EU-AUSTRALIAN WORKSHOP
13-14 SEPTEMBER 2017
OSLO, NORWAY

Energy efficient **M**OF-based **M**ixed-**M**atrix **M**embranes for $\mathbf{C}O_2$ **C**apture

M^4CO_2

FP7 project # 608490

1 January 2014 – 31 December 2017

www.m4co2.eu/

M^4CO_2 project aims

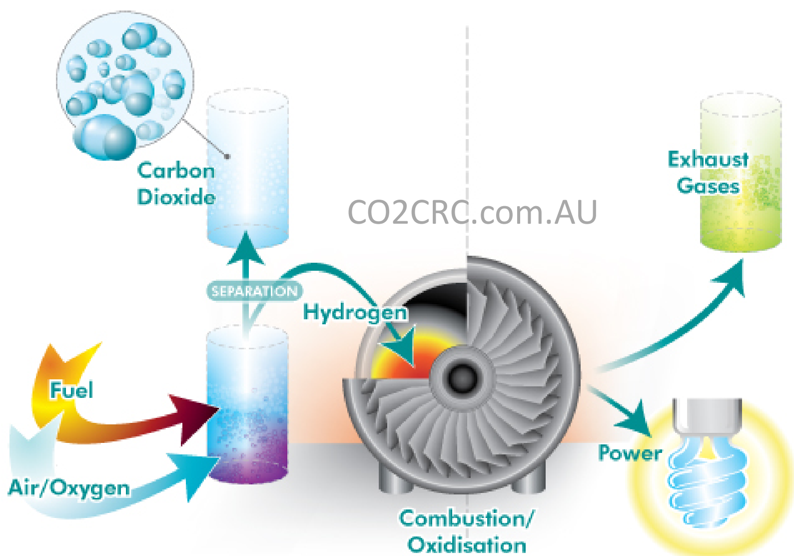
- **Developing & prototyping M**ixed **M**atrix **M**embranes based on highly engineered **M**etal organic frameworks and polymers (**M^4**) for energy efficient **CO_2** Capture
  - Power plants and other energy-intensive industries
  - Pre-combustion and post-combustion applications

- **Target**
  - Highly selective high flux membranes
  - CO_2 capture meeting the targets of the European SET plan (90% of CO_2 recovery at a cost less than 25€/MWh)
    - Internal target 15 €/ton CO_2 (≈ 10-15 €/MWh)

www.m4co2.eu/

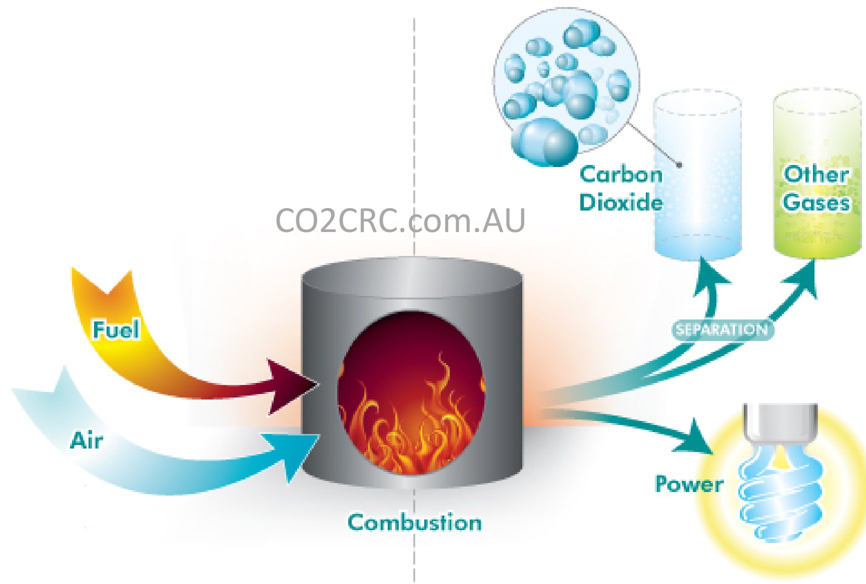
Applications

Pre-combustion CO_2 capture



CO_2 / H_2 mixtures

Post-combustion CO_2 capture



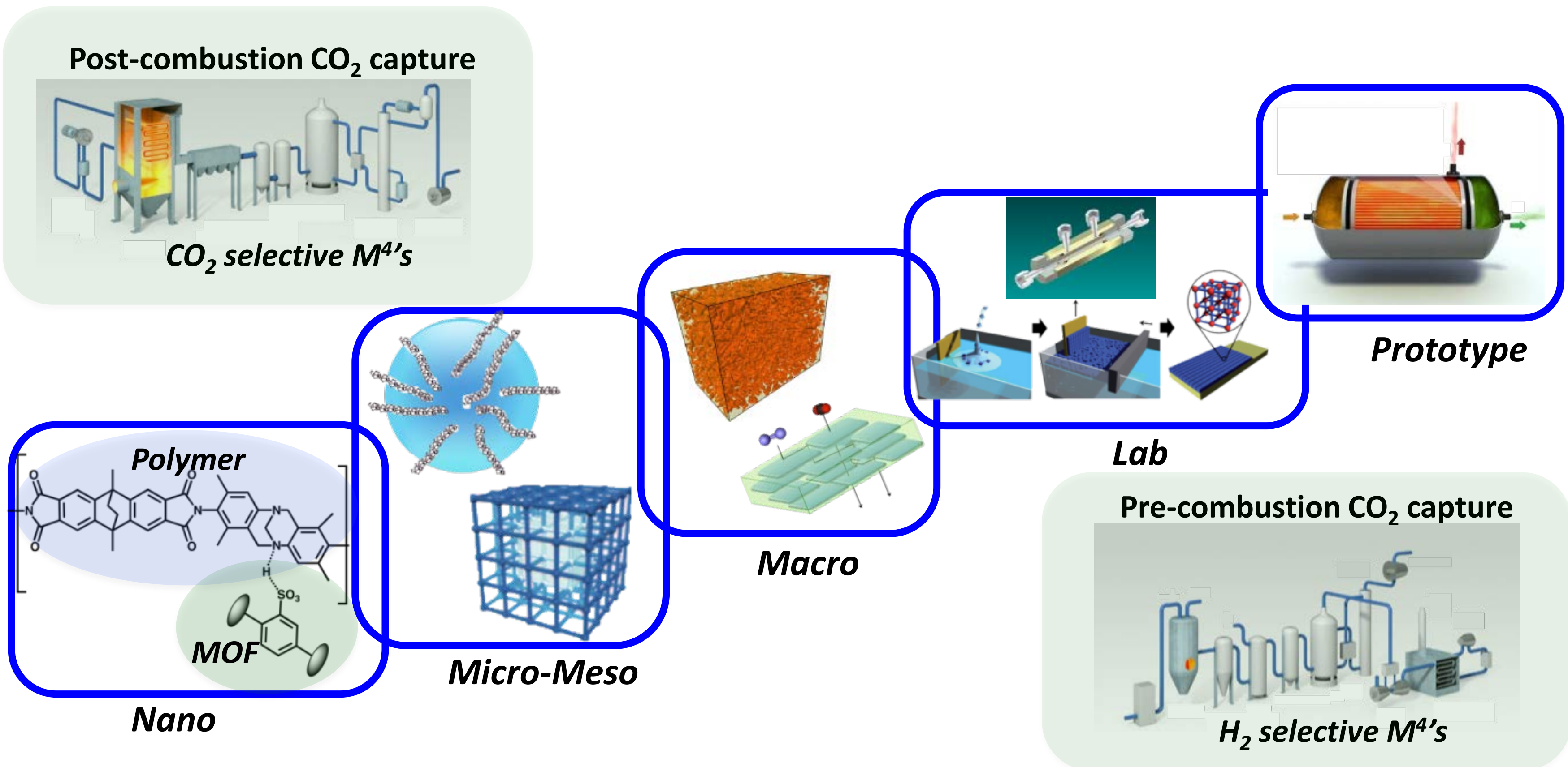
CO_2 / N_2 mixtures

Bio-gas, natural gas upgrading CO_2 / CH_4 mixtures

H_2 selective membranes

CO_2 selective membranes

The Challenge



Partners consortium

TU Delft Delft University of Technology

DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V.

M4CO2

CATO

Tata-Steel

Cementos Portland Valderrivas

tecnalia Inspiring Business

ITM-CNR Istituto per la Tecnologia delle Membrane

The University of Edinburgh

cnrs

Université de Versailles St-Quentin-en-Yvelines

University of St Andrews

Leibniz Universität Hannover

Caesaraugustanae Studium Generale Civitatis

TU Delft Delft University of Technology

Université de Lorraine

TOTAL

ICG Montpellier

Universität Leipzig

polymem membrane manufacturer

HYGEAR

cnrs Aix-Marseille université

UMONS Université de Mons

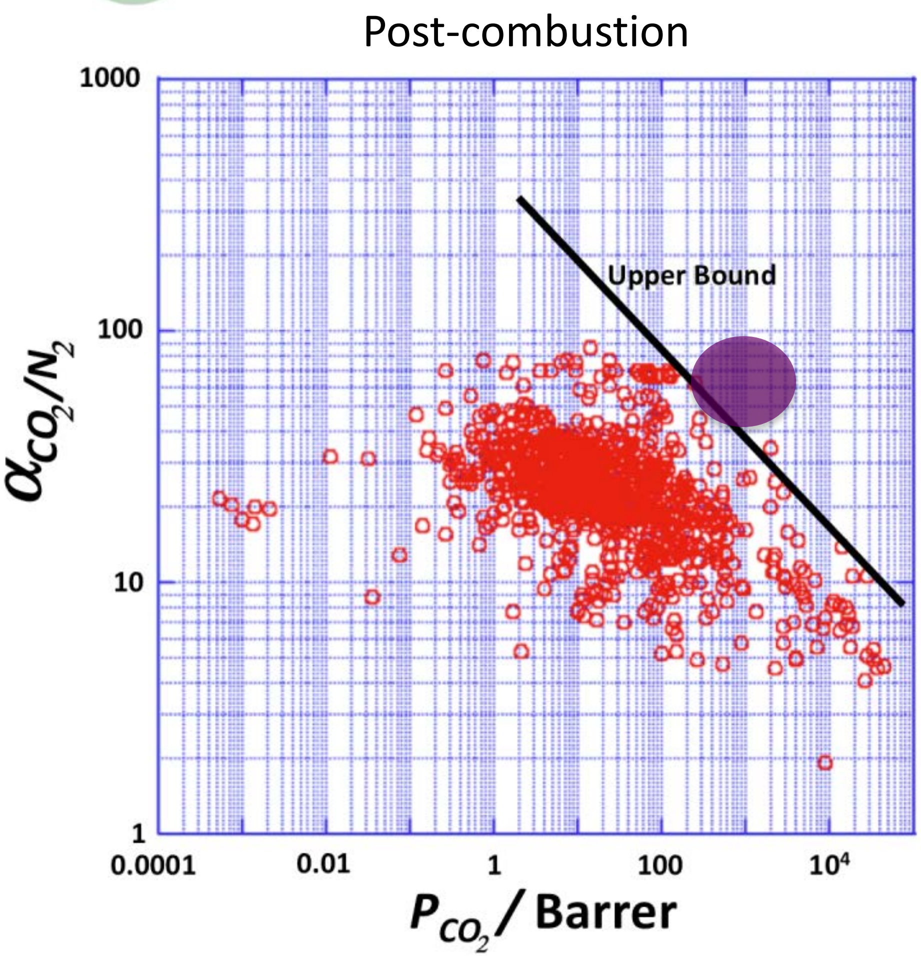
ENSICAEN

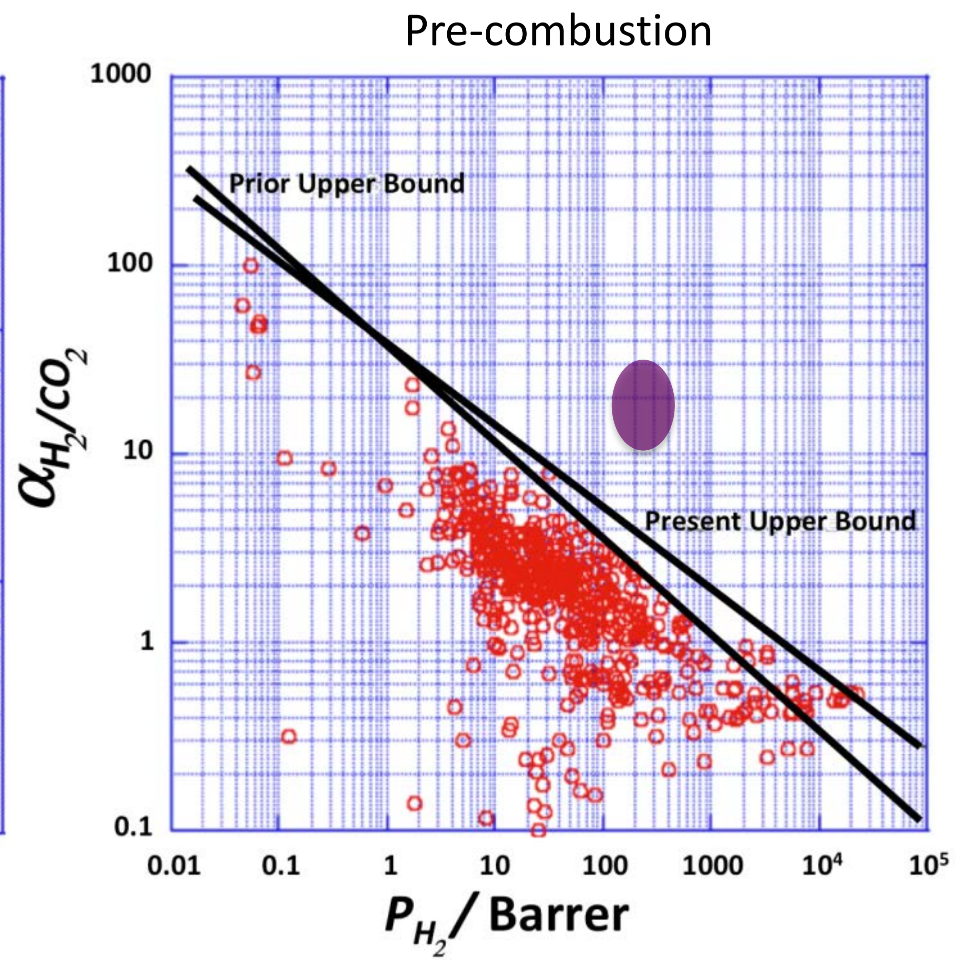
Bulgarian Academy of Sciences 1869

JM Johnson Matthey

Membrane performances - targets

Robeson upper bounds for polymer membranes





Breakthrough in membrane technology

Mixed Matrix Membranes (MMMs)

