MATESA MEETING OSLO, NORWAY, 16 JUNE 2016
UPDATE

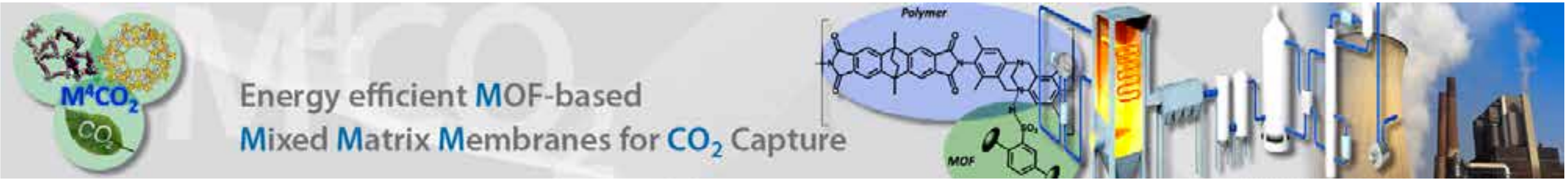
Energy efficient
MOF-based **M**ixed-**M**atrix **M**embranes
for
CO_2 **C**apture

M^4CO_2

FP7 project # 608490

1 January 2014 – 31 December 2017

www.m4co2.eu/

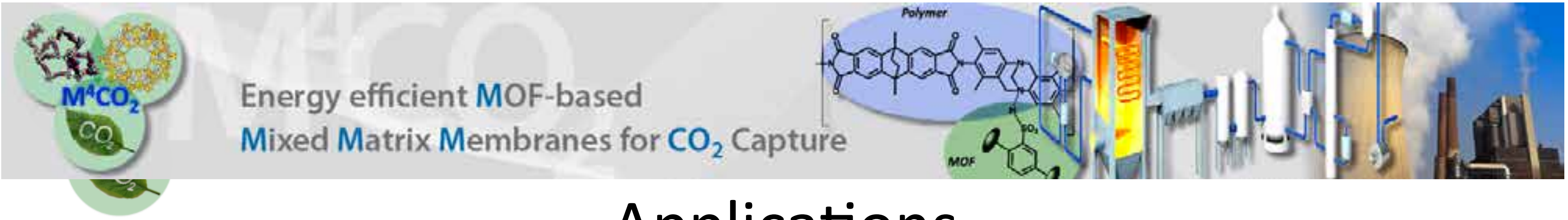


M^4CO_2 project aims

- **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

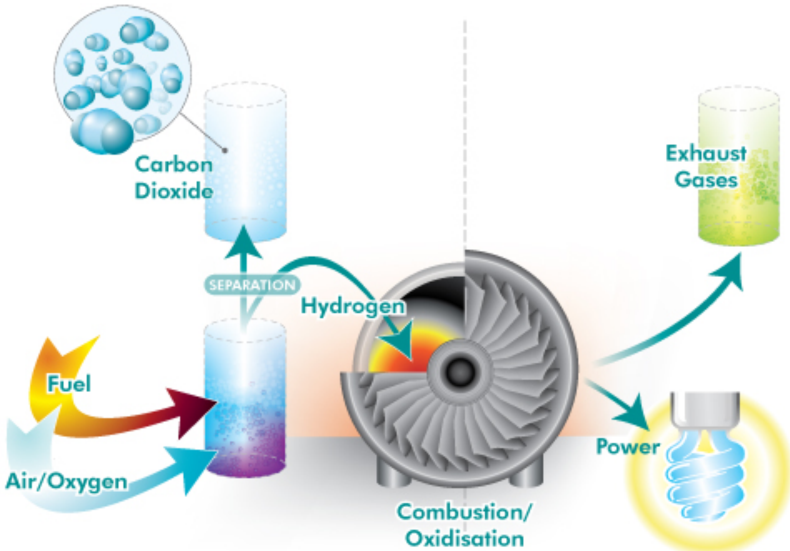
- **Target**
  - Highly selective high flux membranes
  - CO_2 capture meeting the targets of the European SET plan (90% of CO_2 recovery at a cost less than 25€/MWh)
    - Internal target 15 €/ton CO_2 (≈ 10-15 €/MWh)

www.m4co2.eu/



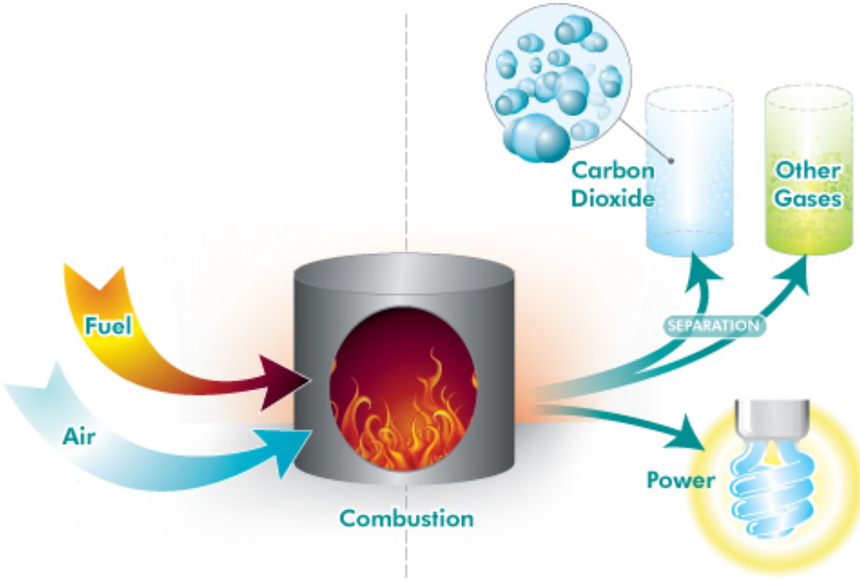
Applications

Pre-combustion CO_2 capture



CO_2 / H_2 mixtures

Post-combustion CO_2 capture



CO_2 / N_2 mixtures

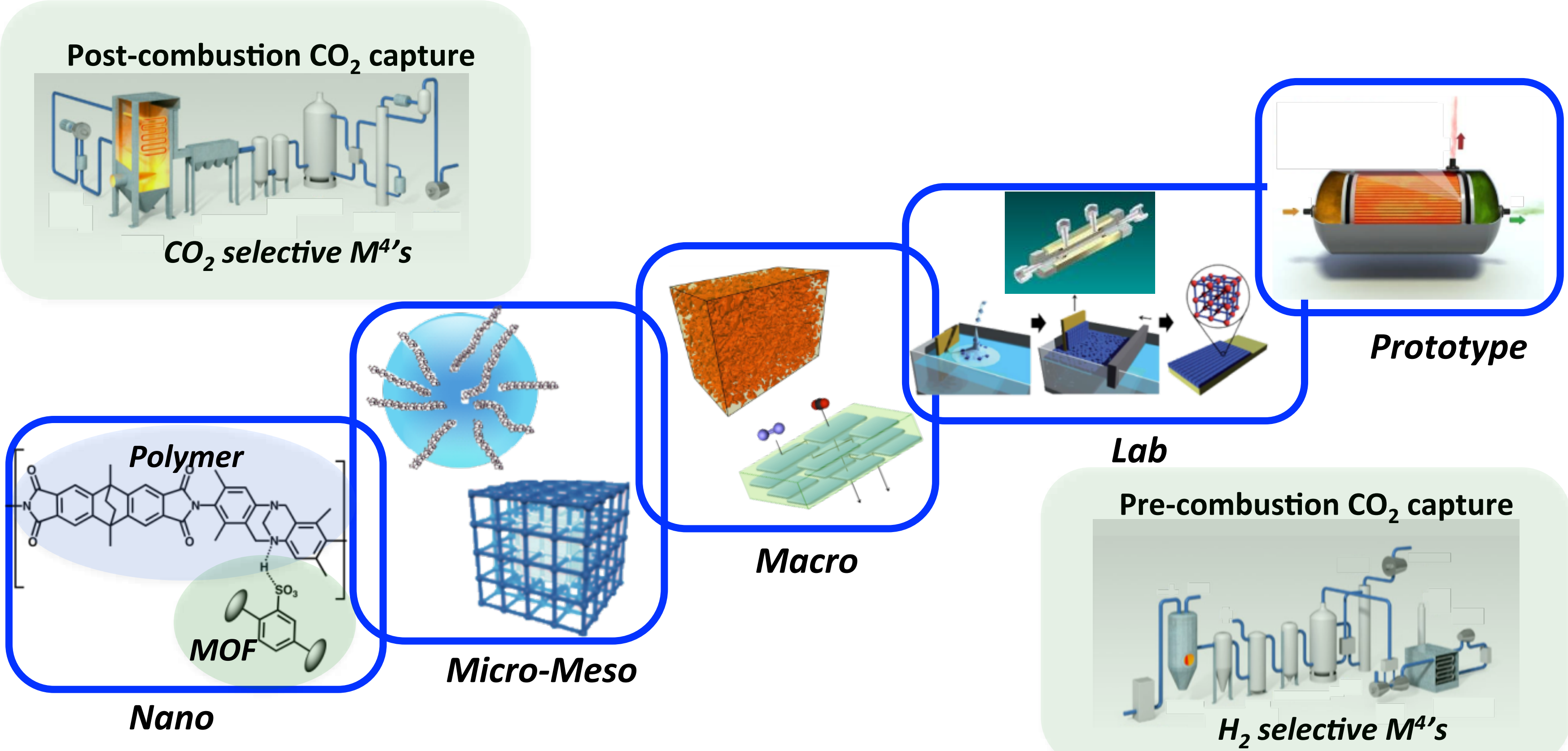
Bio-gas, natural gas upgrading CO_2 / CH_4 mixtures

H_2 selective membranes

CO_2 selective membranes

www.m4co2.eu

The Challenge



Partners consortium

M⁴CO₂

TU Delft Delft University of Technology

DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V.

