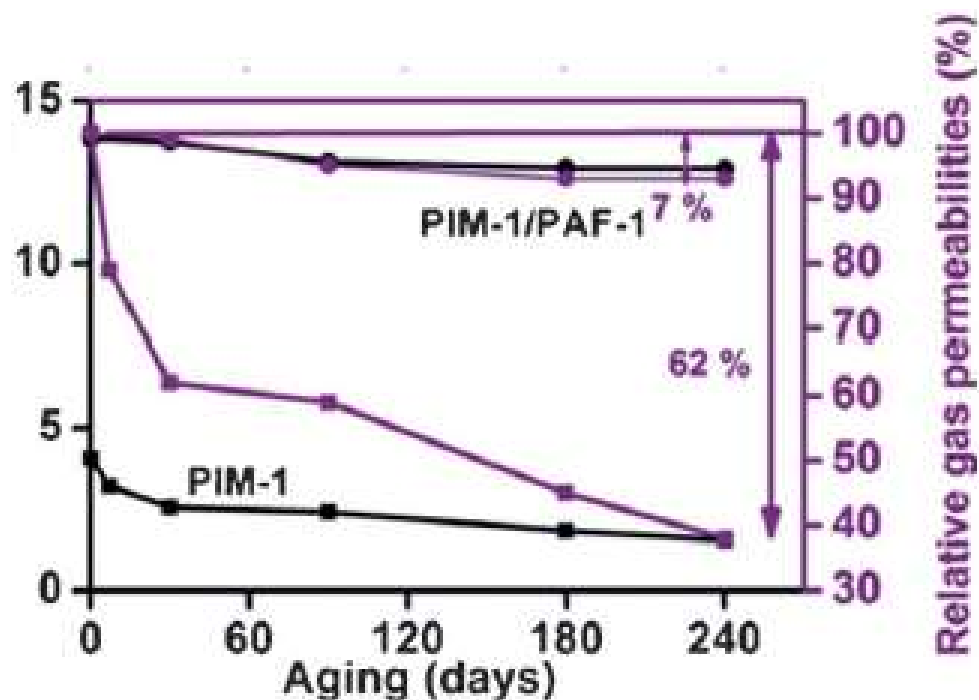
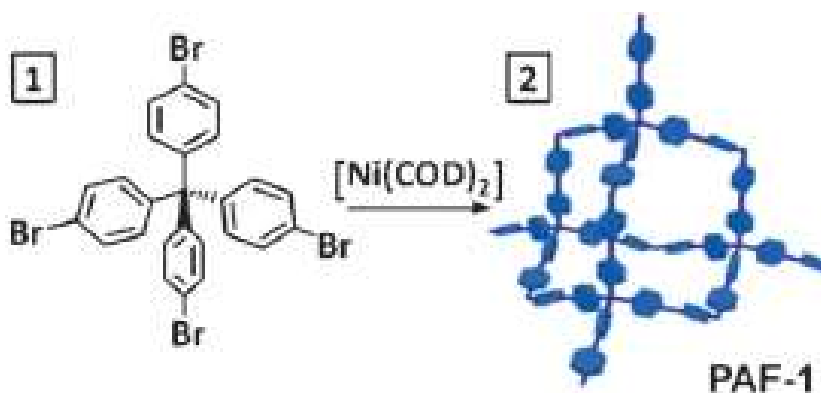


PIM-1 / PAF-1

C.H. Lau *et al.*, *Angew. Chem. Int. Ed.*, 2014, **53**, 5322.

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University of Colorado; Monash University; Australian National University



“Ending aging” in super glassy polymer membranes

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