Polymeric Membranes

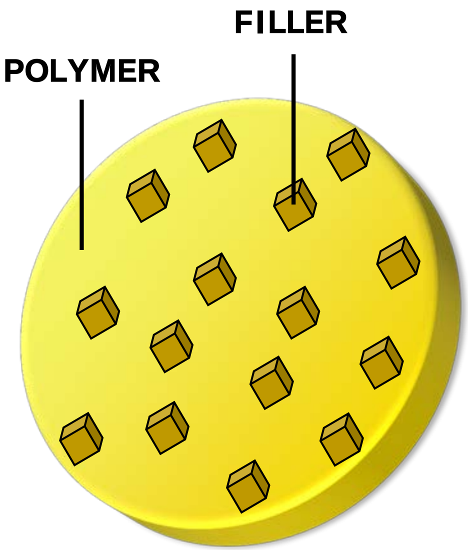
Pros:
- Mechanical stability
- Easy processing and low price

Cons:
- Thermal and chemical stability
- Low permeability

Inorganic Membranes

Pros:
- Chemical stability
- Gas sieving properties

Cons:
- Mechanical stability (brittle)
- Complex processing and expensive



Mixed Matrix Membranes

Filler (Molecular sieve)
+
Matrix (Polymer)

- Mechanical stability
- Easy processing and low price

- Chemical stability
- Gas sieving properties

Chung, T. S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S., *Prog. Polym. Sci.* 32 **(2007)** 483-507
Zimmerman, C. M.; Singh, A.; Koros, W. J., *J. Membr. Sci.* 137 **(1997)** 145-154.

Mixed Matrix Membranes (MMMs)

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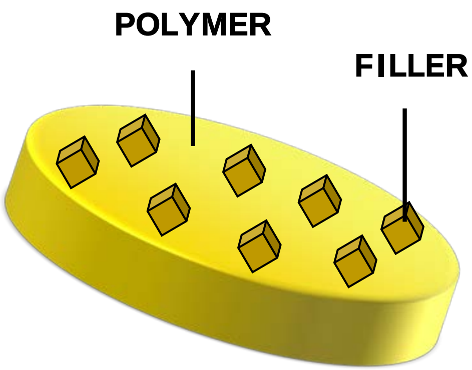
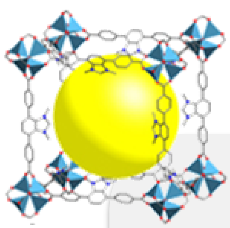




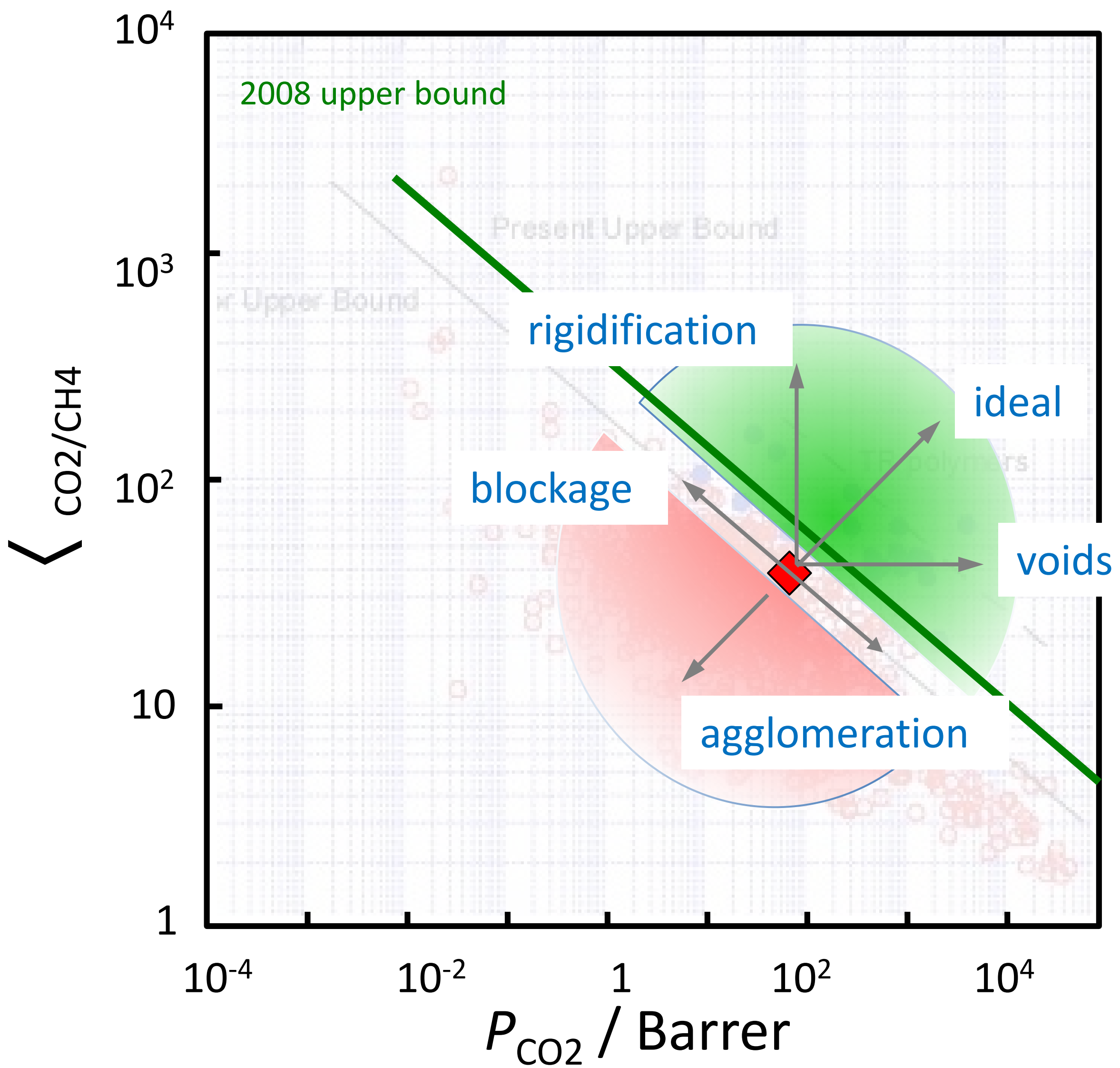
MOFs as fillers

- Molecular sieve properties
- Some MOFs show outstanding CO_2/CH_4 separation properties
- Infinite design possibilities

Good match between filler and matrix is required

J. L. C. Rowsell, O. M. Yaghi, *Microp. Mes. Mater.*, **2004**, *73*, 3-14, and references therein.
E. Stavitski, J. Gascon, F. Kapteijn, et al. *Langmuir*, **2011**, *27*, 3970-3976.

Robeson plot – effect of filler

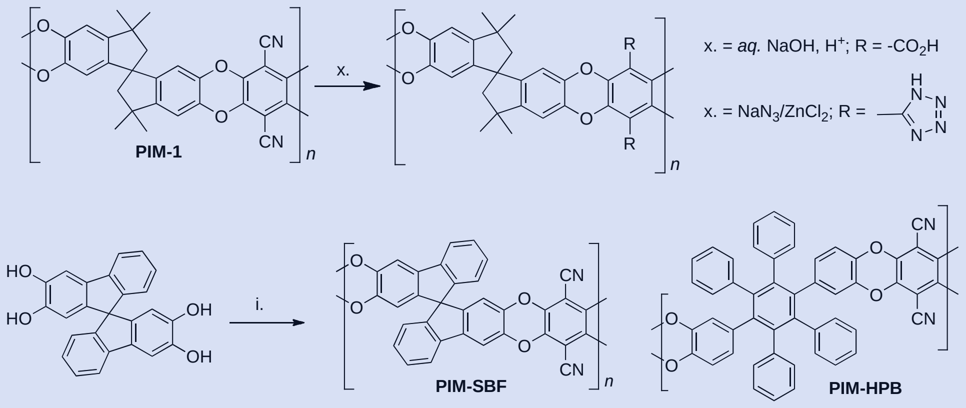


Targets development M^4CO_2 components

- **Identification** of the most interesting MOF – polymer couples for their use in M^4
- **MOF tuning** at the particle level
  - preparation of MOF nanoparticles
  - MOF surface functionalization: synthesis of core-shell fillers
  - synthesis of hierarchical MOF nano-fillers combining meso and micro-pores
  - control of MOF particles with extreme aspect ratios (lamellae)
- Development of new **high flux polymers** bearing tailored functional groups to optimise polymer-MOF interactions
- The **optimization of membrane preparation** conditions
  - Flat sheet, lab scale MOF membranes
  - Langmuir-Blodgett model ultra-thin membranes
  - Hollow fiber (HF) M^4s with thin separating layers for real application
- **Operando studies** –
  - Gaining insight into the separation performance and into the physicochemical properties of the new composites under working conditions
- Accurate **engineering models** based on experimentally determined fundamental parameters to describe permeation through the selected types of M^4
- **Economic evaluation** and **conceptual process designs** for the real life applications of the new membranes

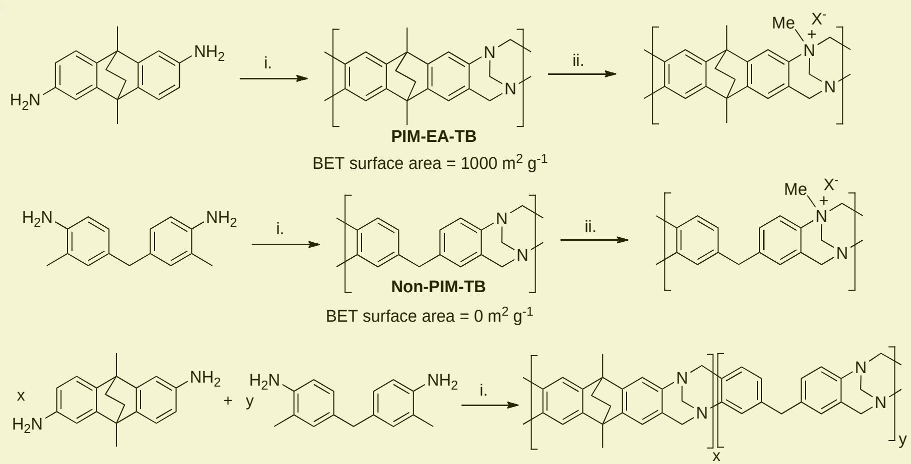
→ **Breakthrough in membrane technology**

WP-2 Polymer development



Post-combustion
High-flux polymers

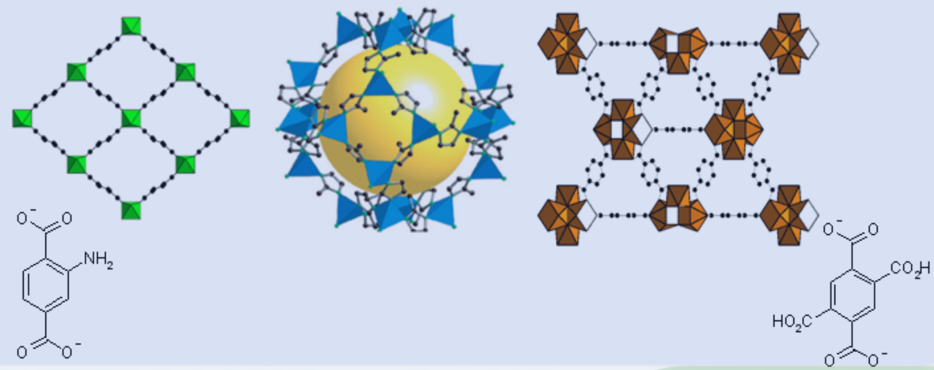
Polyimides of Intrinsic Microporosity (PIM)
PolyBenzImidazoles (PBI)



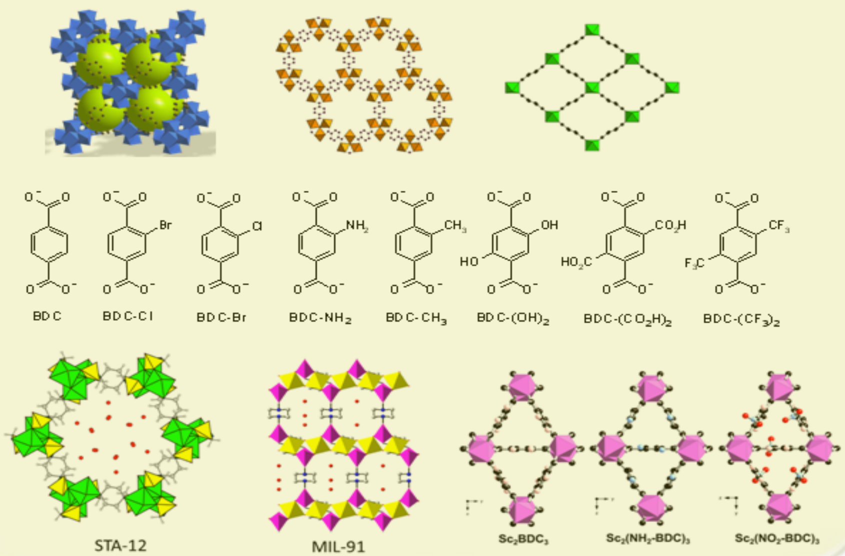
Pre-combustion
High-selectivity polymers