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

CNRS Aix-Marseille Université

UMONS Université de Mons

ENSICAEN

Bulgarian Academy of Sciences 1869

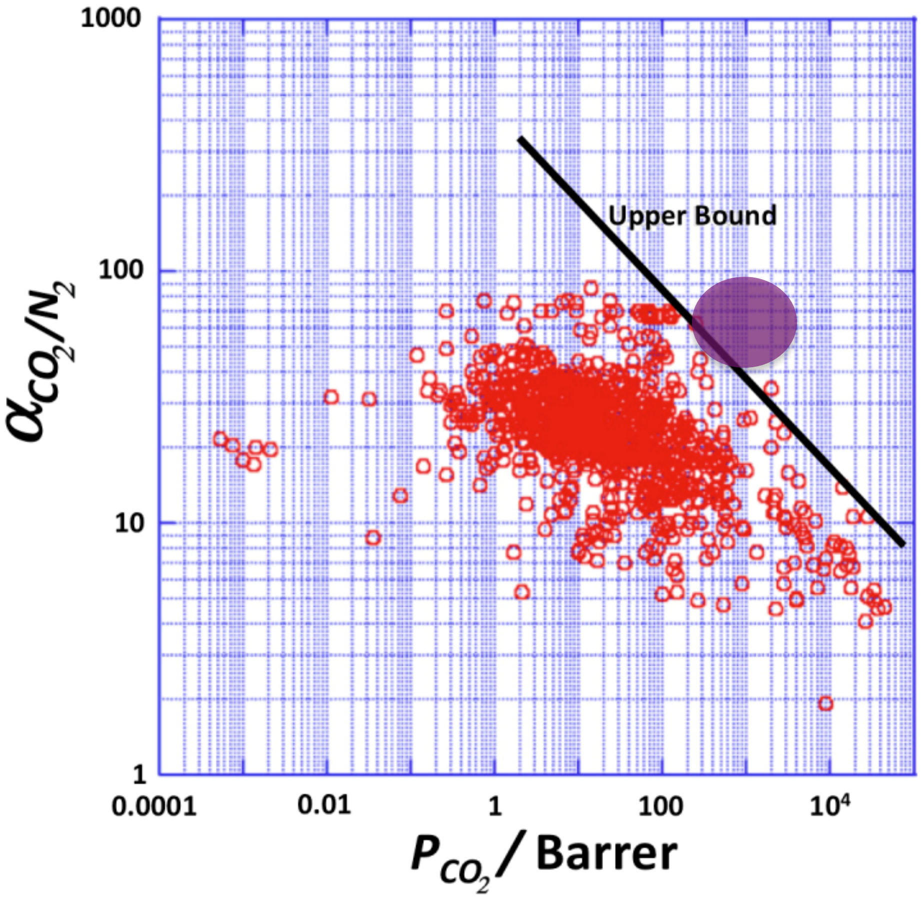
HYGEAR

JM Johnson Matthey

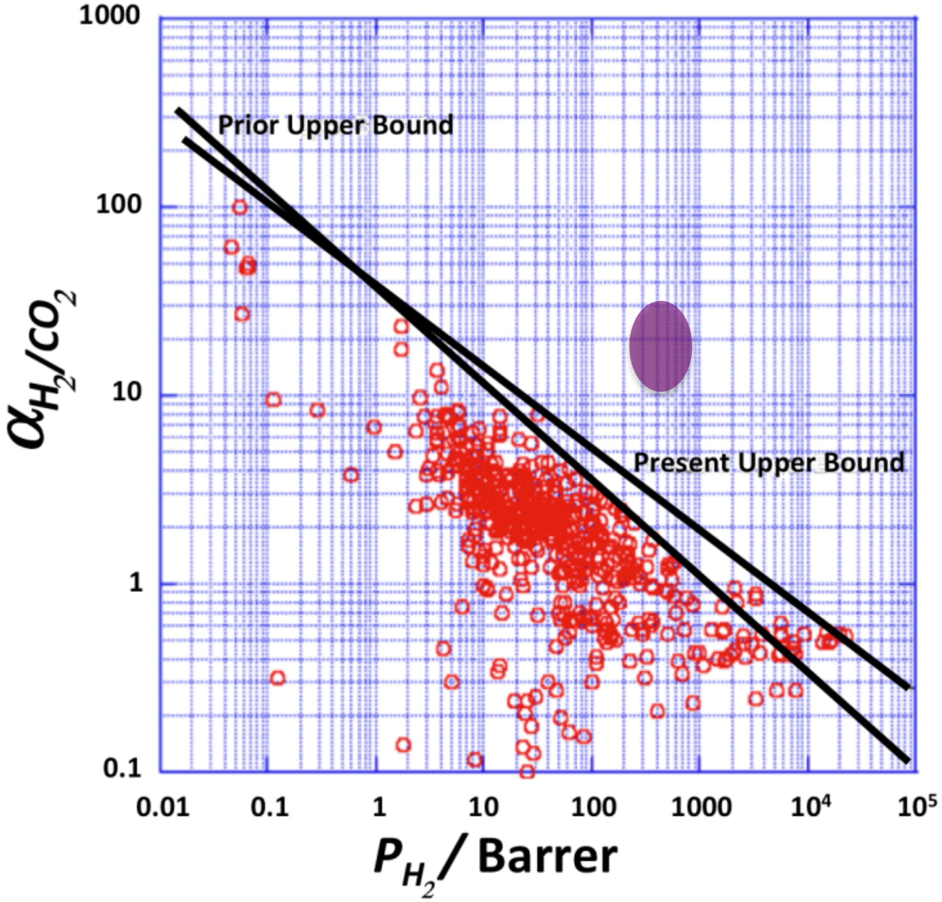
Membrane performances - targets

Robeson upper bounds for polymer membranes

Post-combustion



Pre-combustion



Breakthrough in membrane technology

Mixed Matrix Membranes (MMMs)

Polymeric Membranes

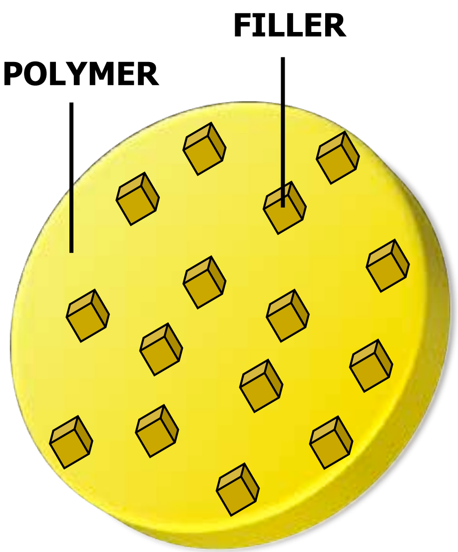
Pros:
- Mechanical stability
- Easy processing and low price

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)

Pros:
- Mechanical stability
- Easy processing and low price

Pros:
- 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.

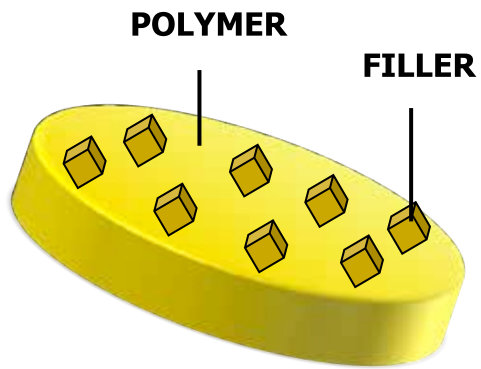
Mixed Matrix Membranes (MMMs)

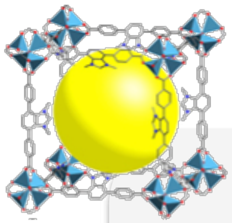
Mixed Matrix Membranes

Filler (Molecular sieve)
+
Matrix (Polymer)

- Mechanical stability
- Easy processing and low price

- Chemical stability
- Gas sieving properties





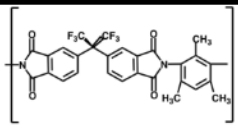
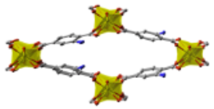
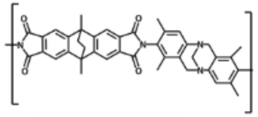
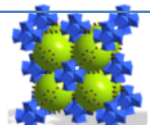
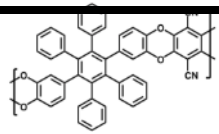
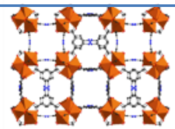
MOFs as fillers

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

Good match between filler and matrix is required

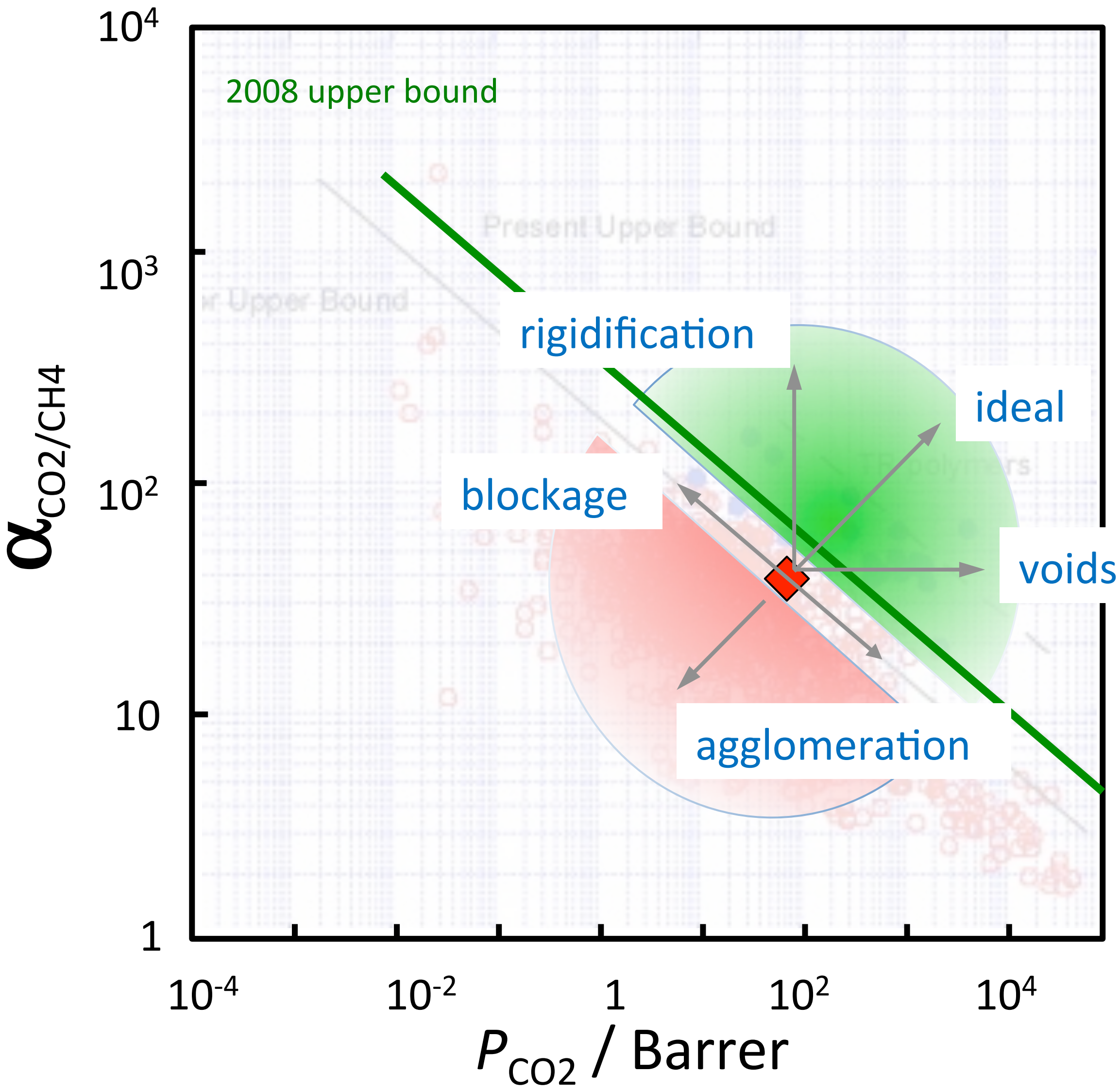
J. L. C. Rowsell, O. M. Yaghi, *Microp. Mes. Mater.*, **2004**, *73*, 3-14, and references therein.
E. Stavitski, J. Gascon, F. Kapteijn, et al. *Langmuir*, **2011**, *27*, 3970-3976.