WP-2 MOF development

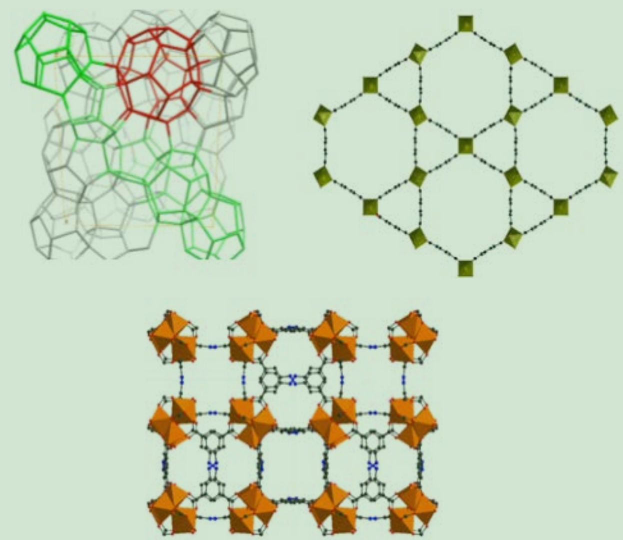
1st Generation



2nd Generation



3rd Generation

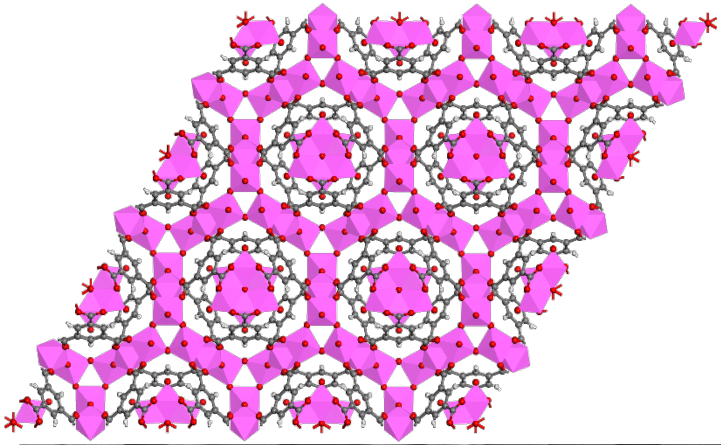


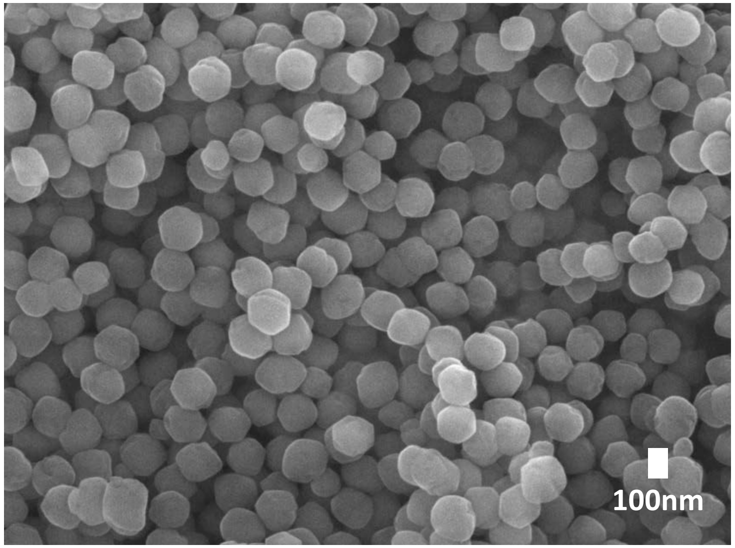
2^{nd} generation nanoMOFs

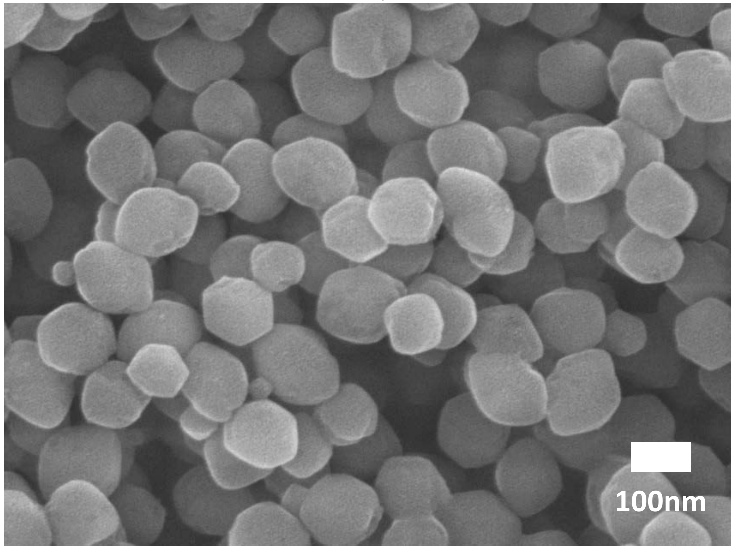
Candidate for 2^{nd} Gen post-combustion which presents good hydrothermal stability and performances under wet conditions

Reflux synthesis in pure water was too difficult to scale-up (low STY)

Optimized reflux synthesis in H_2O/DMF that yields nanoparticles with good yield (100 nm)

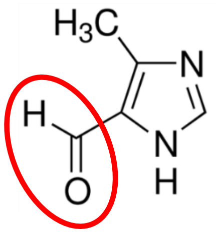


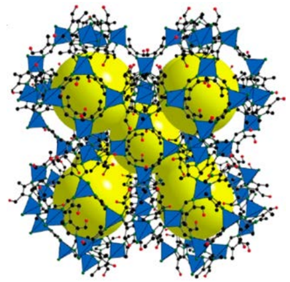


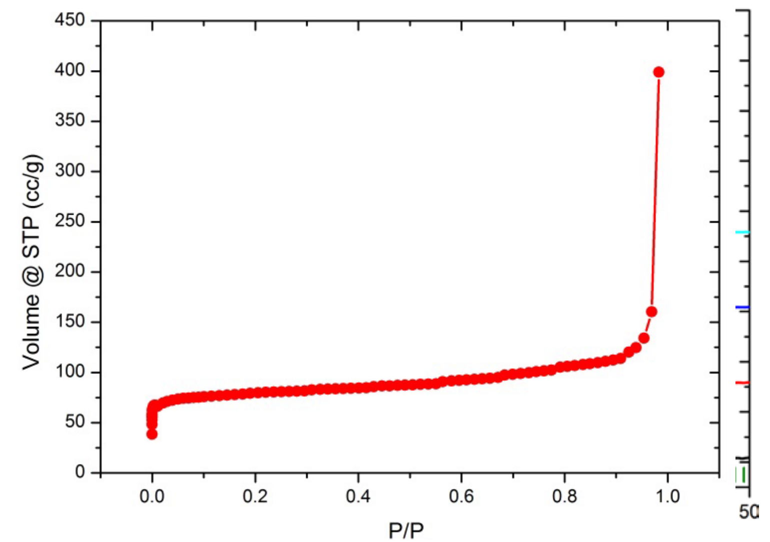


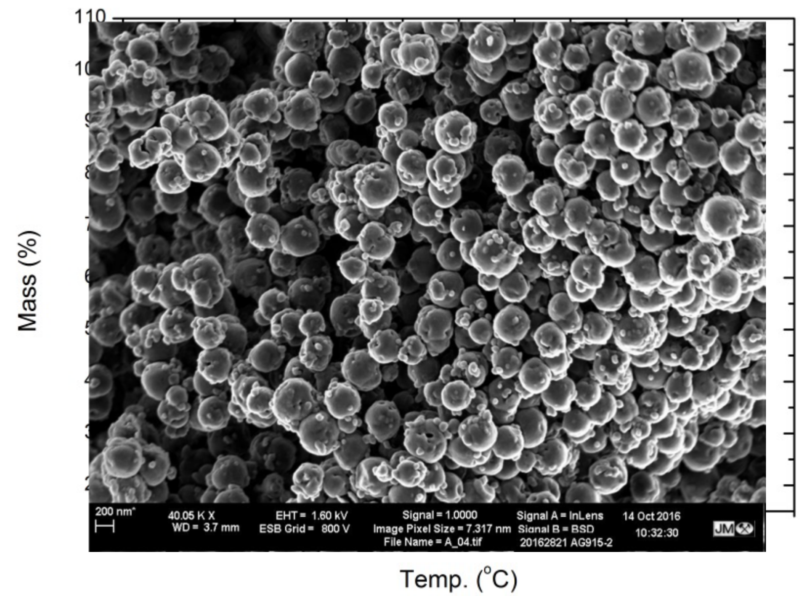
ZIF-94 – scale up synthesis

Johnson Matthey









- Experimentation indicate that the synthesis of ZIF-94 can be improved with a phase pure materials still obtained at [1.5x] initial reaction concentration.
- Above optimal concentrations impurity peaks were observed in the XRD, denoted by *.
- TGA shows good agreement between theory and experimental, thermally stable up to ~275 ^oC.
- N_2 BET surface area = 310 m^2/g.
- SEM indicate nano-MOF was formed consisting of nanospheres ~200 nm in diameter.

Task 4.3 Membrane performance

Journal of Membrane Science 515 (2016) 45–53

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Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Influence of ZIF-8 particle size in the performance of polybenzimidazole mixed matrix membranes for pre-combustion CO_2 capture and its validation through interlaboratory test

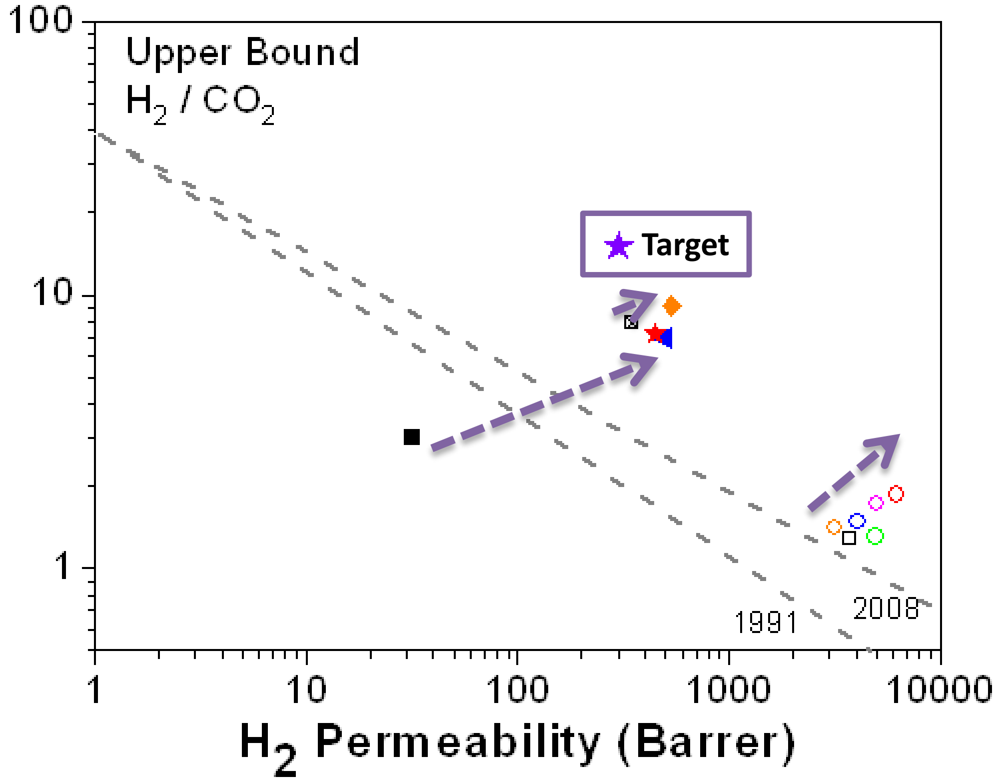
Javier Sánchez-Laínez [a], Beatriz Zornoza [a], Sebastian Friebe [b], Jürgen Caro [b], Shuai Cao [c], Anahid Sabetghadam [d], Beatriz Seoane [d], Jorge Gascon [d], Freek Kapteijn [d], Clément Le Guillouzer [e], Guillaume Clet [e], Marco Daturi [e], Carlos Téllez [a], Joaquín Coronas [a,*]

[a] *Chemical and Environmental Engineering Department and Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain*
[b] *Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität, 30167 Hannover, Germany*
[c] *Johnson Matthey Technology Center, Sonning Common, Reading RG4 9NH, United Kingdom*
[d] *Catalysis Engineering-Chemical Engineering Department, Delft University of Technology, 2628 BL Delft, The Netherlands*
[e] *Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen Normandie, CNRS, 14050 Caen, France*

- Paper from 1st R-R testing: allowed to do complete review of the calculation procedures among TUDELFT, LUH and UNIZAR to verify the GS measurements
- Some discrepancies found:
  - Unify the way of calculating the membrane performance → better coherence with lower average standard deviations (*P* and *S*)
  - Sweep gas has strong influence

Flat sheet membrane performance

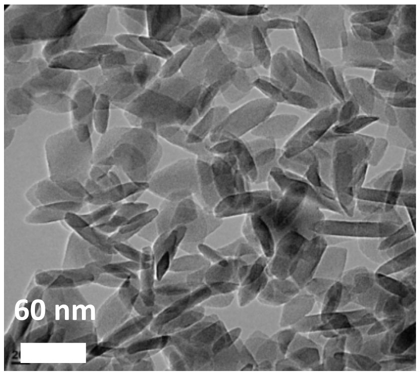
PIM-1 vs PBI and Matrimid based MMMs



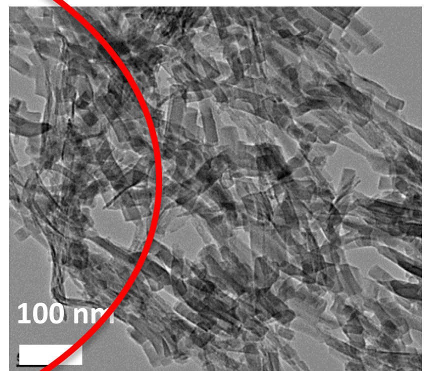
- All PIM-1 membranes surpass the upper-bound (high increase of permeability but reduced selectivity)
- PBI approaches selectivity target