Membrane targets

Membrane Generation	Main components		Scale	Target performance	
				Pre-combustion	Post-combustion
M^4 G-1	Commercial Polymers		Lab	300-1000 GPU P_{H2} > 300 Barrer	500-2000 GPU P_{CO2} > 500 Barrer
	MOF nanoparticles		HF	$a(H_2/CO_2)$ > 15	$a(CO_2/N_2)$ > 50
M^4 G-2	New functionalized polymers		Lab HF	P_{H2} > 400 Barrer	P_{CO2} > 800 Barrer
	Compatibilized MOF nanoparticles		PT	$a(H_2/CO_2)$ > 20	$a(CO_2/N_2)$ > 60
M^4 G-3	New functionalized polymers		Lab	P_{H2} > 500 Barrer	P_{CO2} > 1200 Barrer
	Compatibilized engineered MOF nanoparticles			$a(H_2/CO_2)$ > 30	$a(CO_2/N_2)$ > 70

>>SET targets

Robeson plot – effect of filler

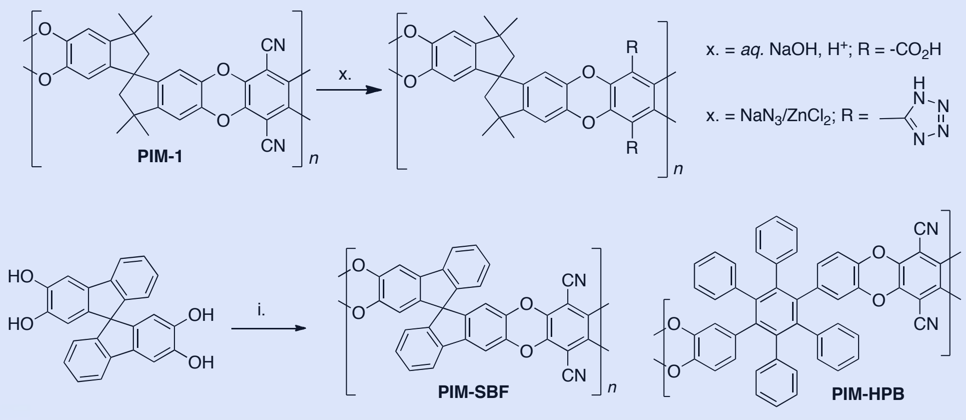


Targets development M^4CO_2 components

- **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
- The thorough **economic evaluation** and **conceptual process designs** for the real life applications of the new membranes

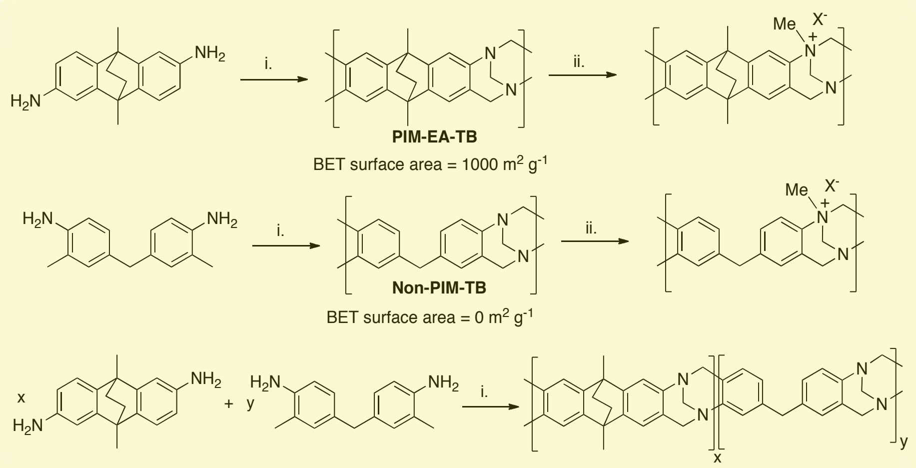
→ **Breakthrough in membrane technology**

WP-2 Polymer development



Post-combustion
High-flux polymers

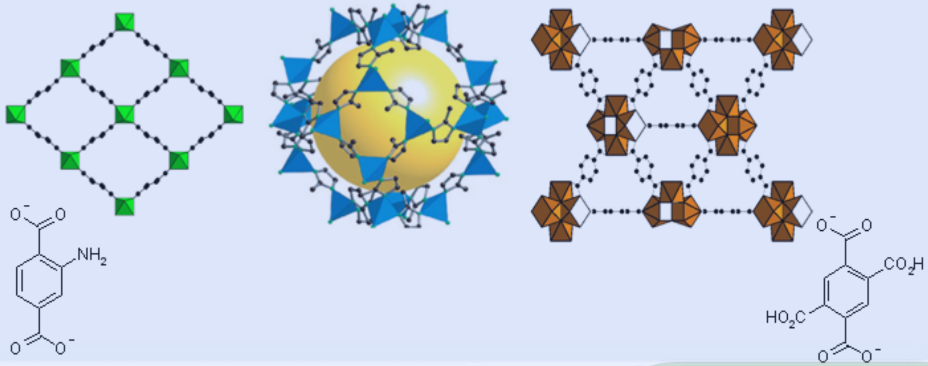
Polyimides of Intrinsic Microporosity
Polybenzimidazoles



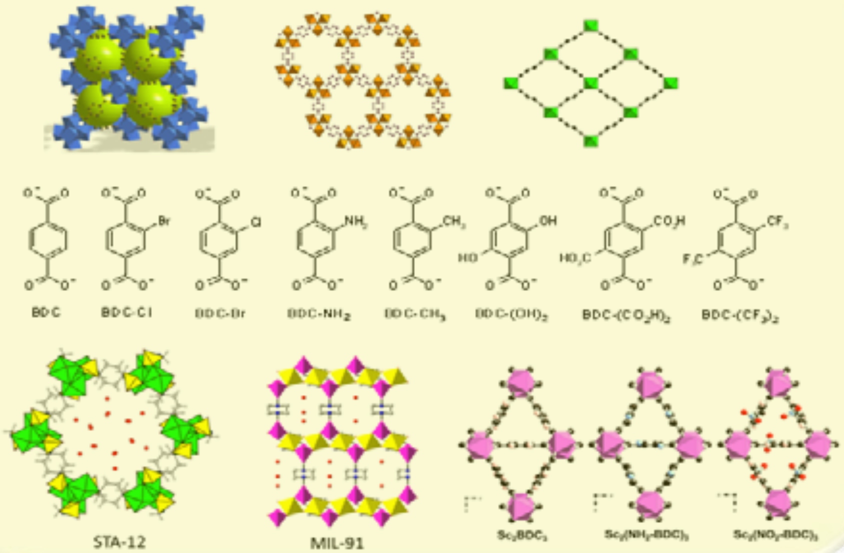
Pre-combustion
High-selectivity polymers

WP-2 MOF development

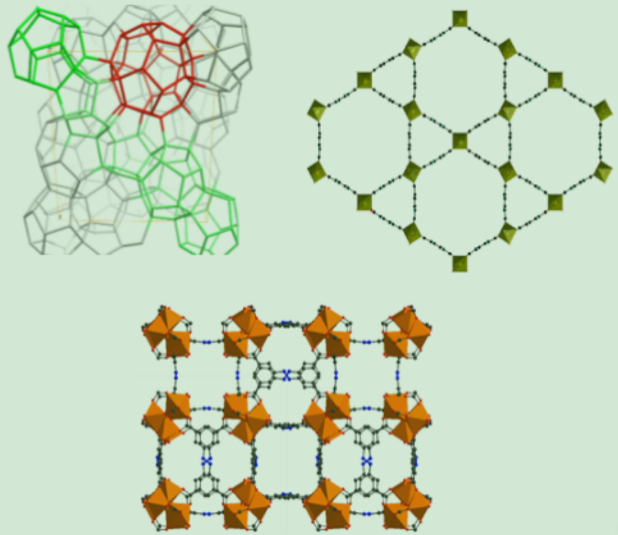
1st Generation



2nd Generation



3rd Generation

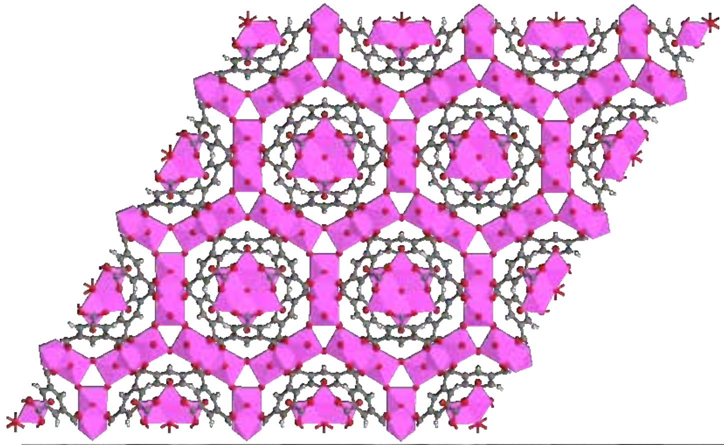


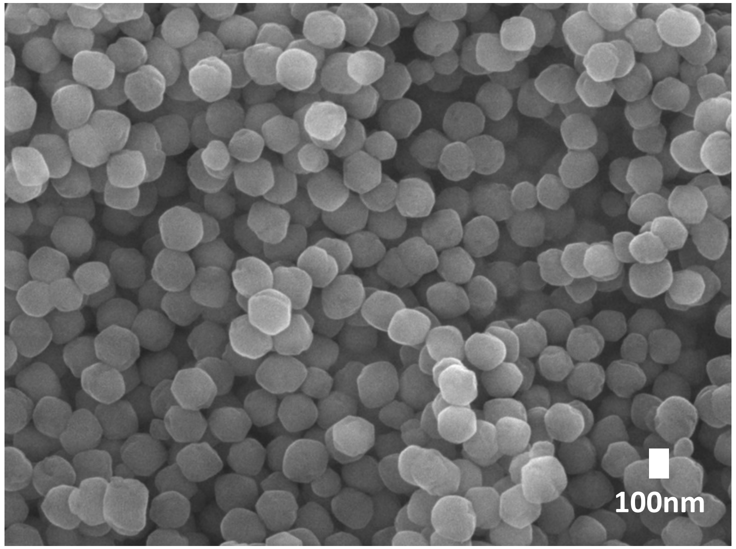
2^{nd} generation nanoMOFs

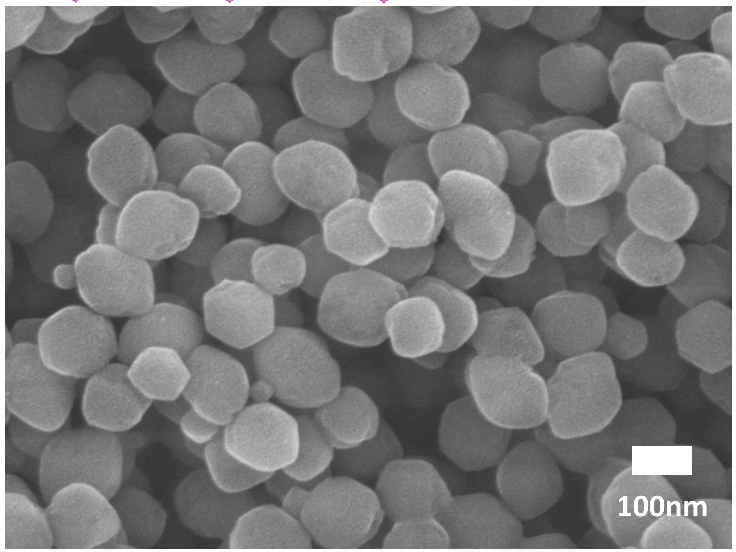
Candidate for 2^{nd} Gen post-combustion which presents good hydrothermal stability and performances under wet conditions