Morphology Effects

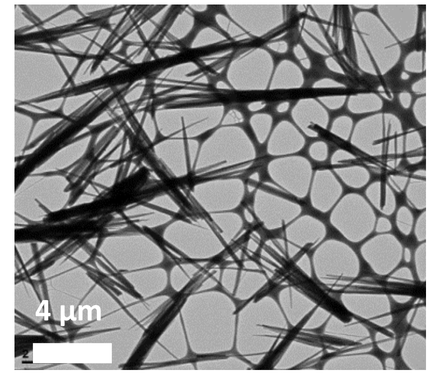
Nanoparticles



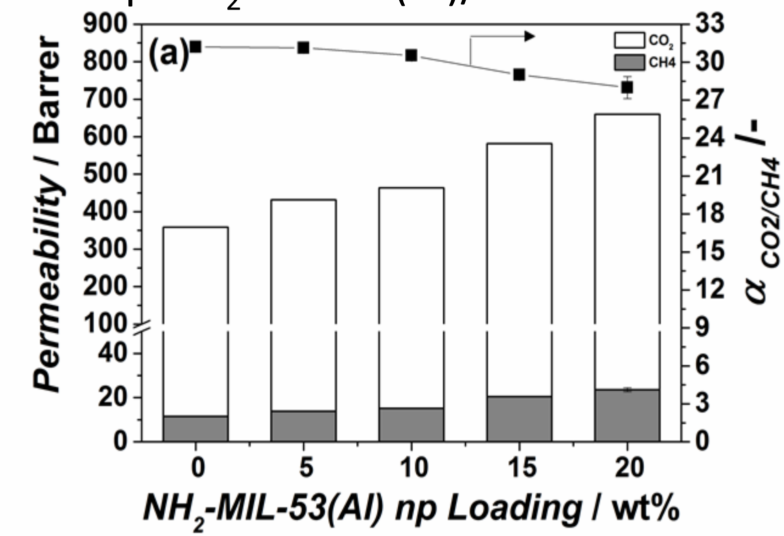
Nanorods



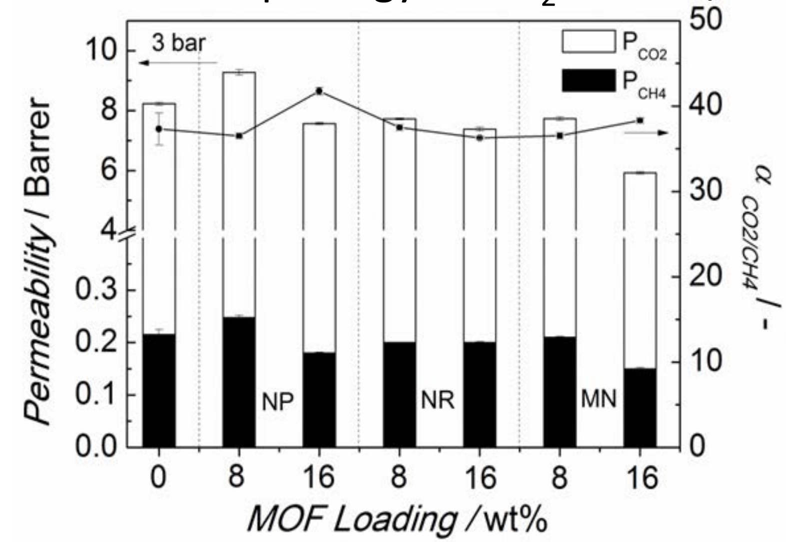
Microneedles



np-NH_2-MIL-53(Al)/6FDA-DAM

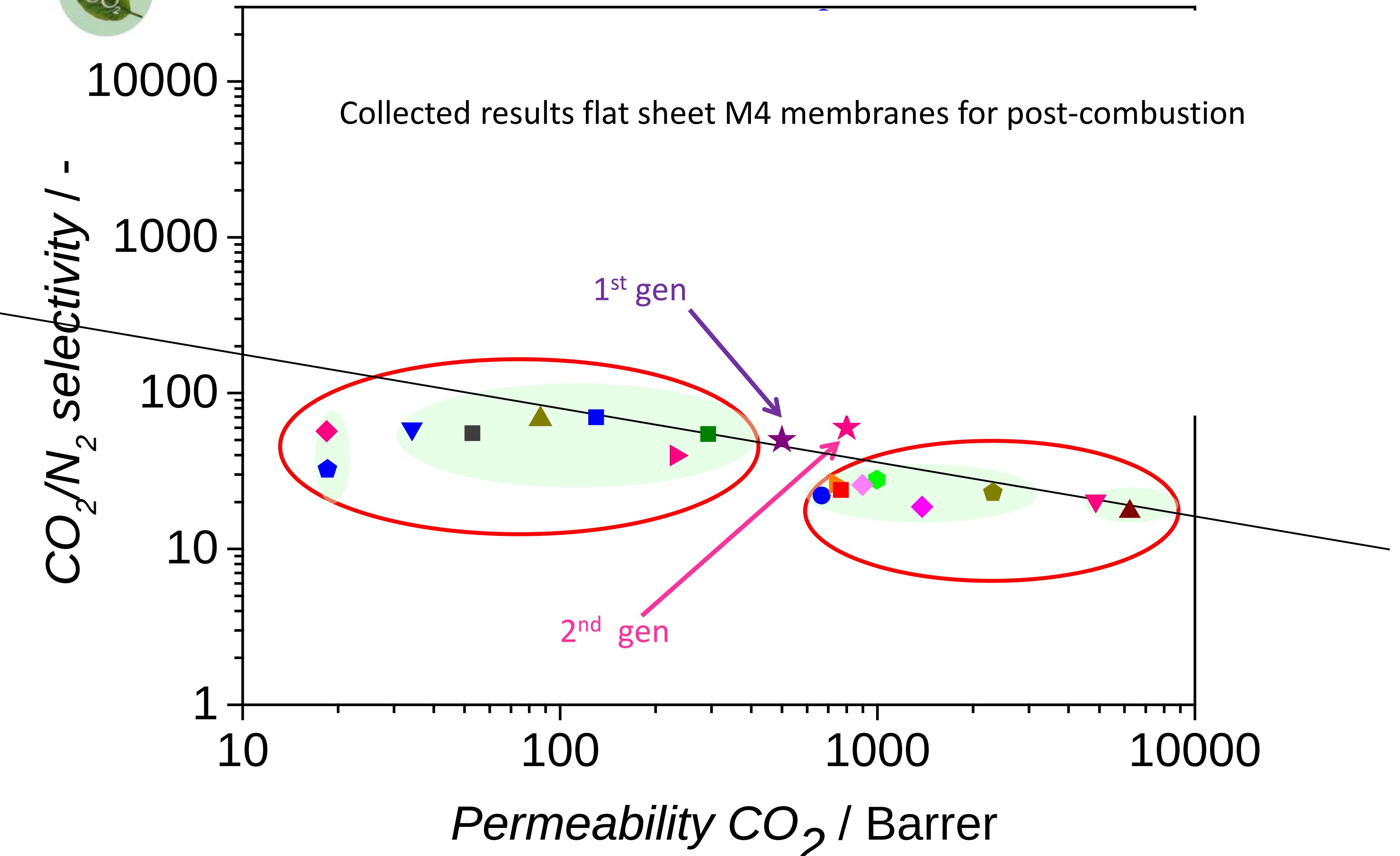


Different morphology of NH_2-MIL-53/Matrimid



Sabetghadam et al, Adv. Func. Mater. 2016

Robeson plot (2008)

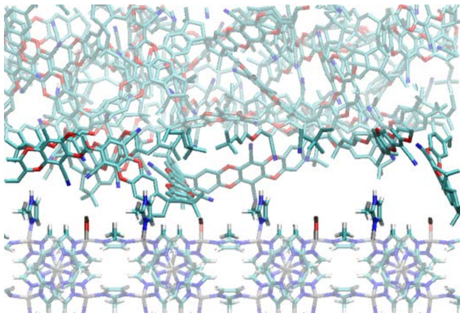


Task Surface Characterization

Rational analysis of series of MOF/Polymer Interfaces

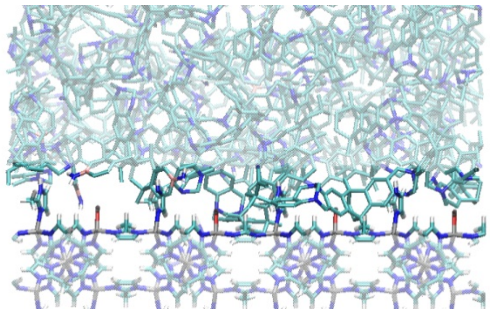
(integrated DFT / MD computational methodology)

PIM-1@ZIF-8



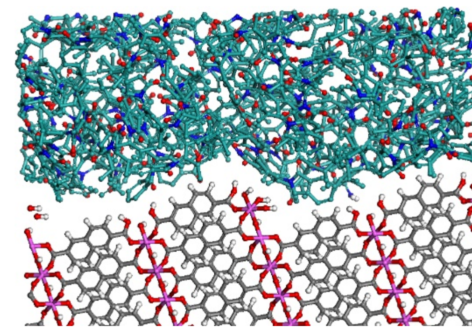
Microvoids

PIM-EA-TB@ZIF-8



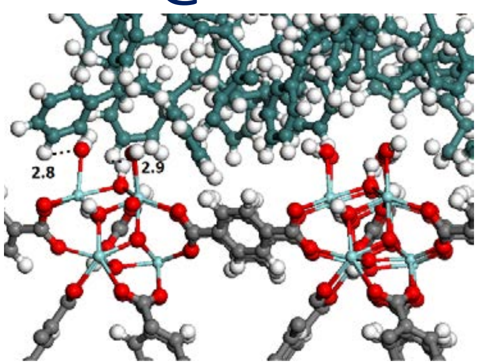
Microvoids

6FDA-DAM@MIL-69



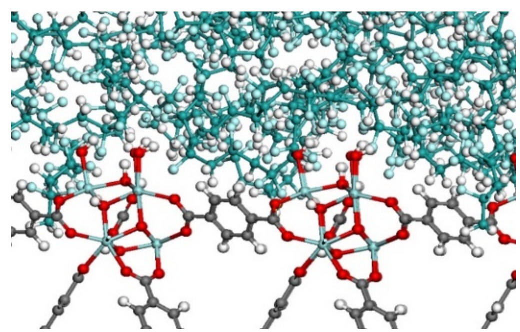
Gap

PS@UiO-66



Intermediate case

PVDF@UiO-66

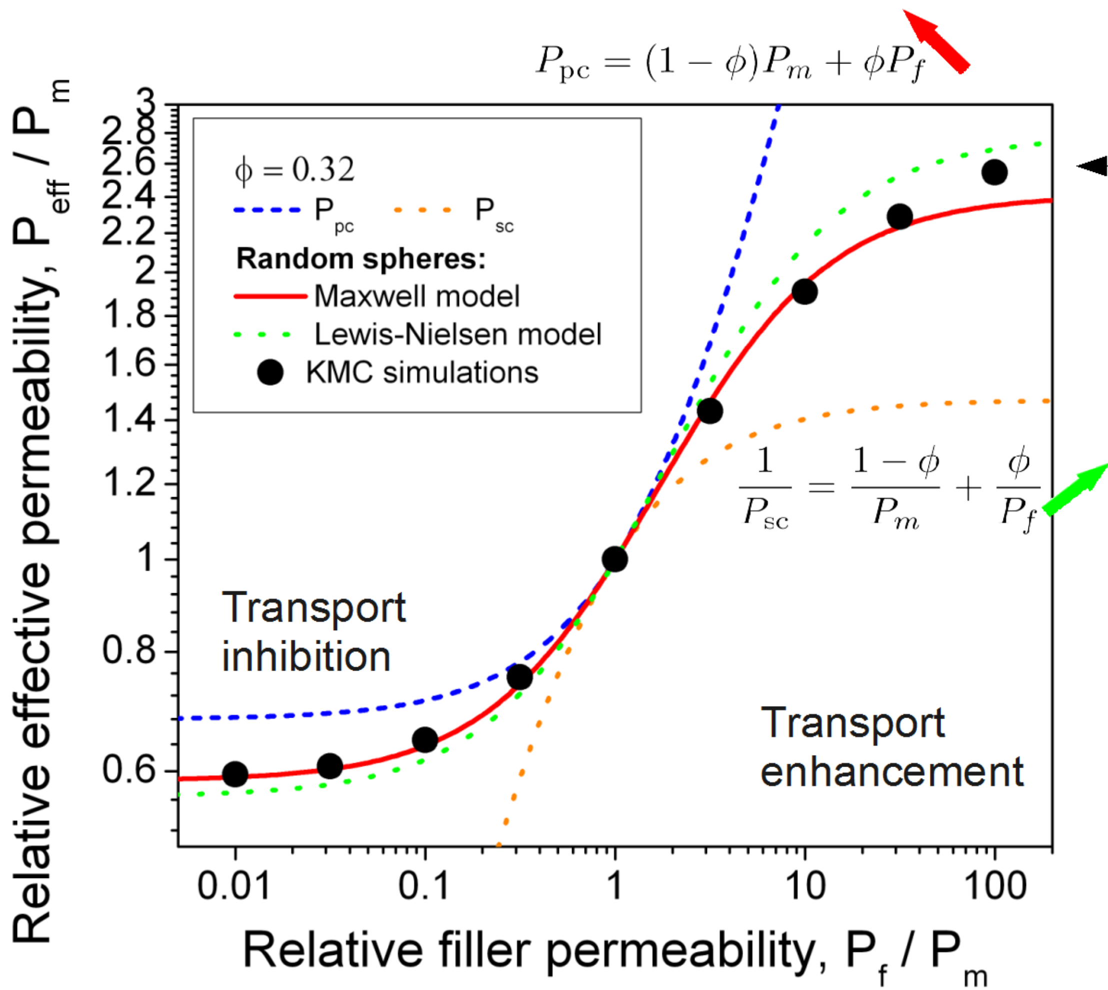


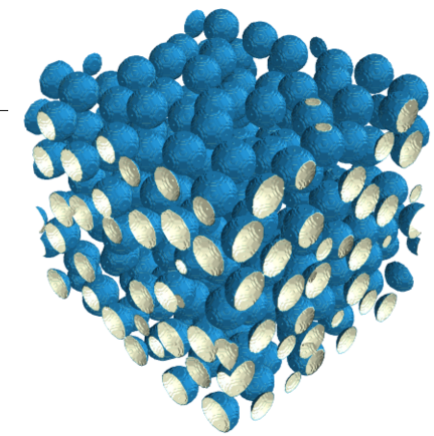
Polymer penetration into the MOF

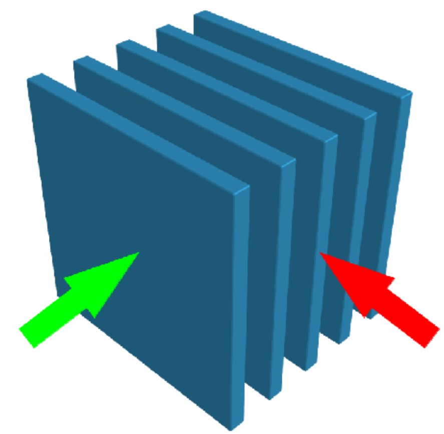
***R. Semino** et al, JACS, to be submitted*

Task Diffusion fundamentals

Transport modification by filler particles







D. Schneider et al., submitted

Task Diffusion fundamentals

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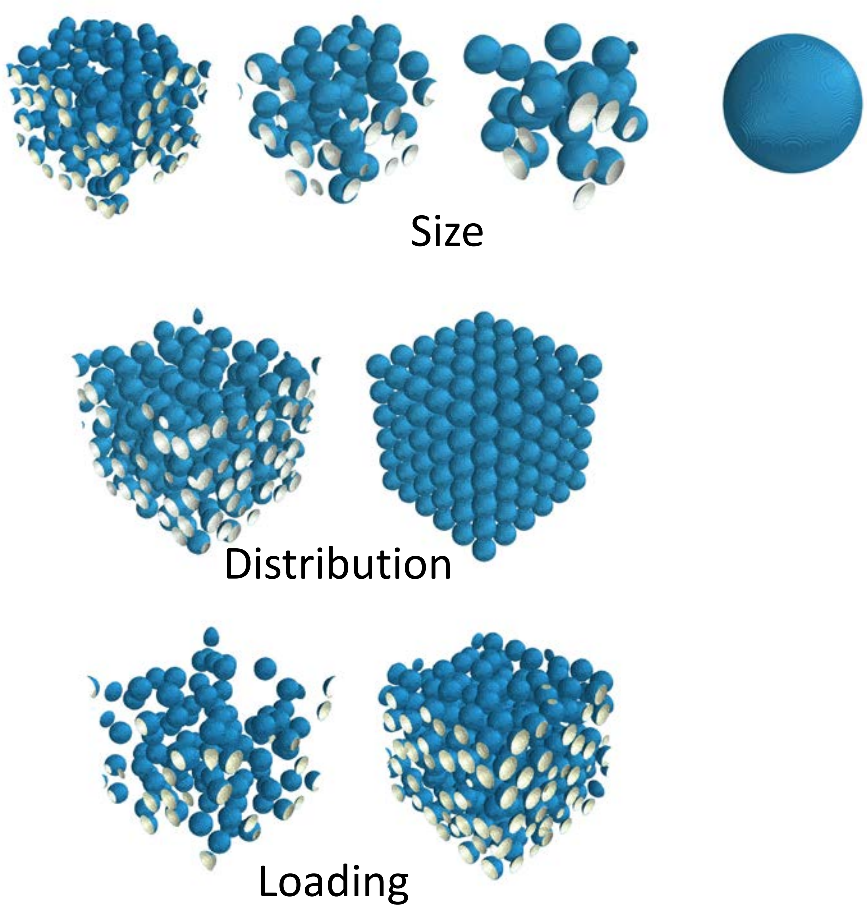
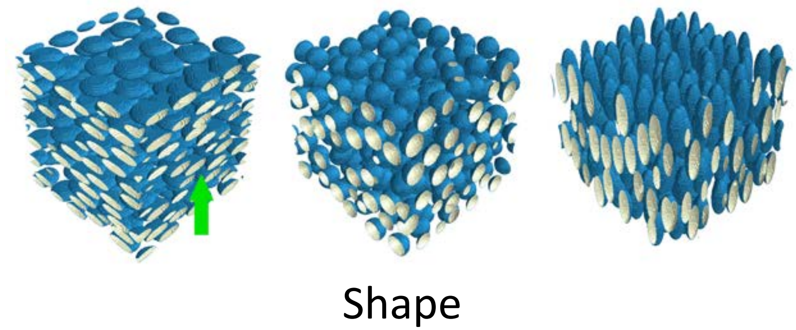
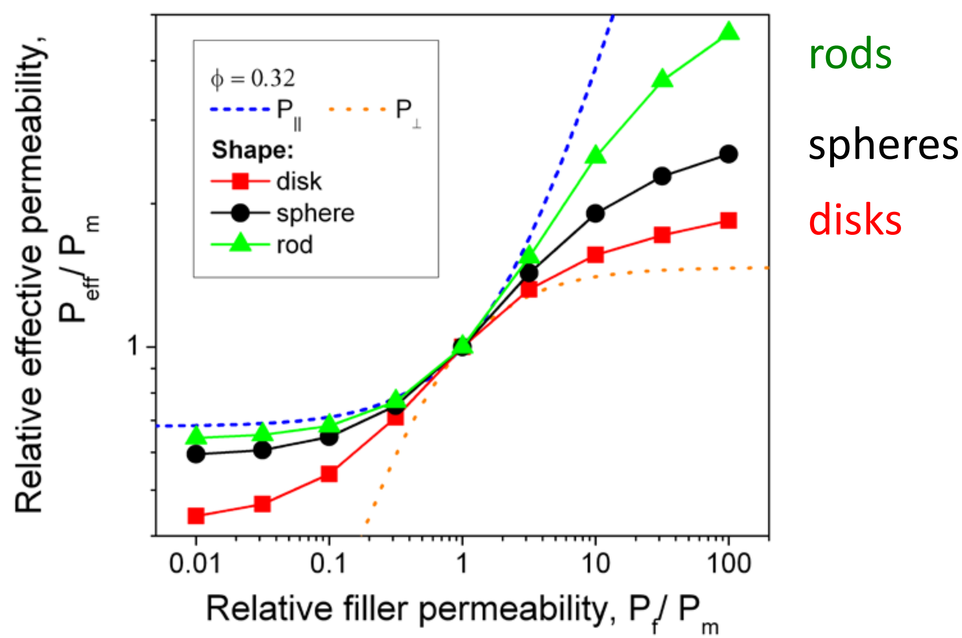


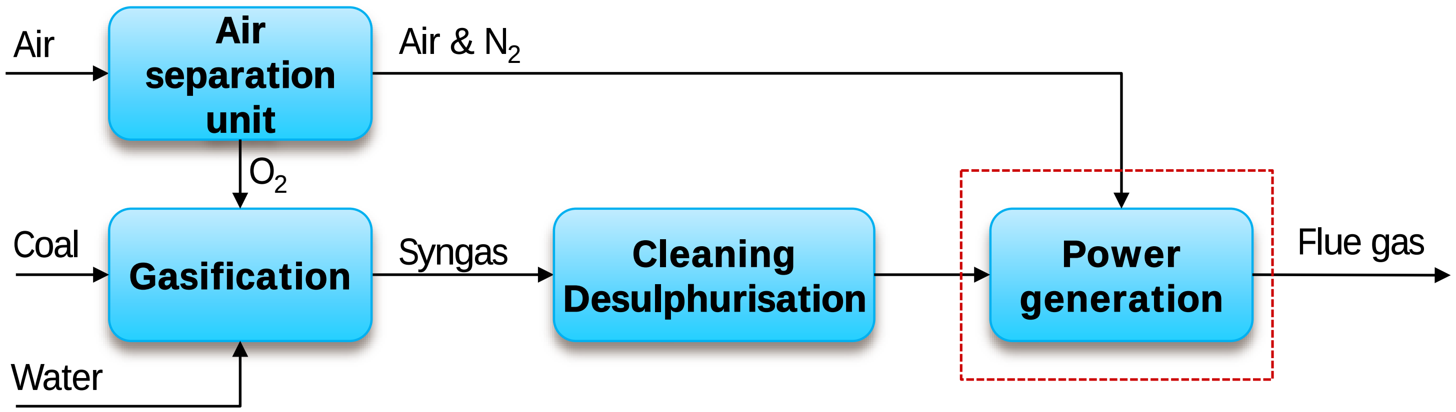




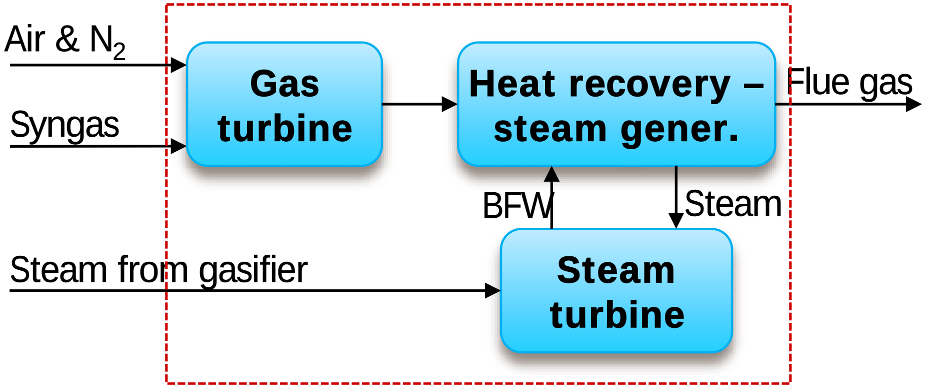
D. Schneider et al., submitted

Reference case

Coal-fired IGCC power plant without CO_2 capture

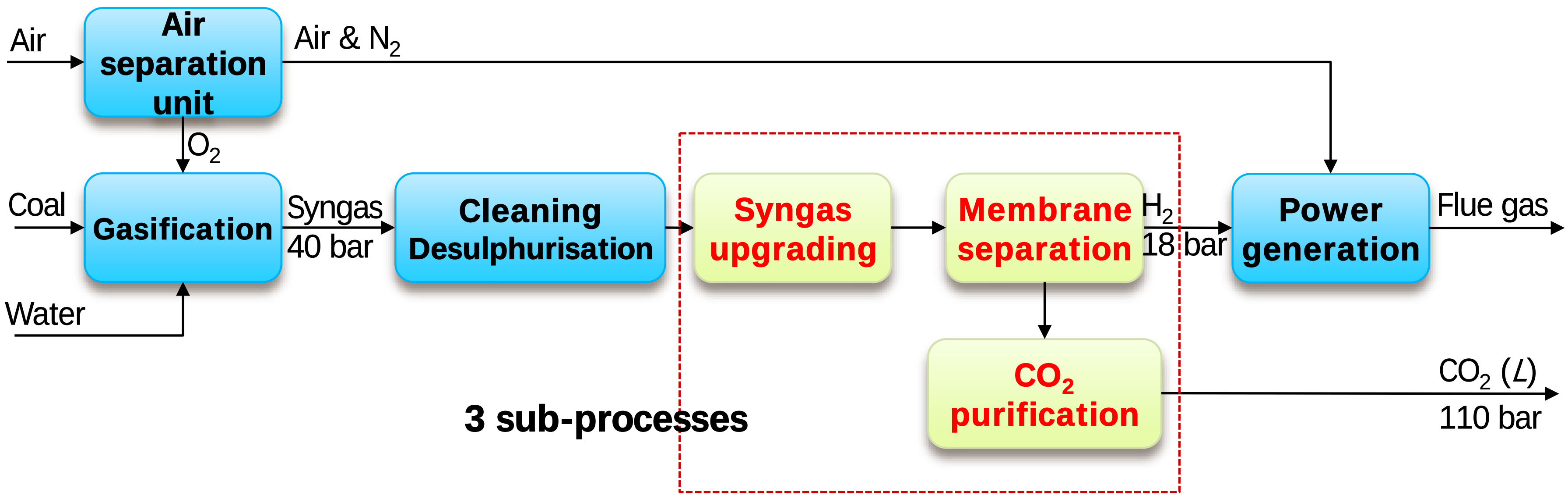


536 MW power output
43% efficiency
3.1 Mt/y CO_2 emissions



Combined Cycle efficiency 54%
Steam cycle efficiency 36%

Basis of design
IGCC plant with pre-combustion capture



- Coal IGCC power plant
- 536 MWe (7450 h/y, Netherlands)
- 3.1 Mt CO_2/y
- CO_2 recovery 90%

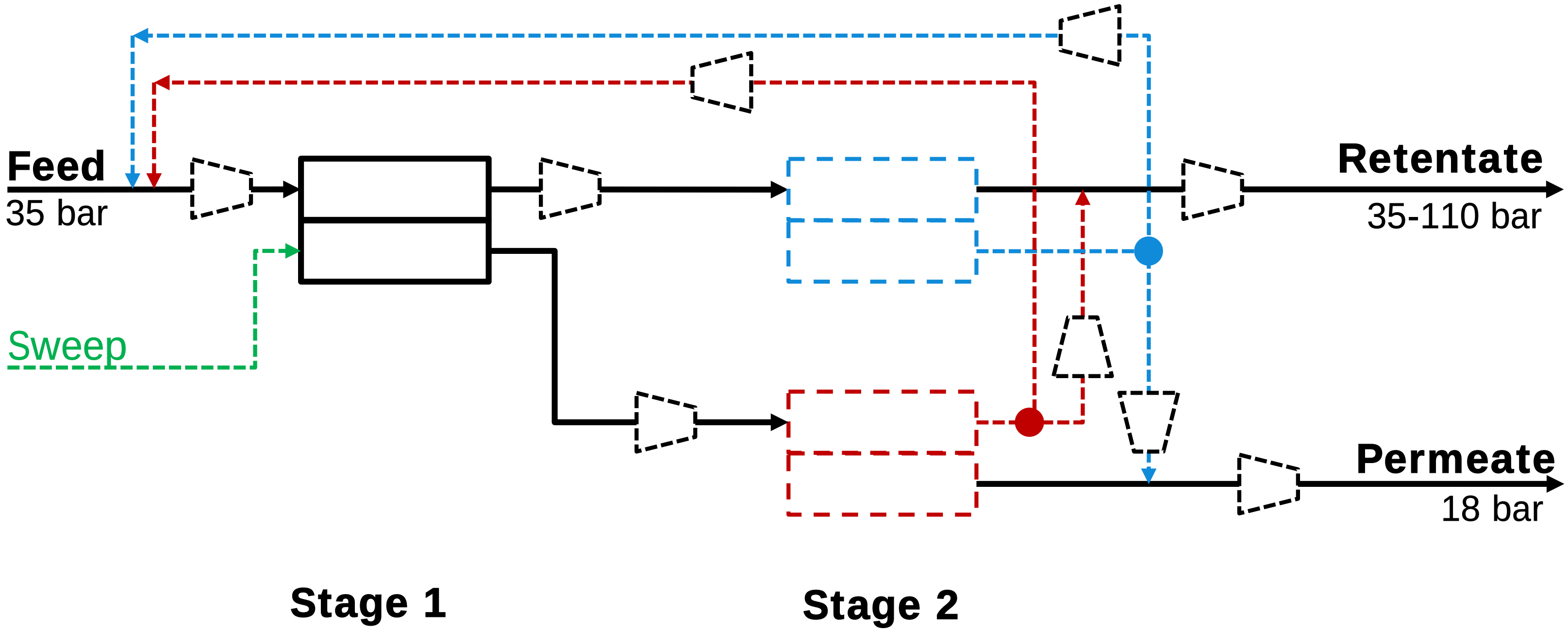
2.78 Mt/y of captured CO_2
?? MW power output
?? % efficiency