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)







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

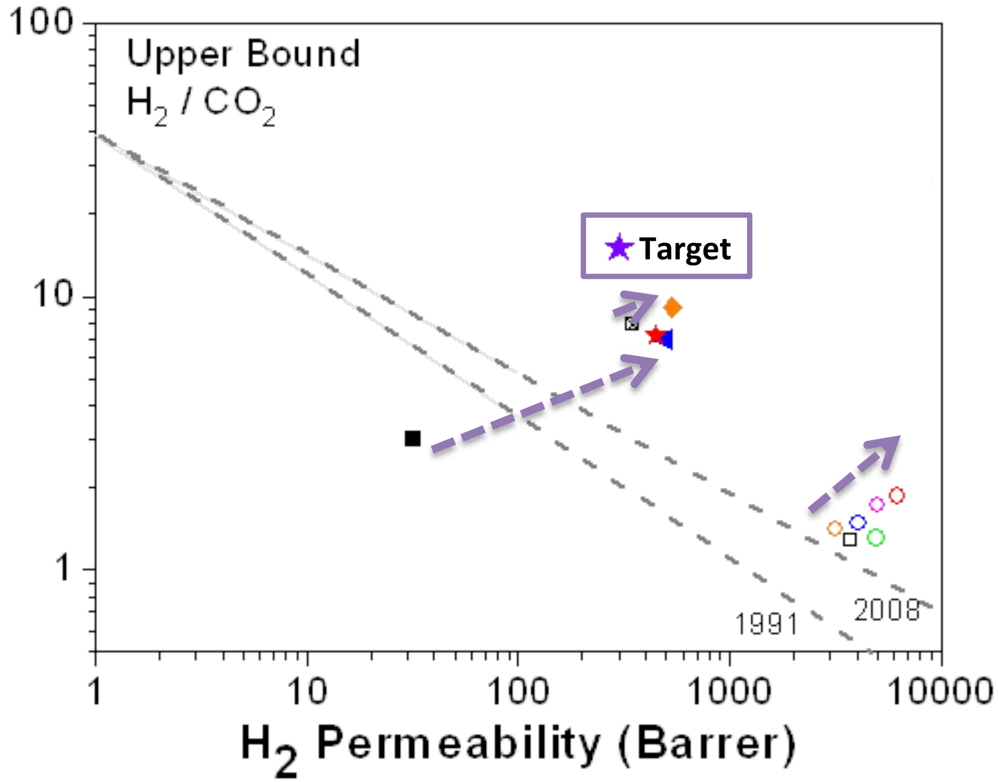
Javier Sánchez-Laínez[a], Beatriz Zornoza[a], Sebastian Friebe[b], Jürgen Caro[b], Shuai Cao[c], Anahid Sabetghadam[d], Beatriz Seoane[d], Jorge Gascon[d], Freek Kapteijn[d], Clément Le Guillouzer[e], Guillaume Clet[e], Marco Daturi[e], Carlos Téllez[a], Joaquín Coronas[a,*]

[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

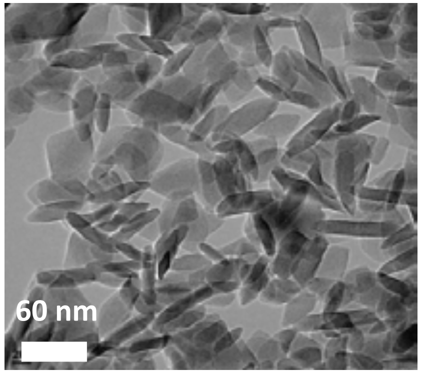
PIM-1 vs PBI and Matrimid based MMMs

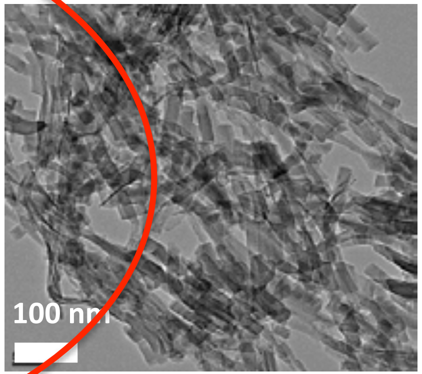


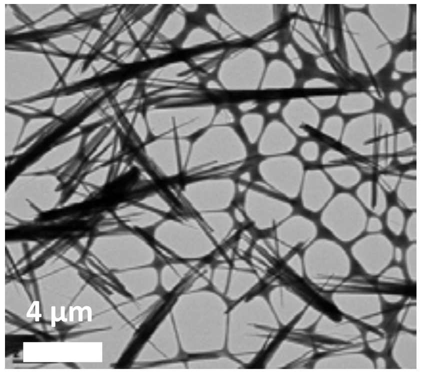
- All PIM-1 membranes surpass the upper-bound (high increase of permeability but reduced selectivity)
- PBI approaches selectivity target

Morphology Effects

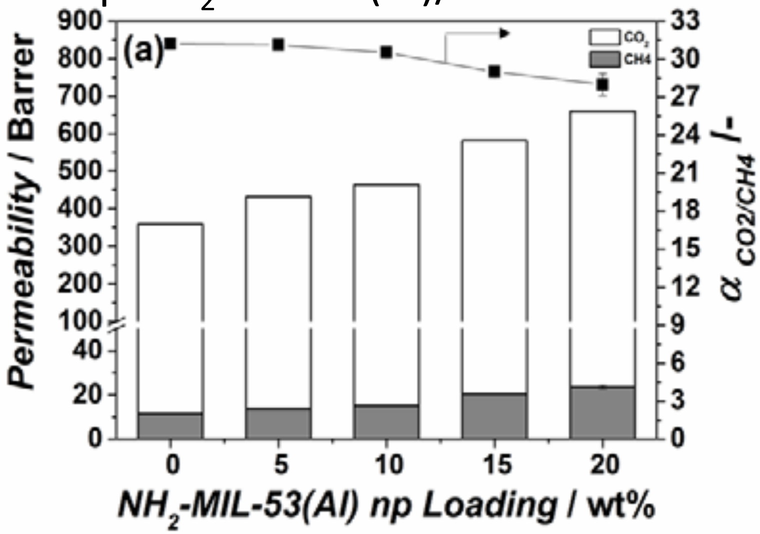
Nanoparticles | **Nanorod** | **Microneedle**