Process options – membrane separation

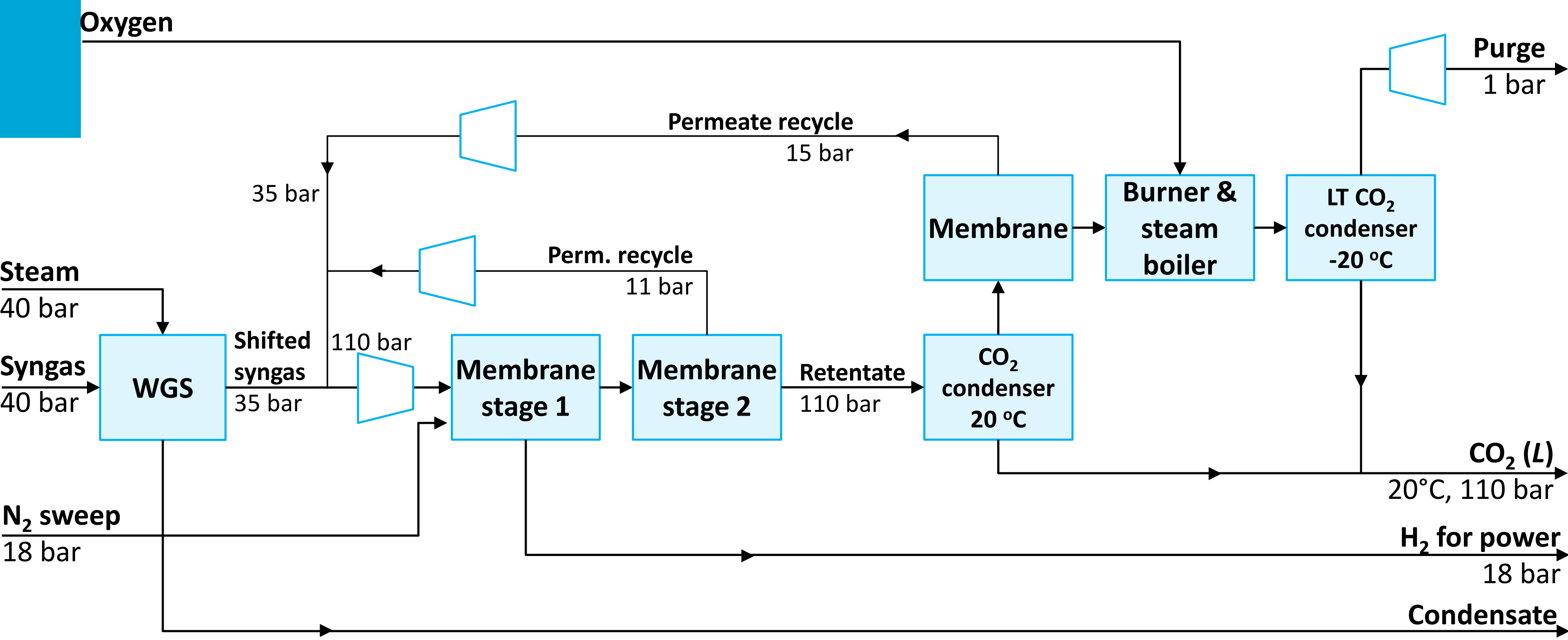
2-stage processes

- ∞ process options
  - # stages
  - pressures feed, permeate
  - Recycles
  - Recovery of species

→ Optimisation problem



Process flow scheme



Optimised scheme

Requires membrane operation at high pressure

Process economics

Designed capture process (110 bar)

- CAPEX 85 M€
- OPEX 25 M€ (excl. electricity)

Cost of captured CO_2 = 15.8 €/t

16.4 €/t 70 bar
18.2 €/t 35 bar

Item	Unit	Without capture	With capture	
Net power output	MW	536	489	-8.8%
Total investment	M€	1148	1233	
Specific investment	€/kW	2141	2522	
Cost of electricity	€/MWh	68.4	80.4	+17.6%, 12 €/MWh

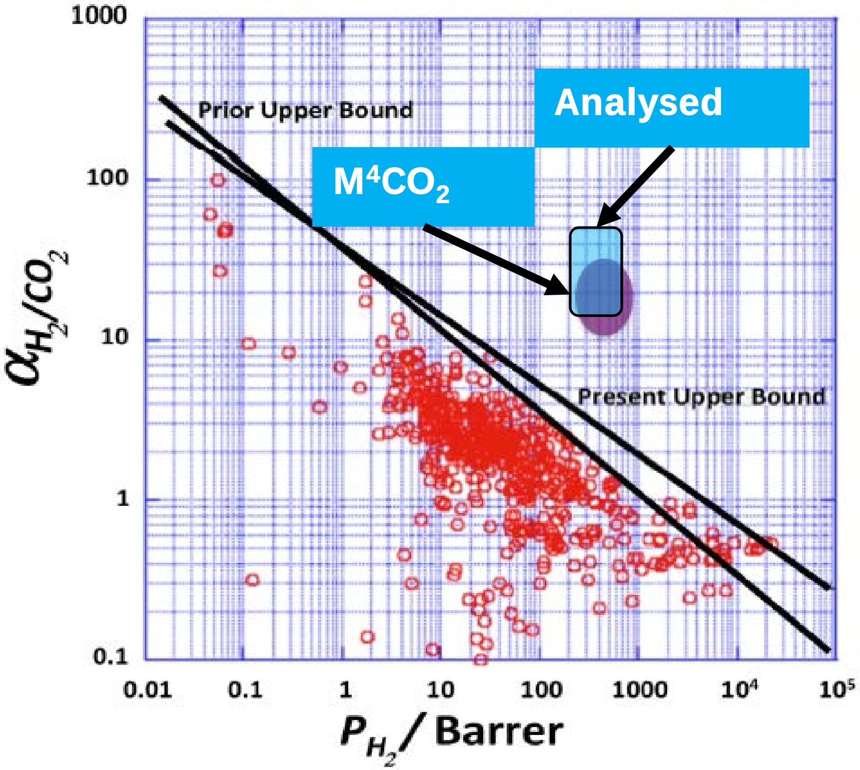
Profitability in 2030 (30 €/t CO_2)

- in 2015 not profitable (7 €/t CO_2)
- ROI = 23%
- Payback time = 3.5 years

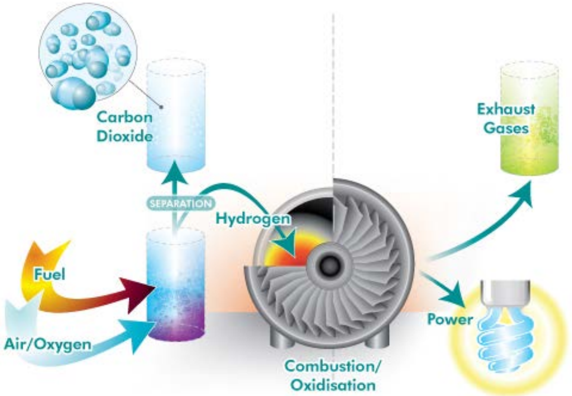
Sensitivity analysis

- CO_2 capture cost vs. Membrane performance
- → recommend further R&D

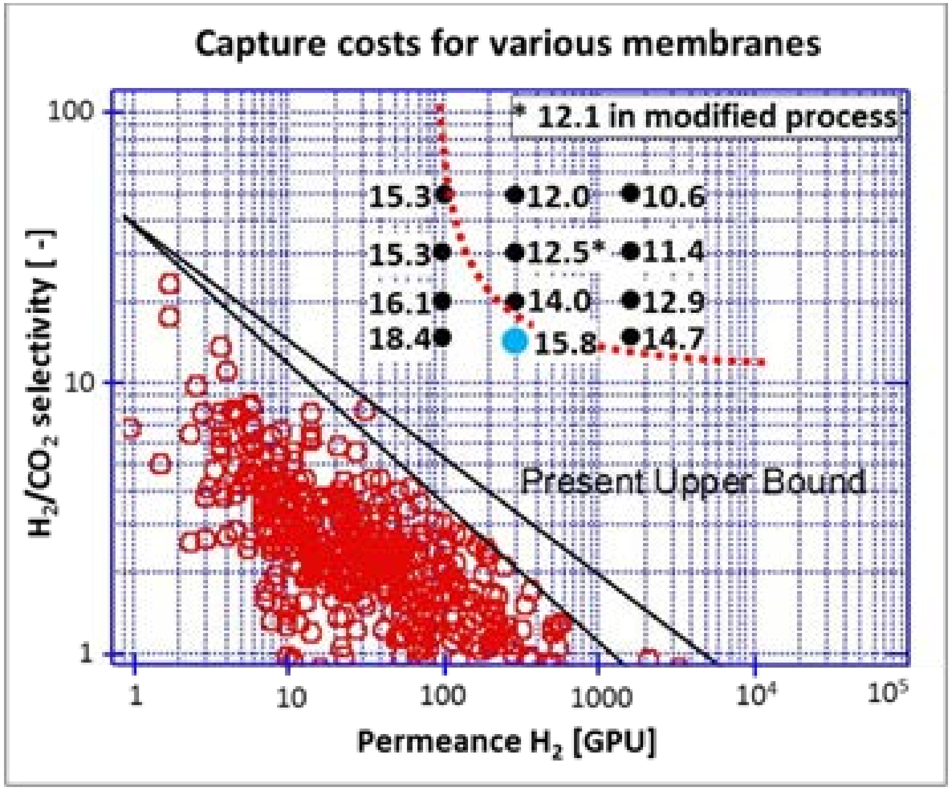
Analysed membranes	
Permeance (GPU)	Selectivity
100-1700	15-50



Pre-combustion concept design



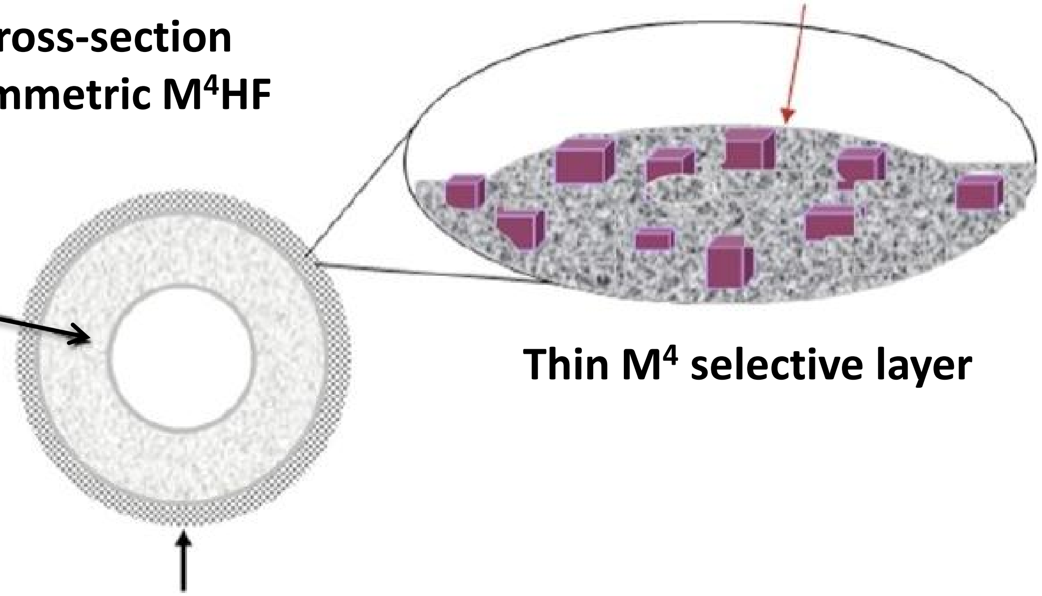
Sensitivity Analysis

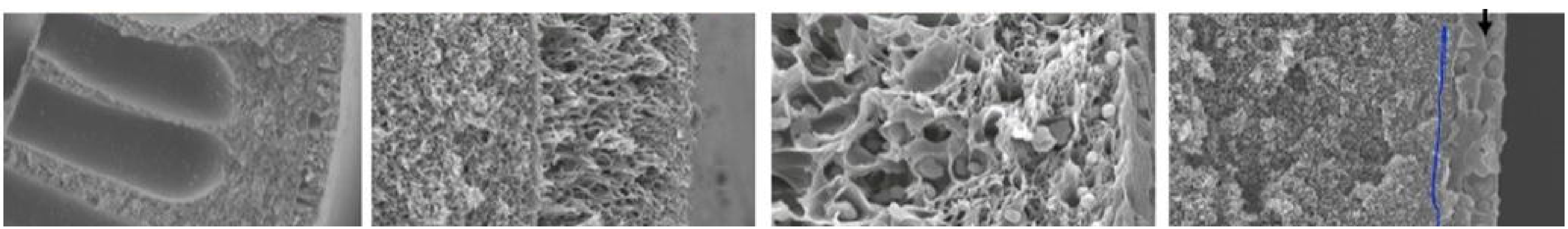


Improvement of selectivity will allow capturing for <15 €/t

Permeability high enough
Selectivity >30 not useful

Hollow Fibre (HF) membranes

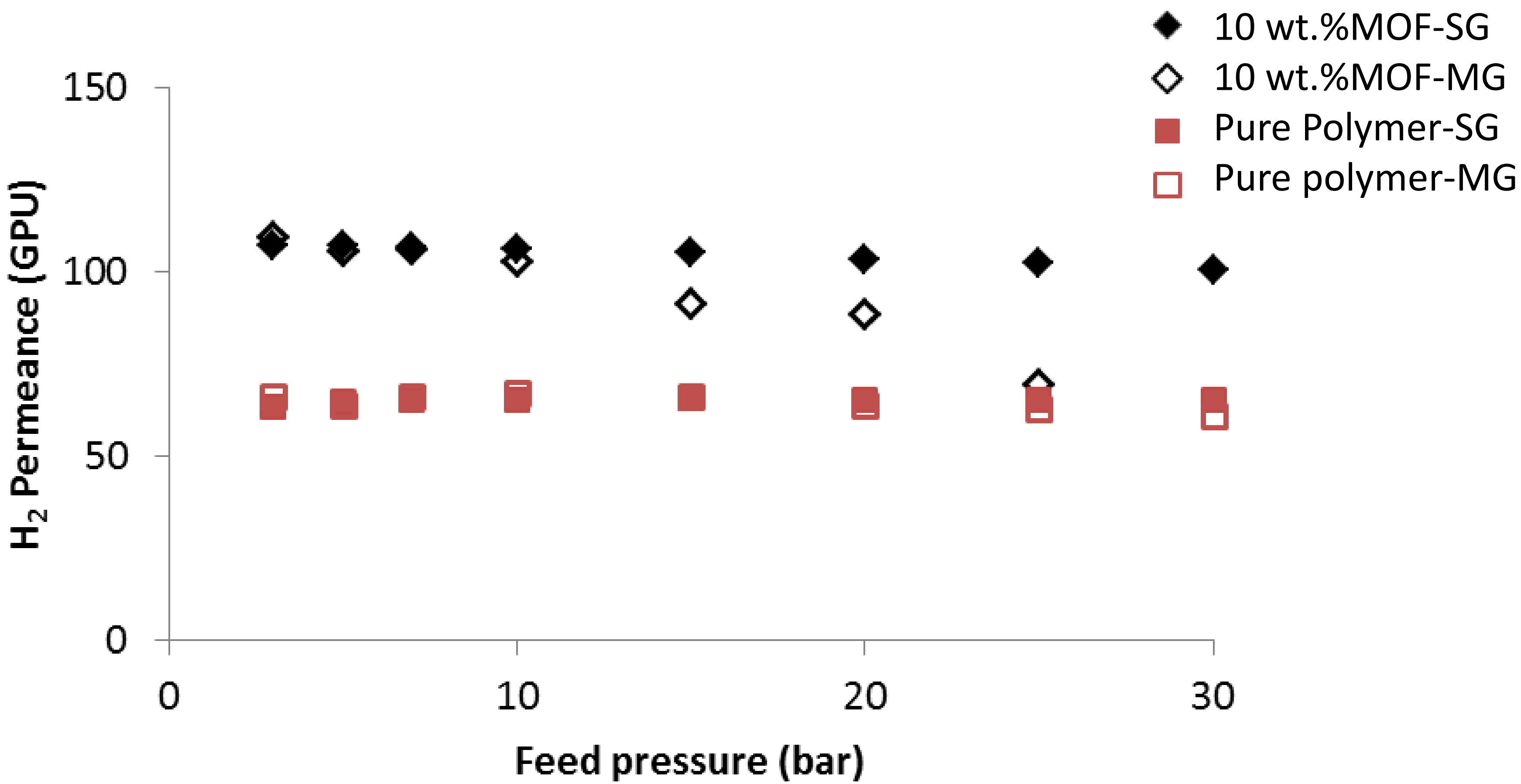




First performance of M4-HFMs

Single and Mixed gas permeation

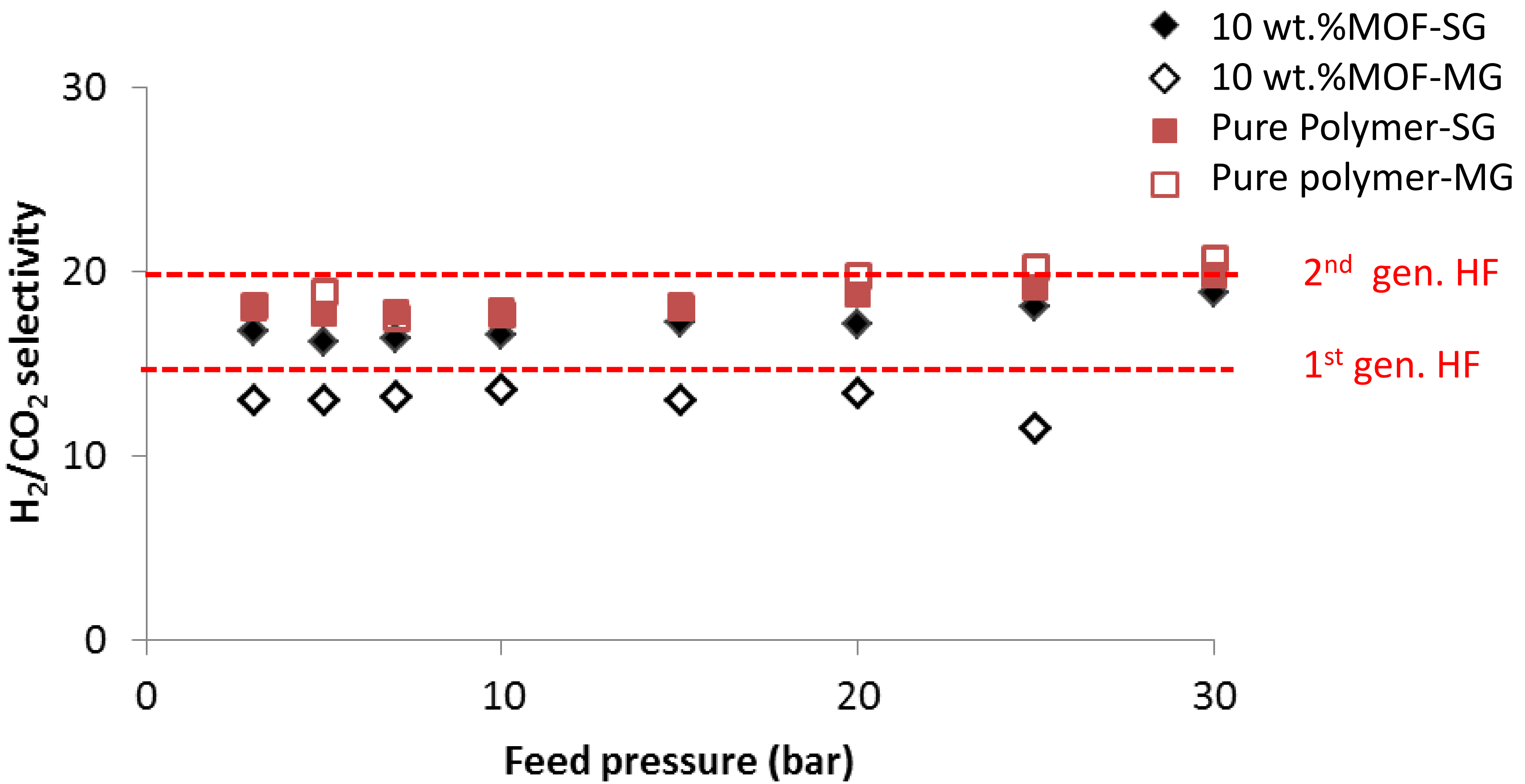
Single Gas (SG) and Mixed Gas (MG) 50%H_2/50%CO_2 @ 150ºC



First performance of M4-HFMs

Single and Mixed gas permeation

Single Gas (SG) and Mixed Gas (MG) 50%H_2/50%CO_2 @ 150ºC



Independently confirmed by partner

ITM-CNR
Istituto per la Tecnologia delle Membrane

Constant velocity dip-coating

Proof of principle – lab scale
‘Pull-through coater’

The fiber is fixed between the clamps of a tensile tester and is pulled out from the polymer solution at a controlled speed.

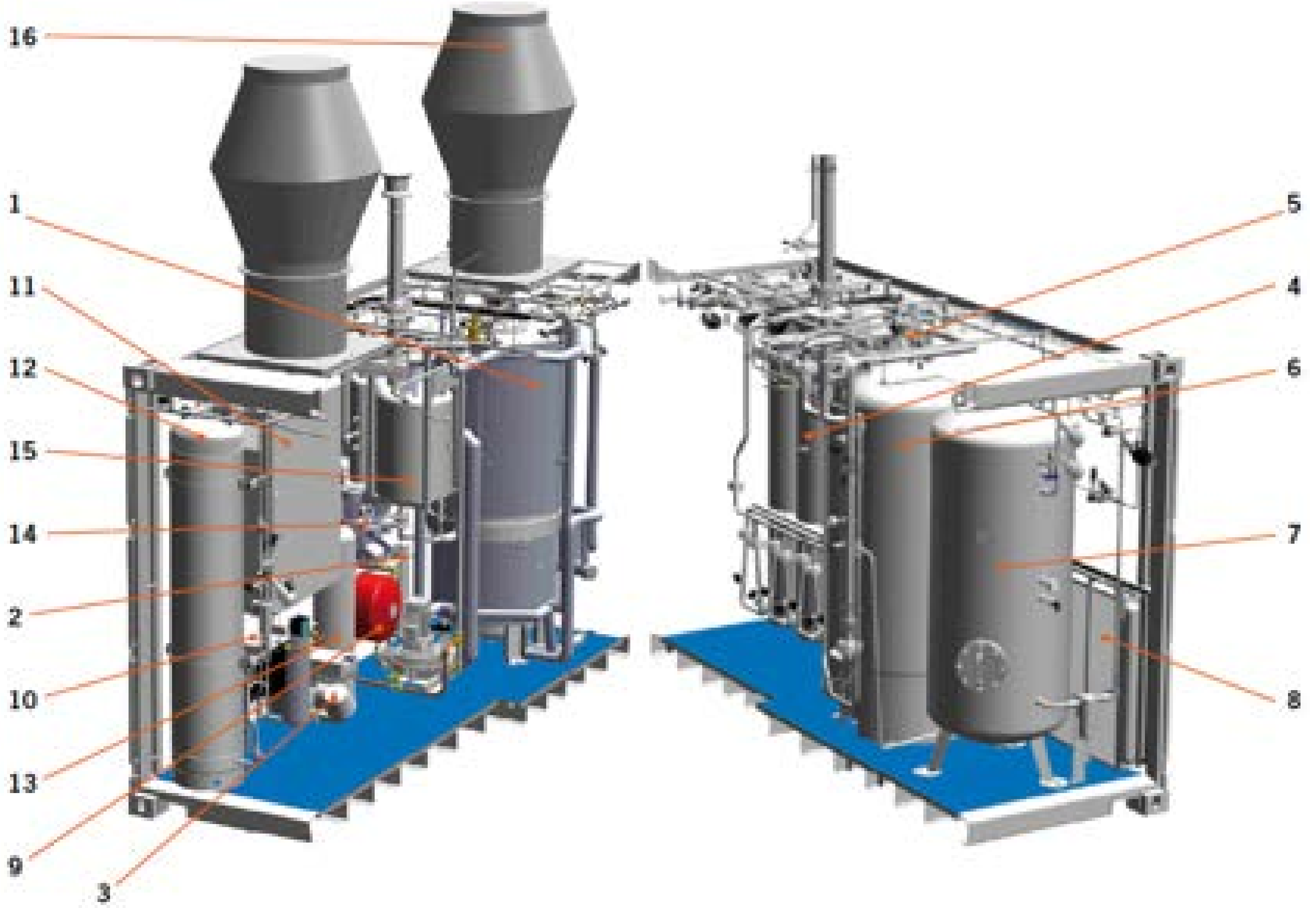
This automatic device, having a working height of ca. 1 meter, can be applied to coat

- fibers with a length even larger than 50 cm, or continuously
- working at a speed that can be varied in a quite large range (e.g., 1 - 500 mm/min).