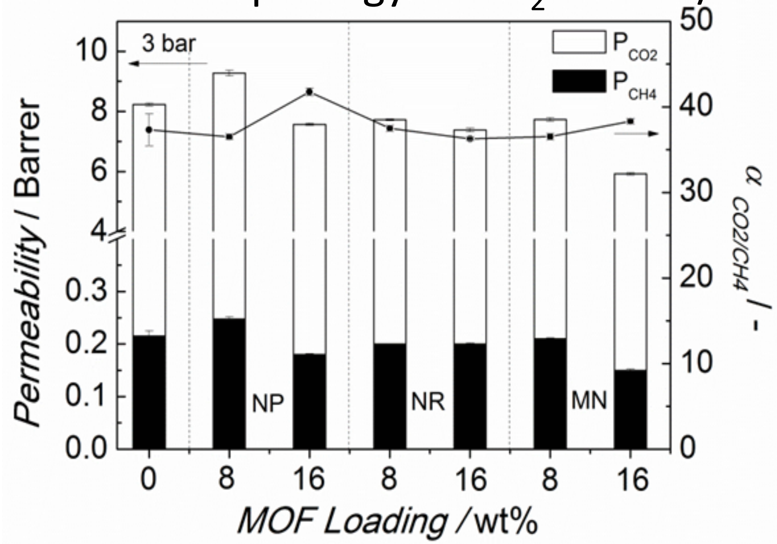




np-NH_2-MIL-53(Al)/6FDA-DAM

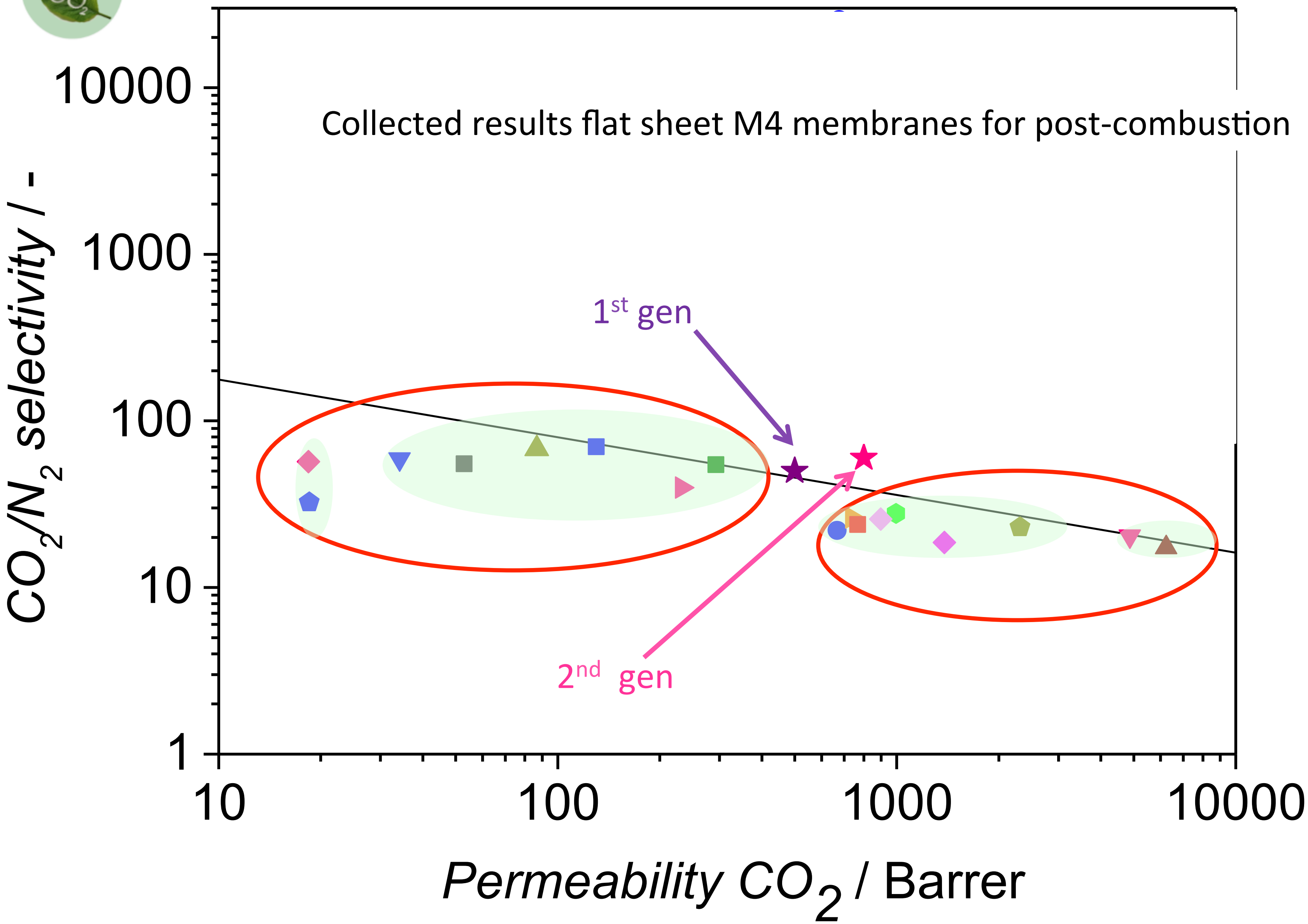


Different morphology of NH_2-MIL-53/Matrimid



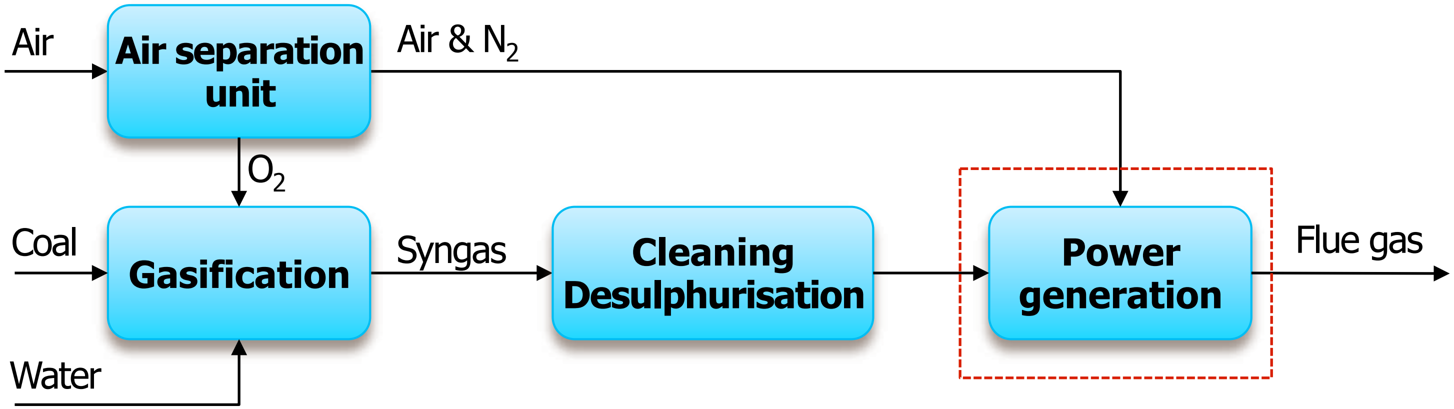
Sabetghadam et al, Adv. Func. Mater. 2016

Robeson plot (2008)

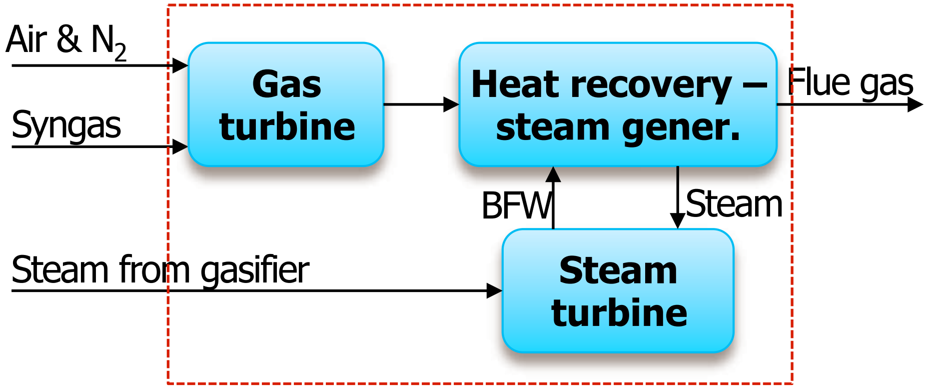


Reference case

Coal-fired IGCC power plant without CO_2 capture

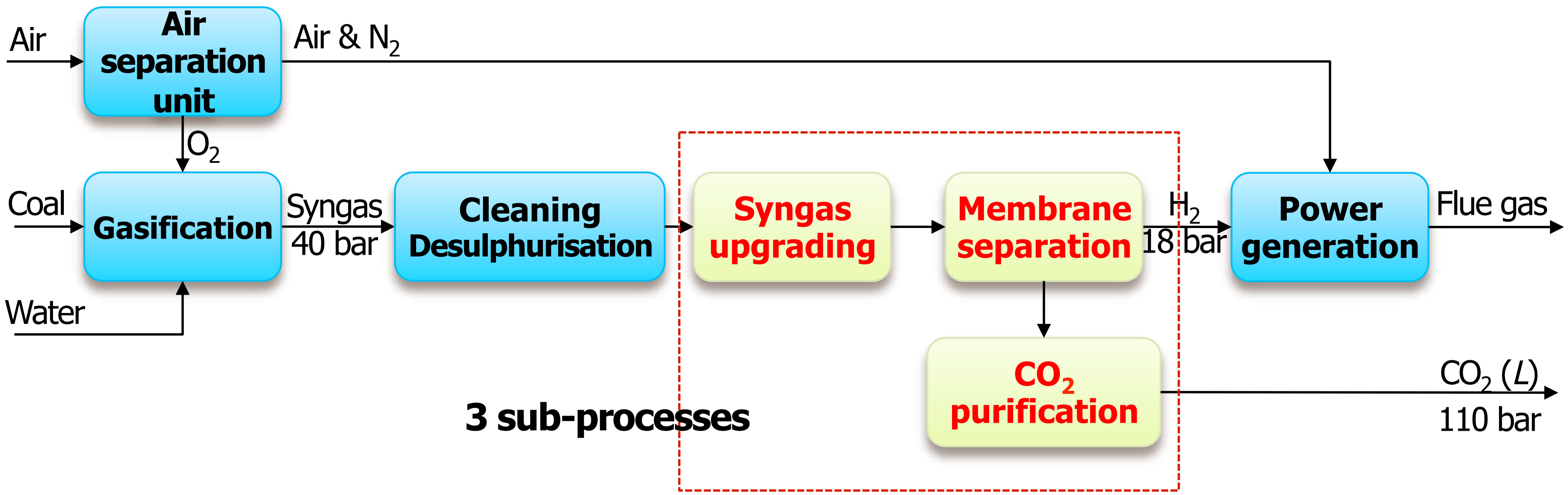


536 MW power output
43% efficiency
3.1 Mt/y CO_2 emissions



Combined Cycle efficiency 54%
Steam cycle efficiency 36%

Basis of design
IGCC plant with pre-combustion capture



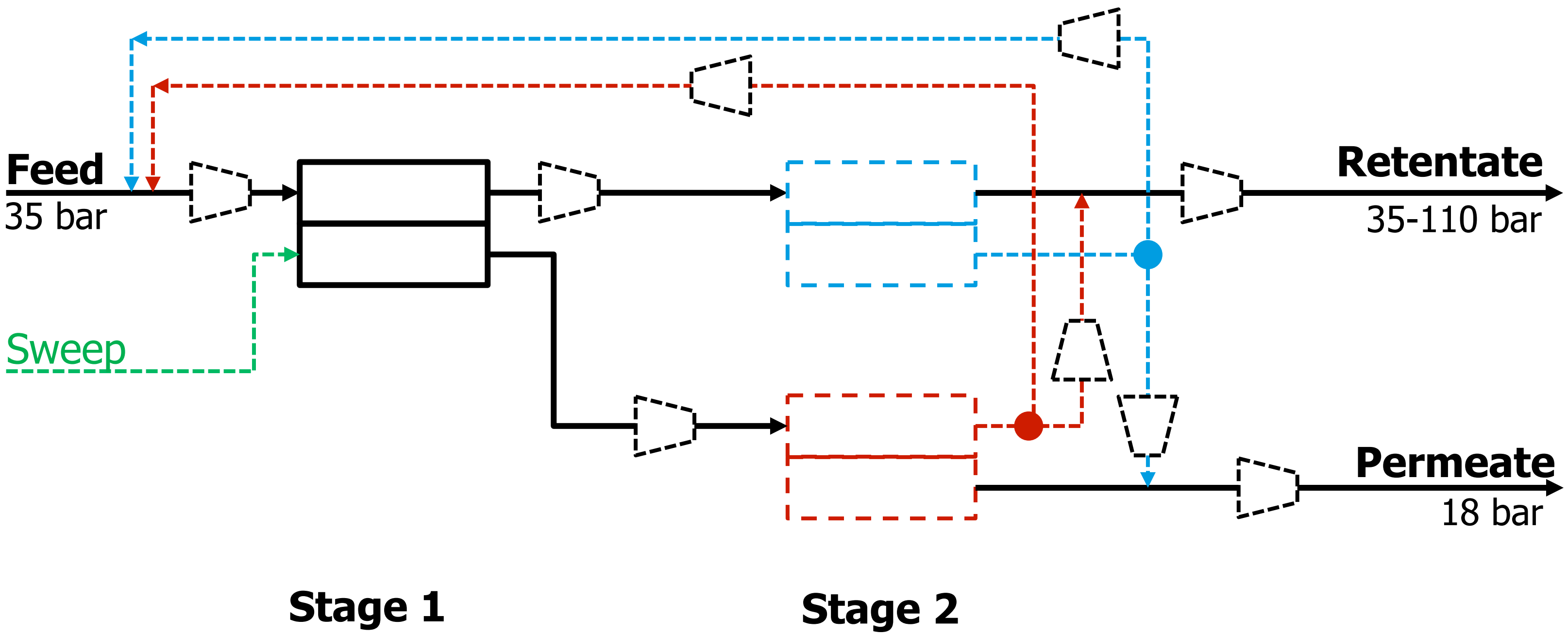
2.78 Mt/y of captured CO_2
?? MW power output
?? % efficiency

Process options – membrane separation

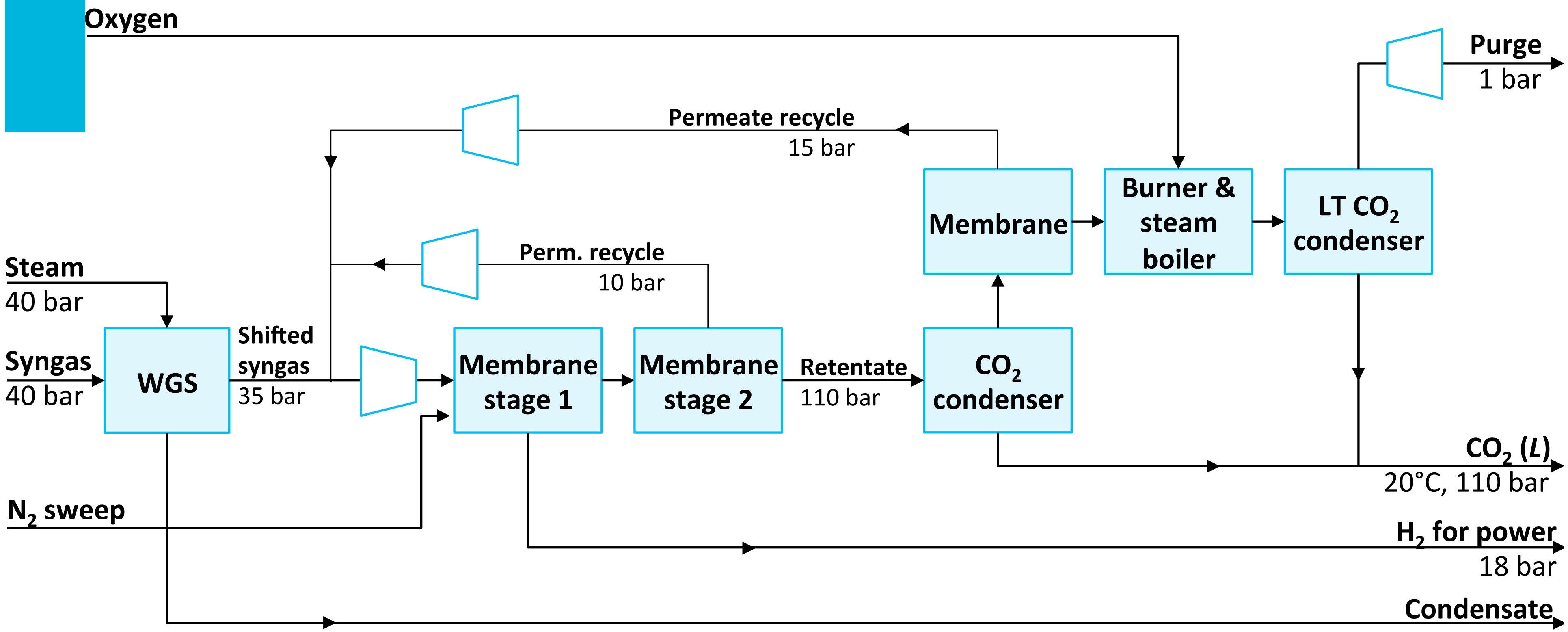
2-stage processes

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

→ Optimisation problem



Process flow scheme



Optimised scheme

PROCESS ECONOMICS (1ST GEN. MEMBRANES)

Designed capture process

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

Cost of captured CO_2 = 15.8 €/t

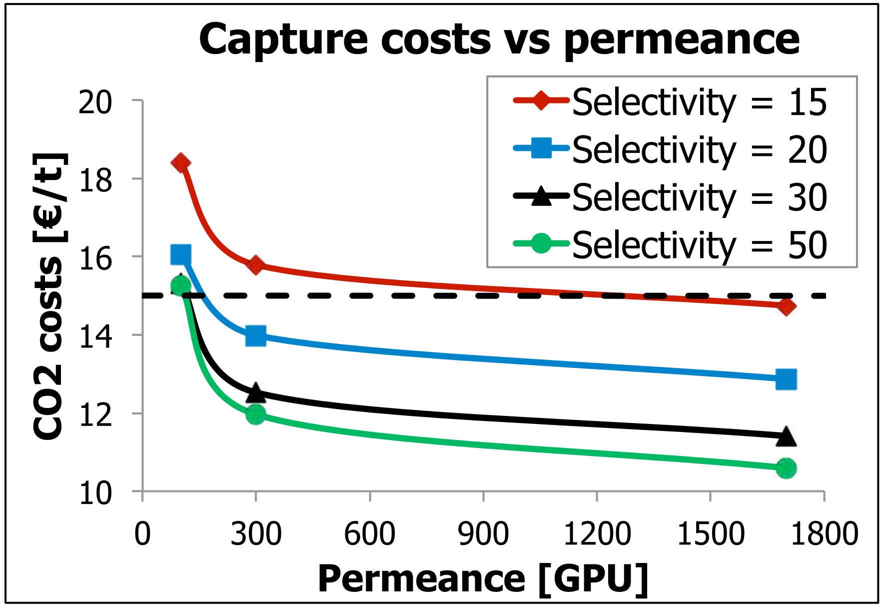
16.4 €/t 70 bar
18.2 €/t 35 bar

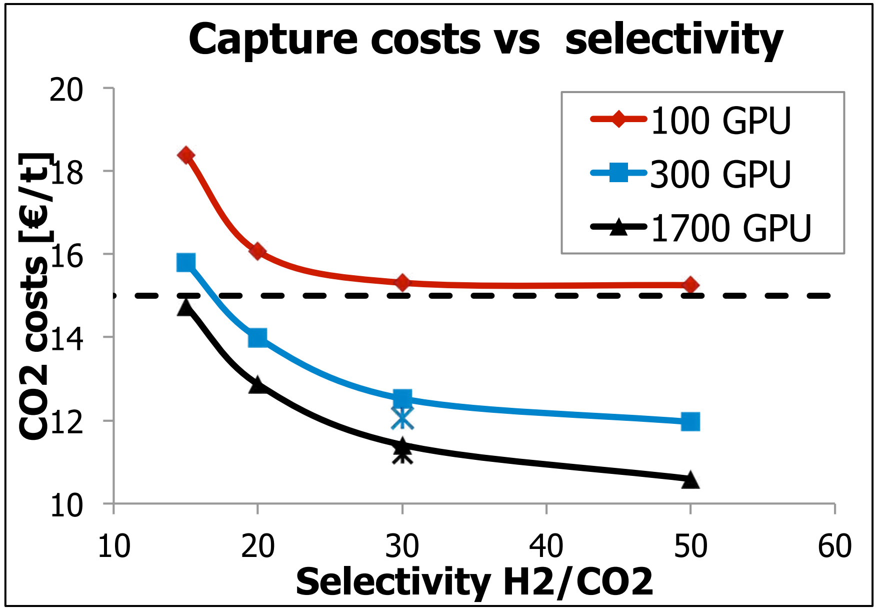
Item	Unit	Without capture	With capture
Net power output	MW	536	489
Total investment	M€	1148	1233
Specific investment	€/kW	2141	2522
Cost of electricity	€/MWh	68.4	80.4

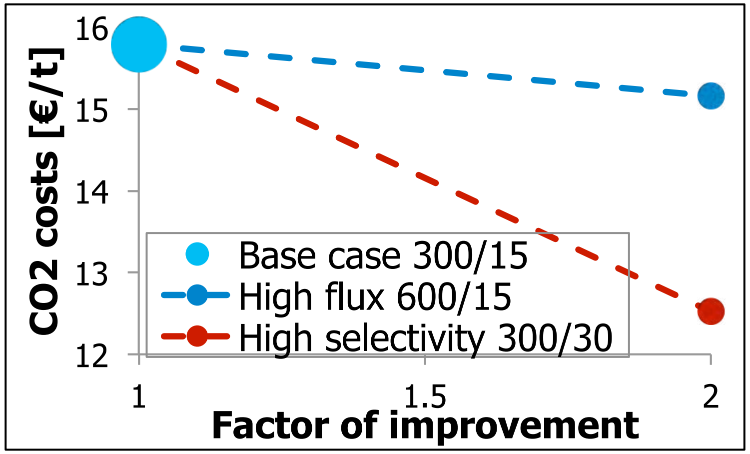
Profitability in 2030 (30€/t CO_2)

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

Sensitivity analysis







Little improvement of selectivity will allow capturing for <15 €/t

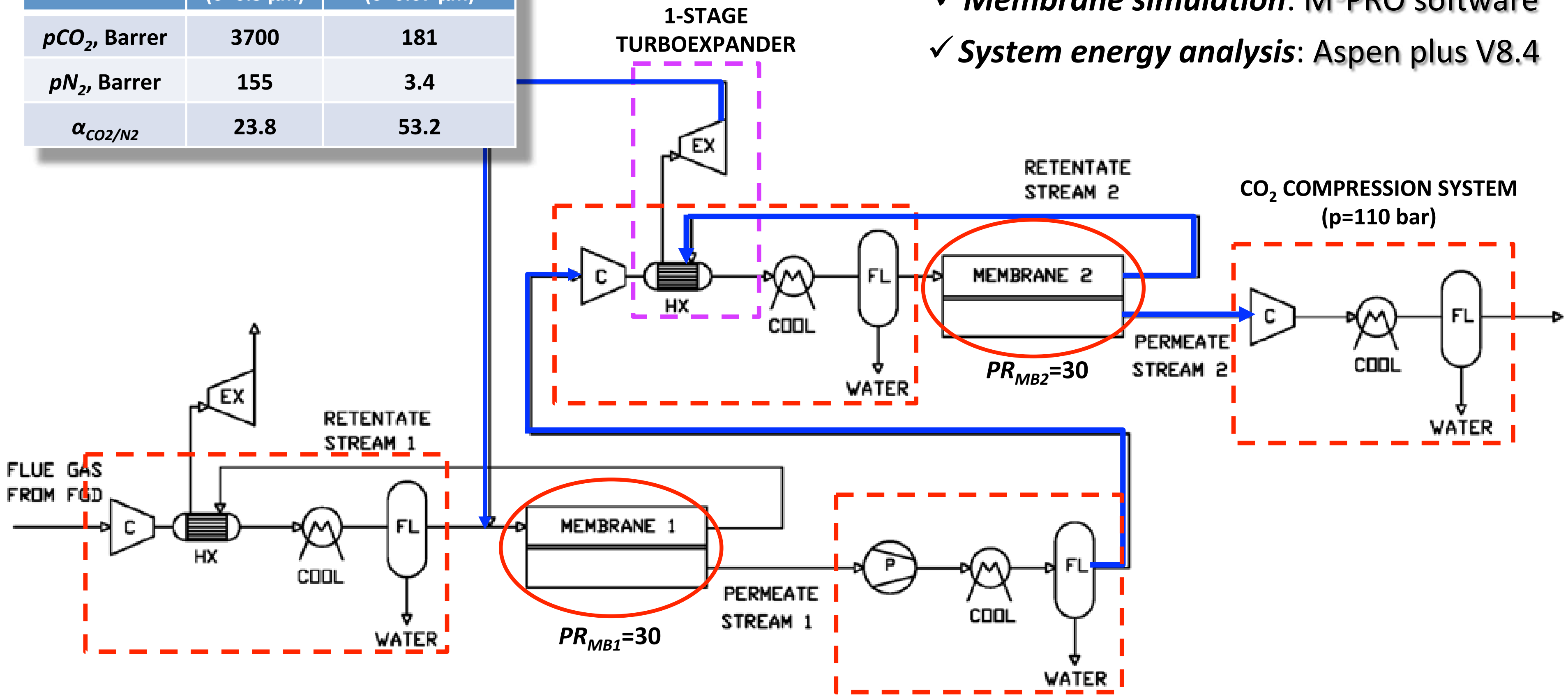
Permeability high enough
Selectivity >30 not useful