Modules manufacturing at Polymem

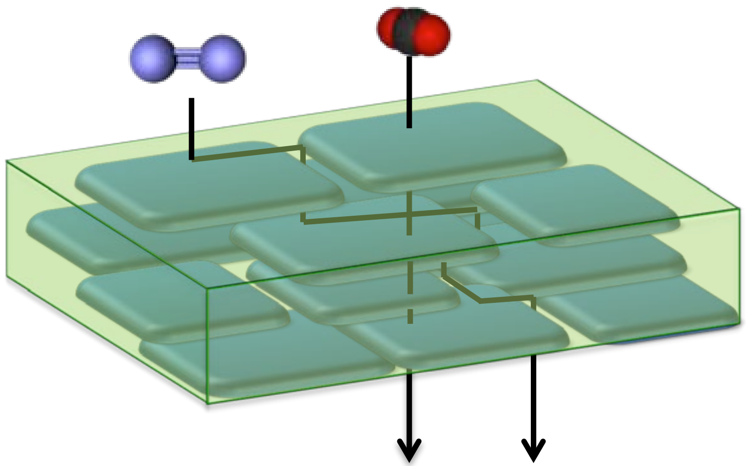
Pre-combustion module (100 fibres, 80 cm) to be tested at Hygear

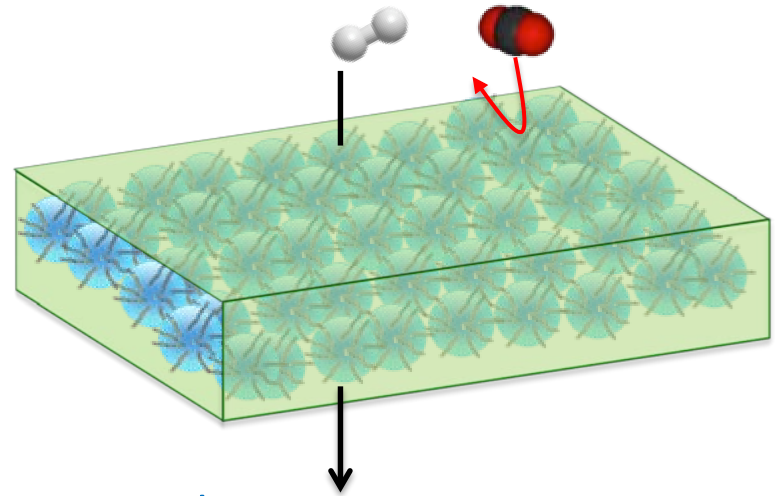
Experimental infrastructure



1. Reformer unit and burner
2. Water Gas Shift assembly
3. Burner blower
4. PSA vessels
5. DI water storage
6. Off gas storage
7. H_2 storage
8. After cooler
9. Coolant Expansion vessel
10. Water Purification system
11. Electronics cabinet
12. Desulphurization system
13. Mixed bed filter
14. Water pumps
15. Steam generator
16. Jetcap

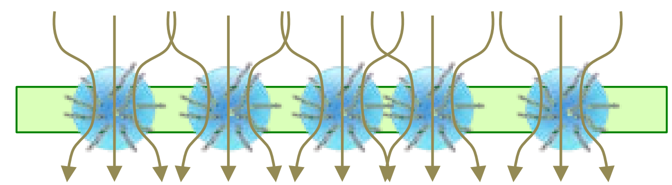
Flux - Selectivity improvements





Selective polymers:

- Flux improvements
  - Hollow spheres
  - Mesoporous, good adsorption
- Shorter effective path-lengths

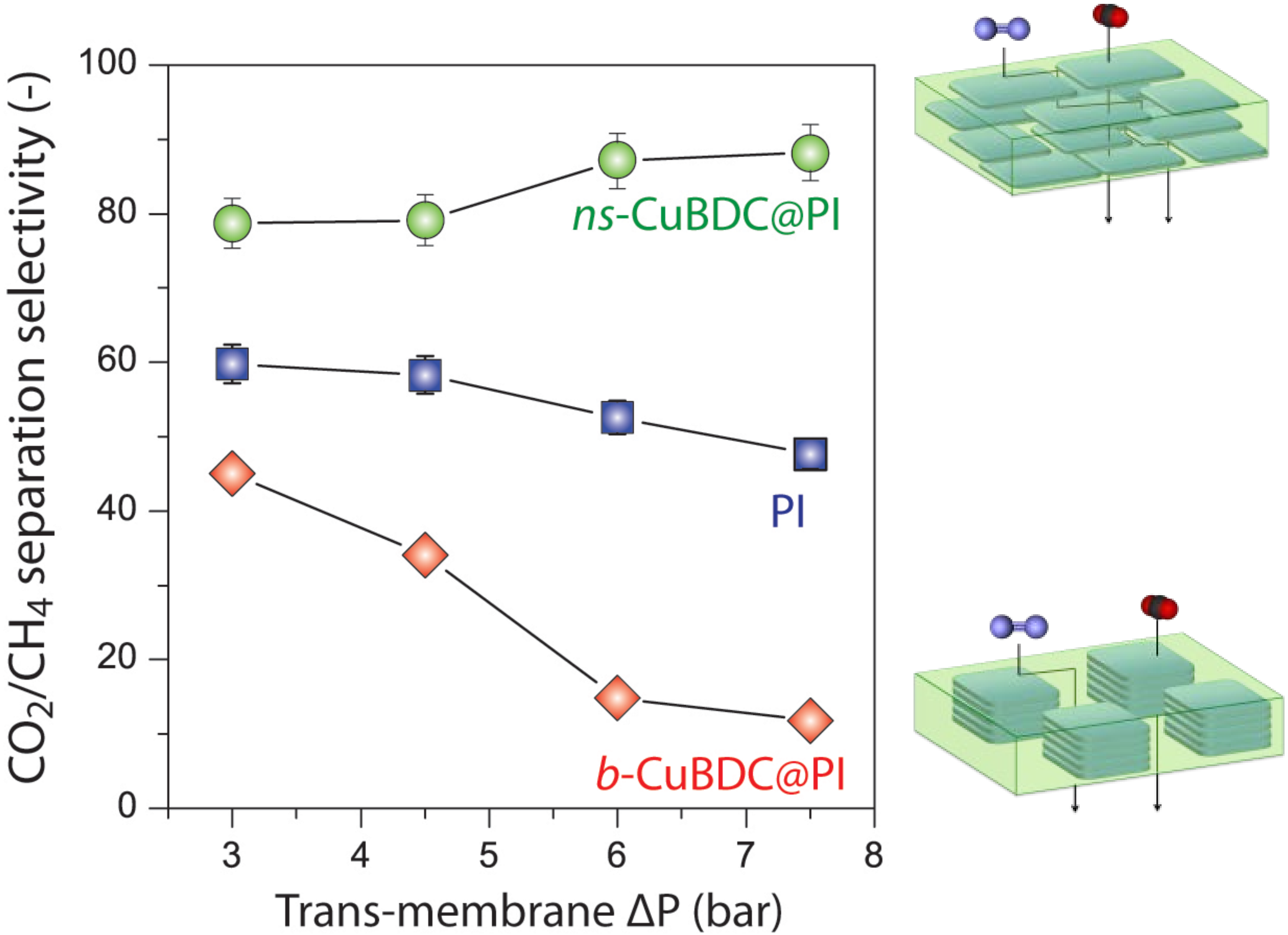


- Percolation membranes

High flux polymers:

- Selective fillers
  - Increased path-lengths
    - tuned aspect ratio
  - Adsorption selective

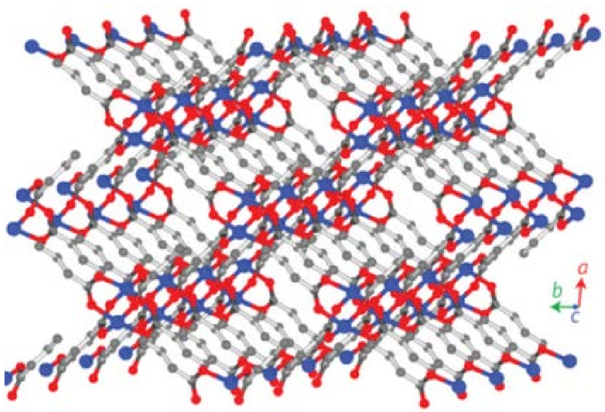
Separation performance

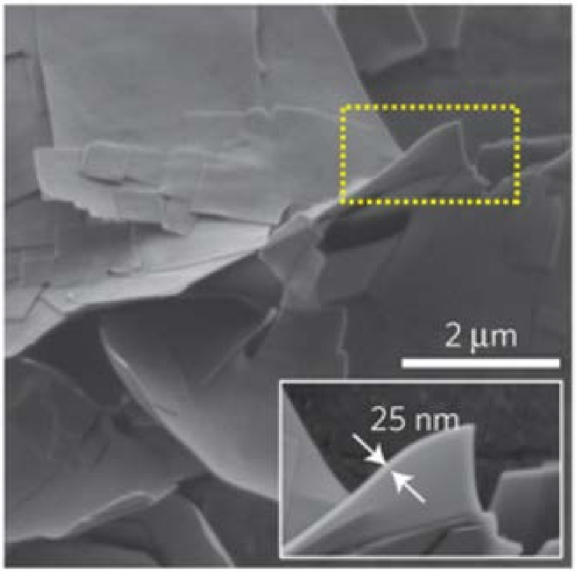


Rodenas *et al.* Nature Materials 14, 48–55 (2015)

Cu-BDC/Matrimid

WP4





Aged (3 years) Cu-BDC platelet/Matrimid (15/85 CO_2/N_2 mixed gas @ 25 °C heat treated @ 180 °C)

Membrane (wt%)	*Δp*(bar)	CO_2 (Barrer)	N_2 (Barrer)	α (CO_2/N_2)
0	1	9 ± 0	0.4 ± 0.0	23± 1
8	1	18 ± 0	0.3 ± 0.0	57 ± 1
8	2	14 ± 0	0.3 ± 0.0	46 ± 2

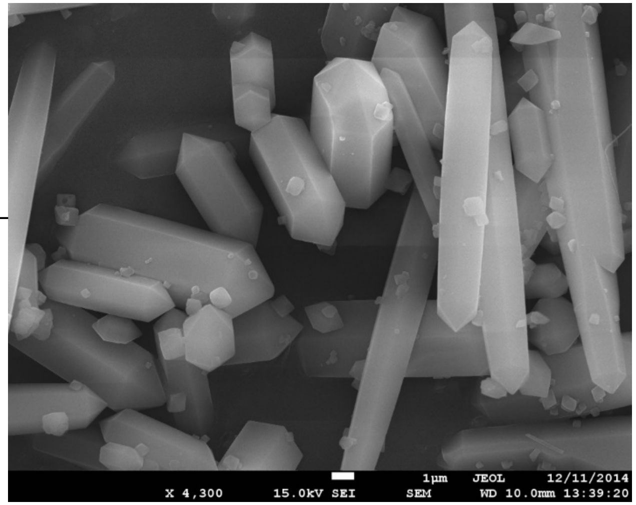
- Permeability (low) and selectivity both improved with MOF
- Stable system

Rodenas et al, Nat. Mater. 2015

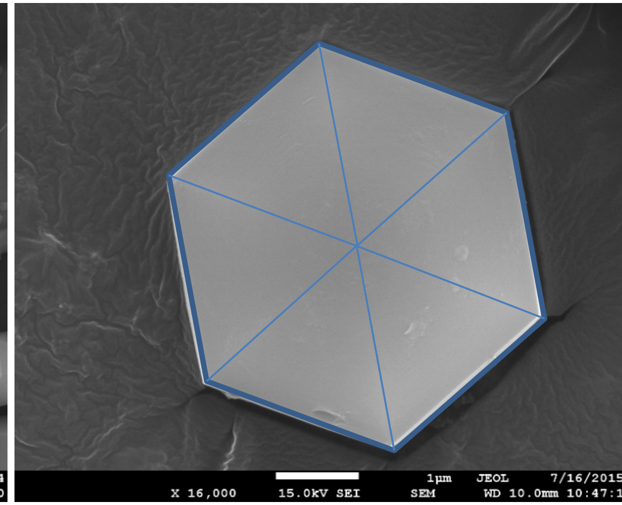
MIL-96(Al)

3^{rd} generation nanoMOFs

__Hydrothermal__
Hexagonal rods

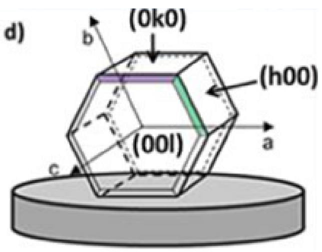


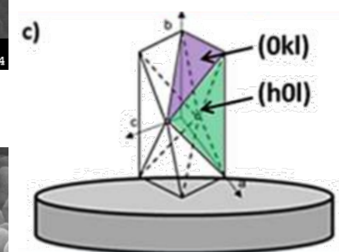
Up to 20μm long



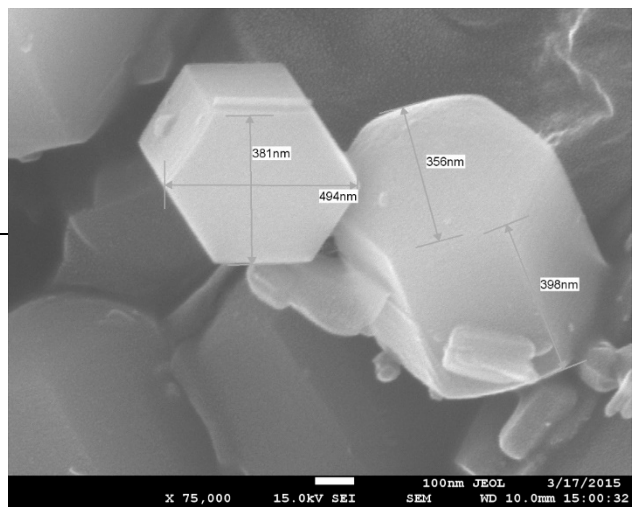
Up to 300nm thick

__Microwave__
Hexagonal platelets

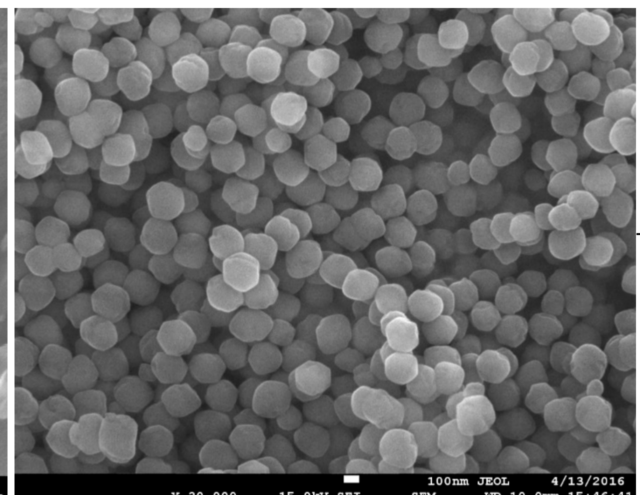




__Reflux H_2O__
nano rods



Intermediate shape



150nm

__Reflux H_2O/DMF__
nano spheres

Control of morphology influencing diffusion properties

A. Knebel *et al*, *ACS Appl. Mater. Interfaces*, 8, 7536, 2016

M^4CO_2 status – Summer 2017

- Project runs in-line with planning
- Process designs guide development direction
  - Selectivity strongest sensitivity
- 1st and 2nd generation materials identified – proof-of-principle PT
  - Development lamellar and layered 3rd generation materials
  - MOF stabilized in M4's (3 year)?
- Uniformity in membrane testing
- Hollow fibre membrane manufacture
  - Pre-combustion selectivity specs reached
  - Films and HF differ in performance
- Supporting studies provide
  - Insight in performance, polymer-MOF interaction, adsorption and diffusion, morphology
  - New experimental and modeling techniques in-situ performance studies

>90 dissemination items

Scale up challenging

Follow-up NMBP projects under negotiation

We cordially invite you to