Dual-stage membrane system layout

	PIM-1 (δ=0.3 μm)	*Polyactive™1500* (δ=0.07 μm)
pCO_2, Barrer	3700	181
pN_2, Barrer	155	3.4
$\alpha_{CO2/N2}$	23.8	53.2

✓ ***Membrane simulation***: M^3PRO software

✓ ***System energy analysis***: Aspen plus V8.4



➢ Permeate from the 1st stage is recompressed up to 30 bar and sent to the 2nd stage

➢ Retentate from the 2nd stage is recirculated back to the 1st membrane stage

➢ Permeate from the 2nd stage is sent to CO_2 compression system

Conclusions – Post combustion 2-stage CC

- ❑ Evaluation of opportunities for improving techno-economic performances of dual stage membrane systems, varying the *membrane separation properties*, *pressure ratio* and *system layout*

- ❑ There exists an optimal pressure ratio, allowing to minimize specific energy requirement (E_{TOT}) and cost of CO_2 capture (c_{CO2})

- ❑ Energy and economic performances can be further improved eliminating the energy recovery system at second membrane stage and operating with $PR_{MB-1}>PR_{MB-2}$

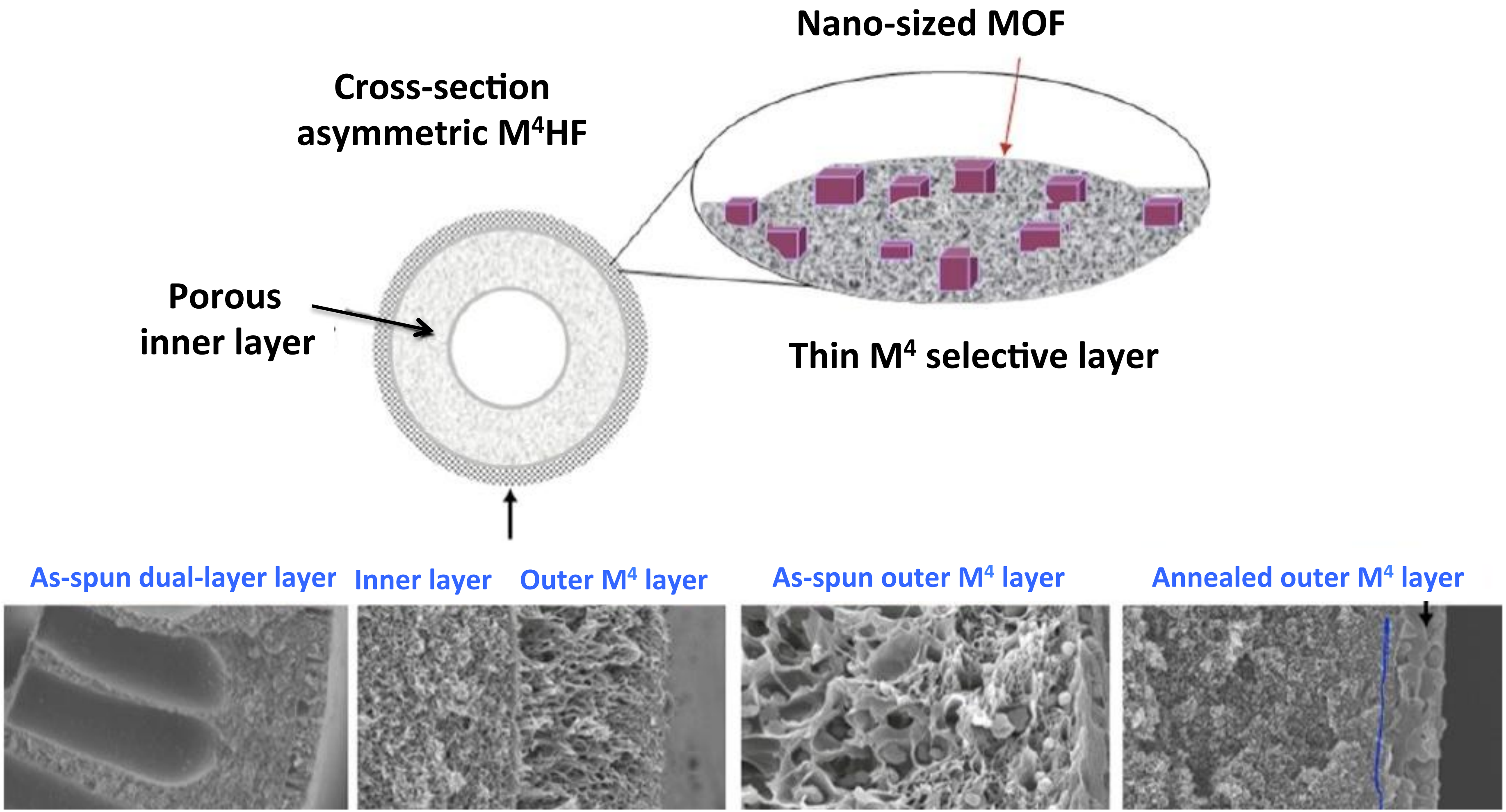
- ❑ Flue gas from coal-fired power plant

	$PR_{MB-1}>PR_{MB-2}$	
Membrane type	Polyactive	Improved membrane
Design conditions	min: E_{TOT}, c_{CO2}	min: E_{TOT}, c_{CO2}
$PR_{MB-1, opt}$	22.5	15
E_{TOT}, kWh/tonne	293	238
$CO_{2, em}$, kg/MWh	110.6	104.9
c_{CO2}, €/tonne	24.6	20.6

- ❑ Flue gas from natural gas boiler

	$PR_{MB-1}>PR_{MB-2}$	
Membrane type	Polyactive	Improved membrane
Design conditions	min: E_{TOT}, c_{CO2}	min: E_{TOT}, c_{CO2}
$PR_{MB-1, opt}$	25	20
E_{TOT}, kWh/tonne	395.5	298.3
$CO_{2, em}$, kg/MWh	21	21
c_{CO2}, €/tonne	60.0	49.4

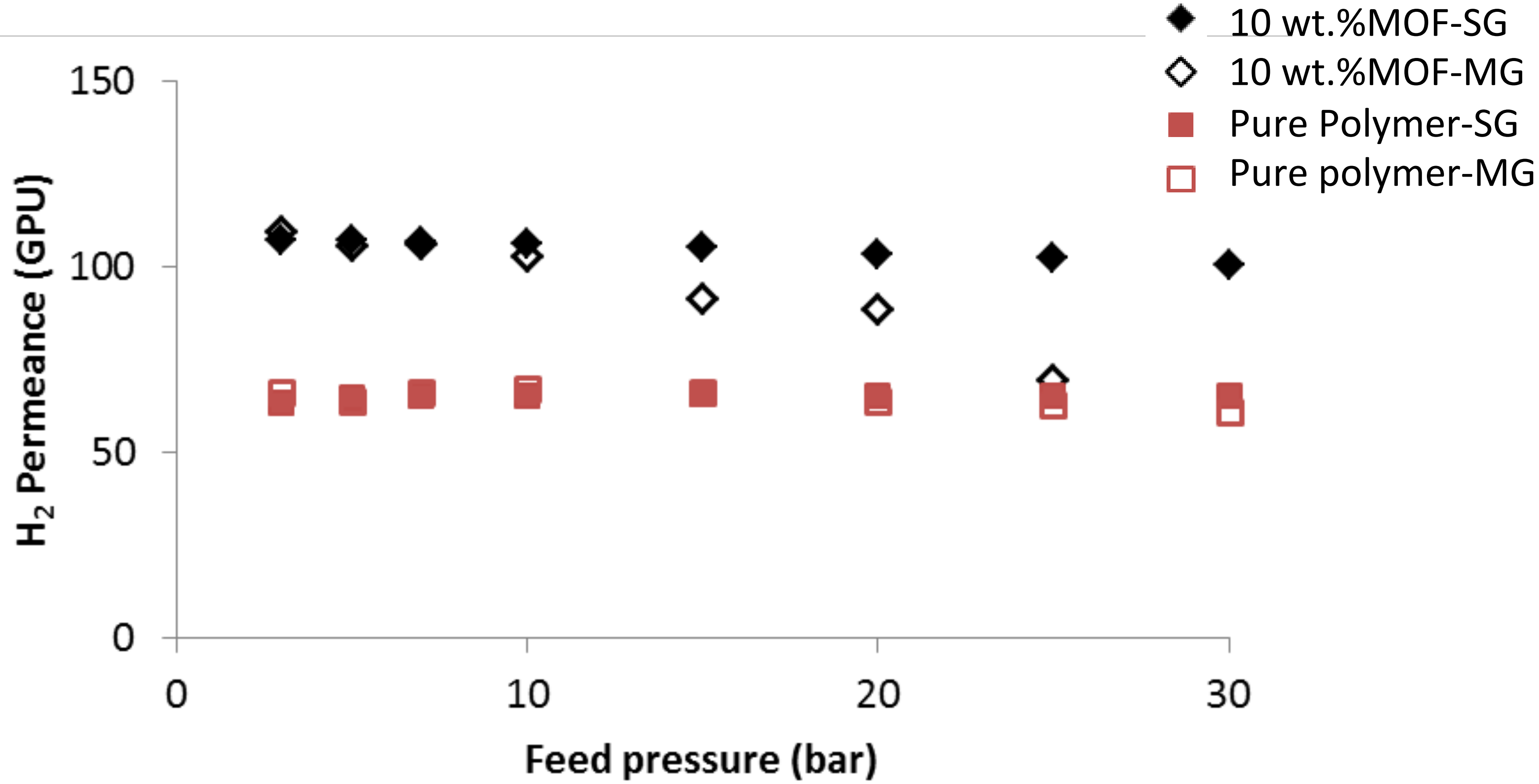
Hollow Fibre (HF) membranes



First performance of M4-HFMs

Single and Mixed gas permeation

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



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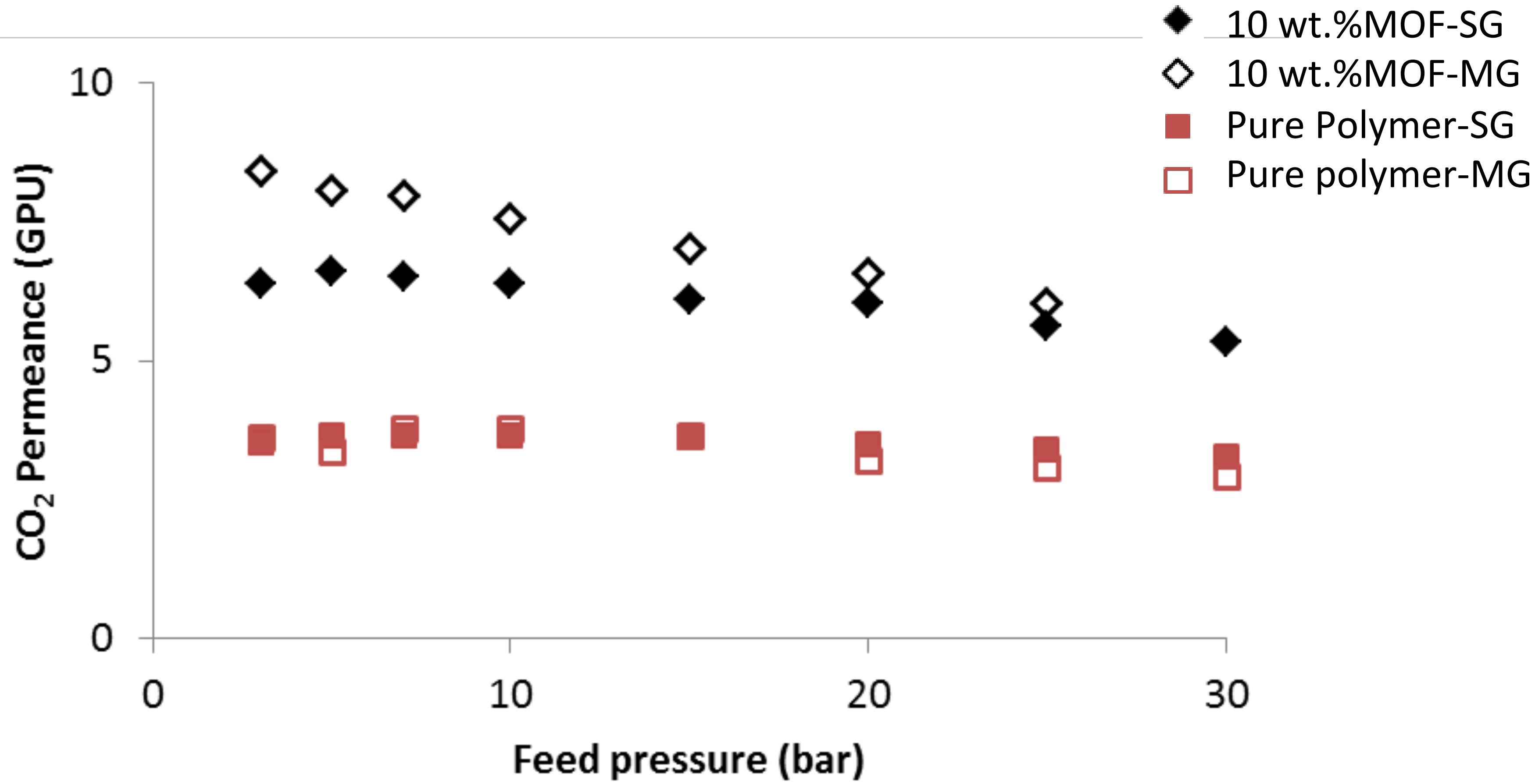

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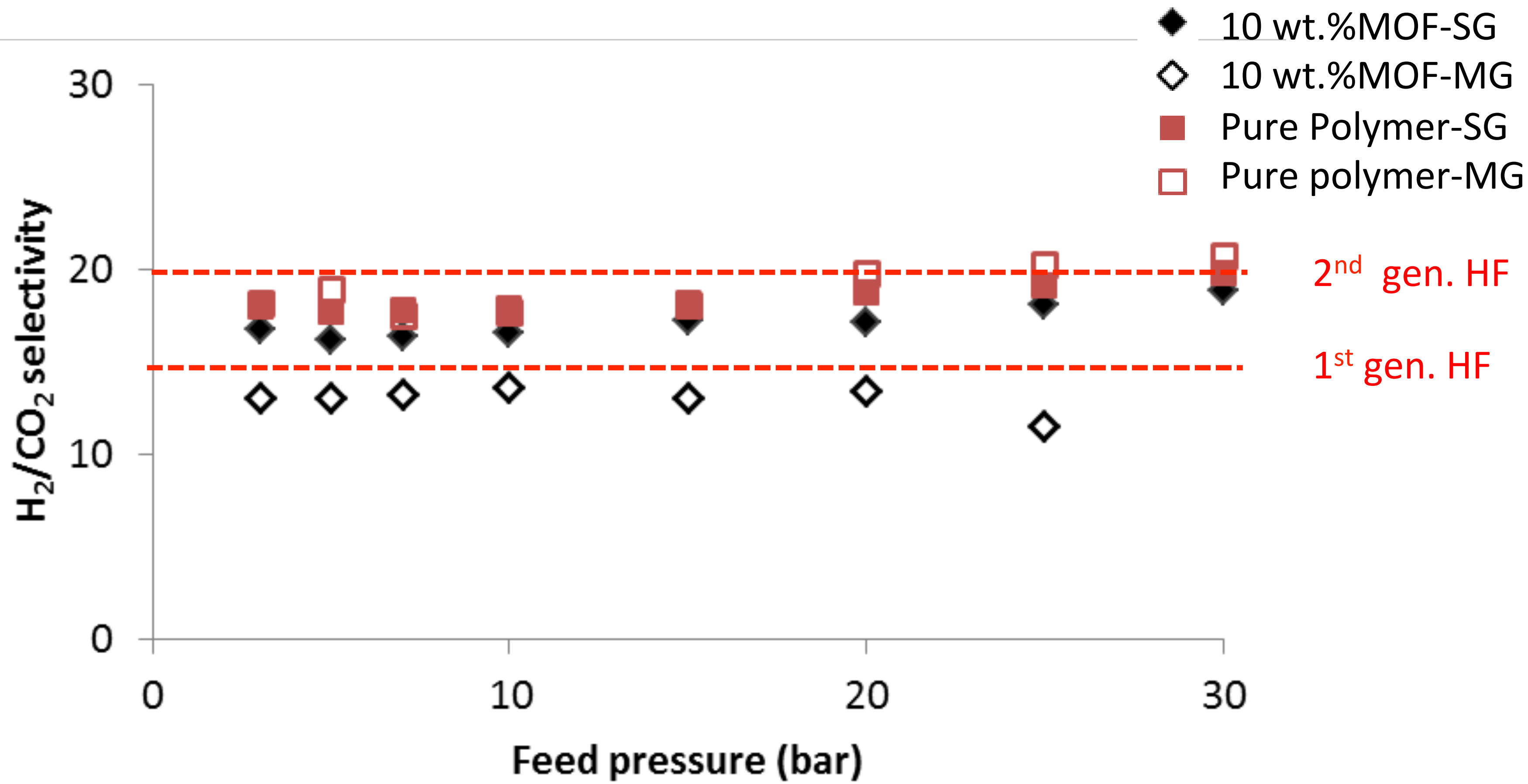
Single and Mixed gas permeation

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



Performance of M4-HFMs

HFs from TECNALIA
Module from UNIZAR
Sealed at UNIZAR

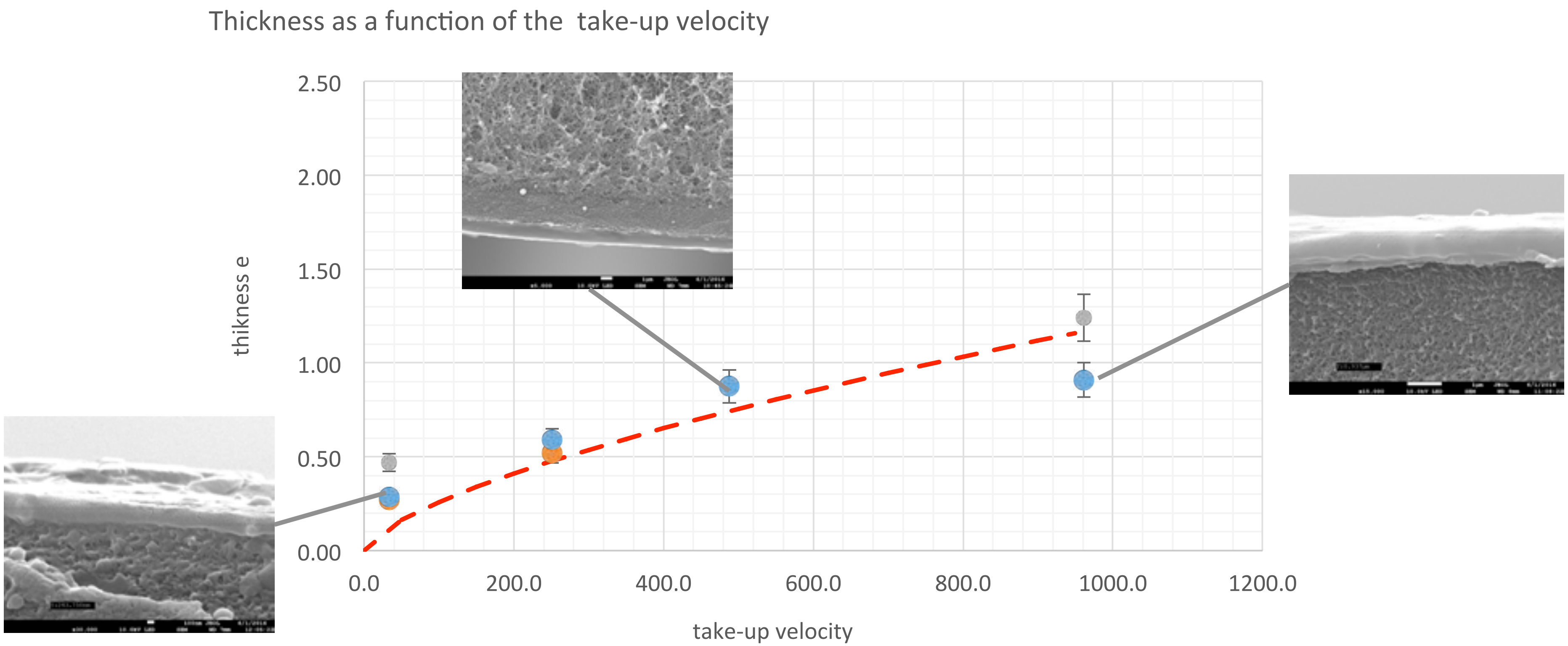
Preliminary results

Test confirmation partner

Membranes	Temperature (ºC)	Pressure (bar)	Permeabillity H_2 (GPU)	Permeabillity CO_2 (GPU)	Selectivity H2/CO2
5 wt% MOF	150	1	46,2	2,3	20,6
		2	44,6	2,2	20,5
		3	45,1	2,2	21,0
		4	43,0	2,1	20,5

Development of M4HFMs

“Composite membrane elaboration”



- Small influence of the % concentrations tested so far
- Thickness increases with velocity. Very predictable
- Low velocity for thickness lower than 0.5 µm
- Influence of drying temperature to be evaluated

Constant velocity dip-coating

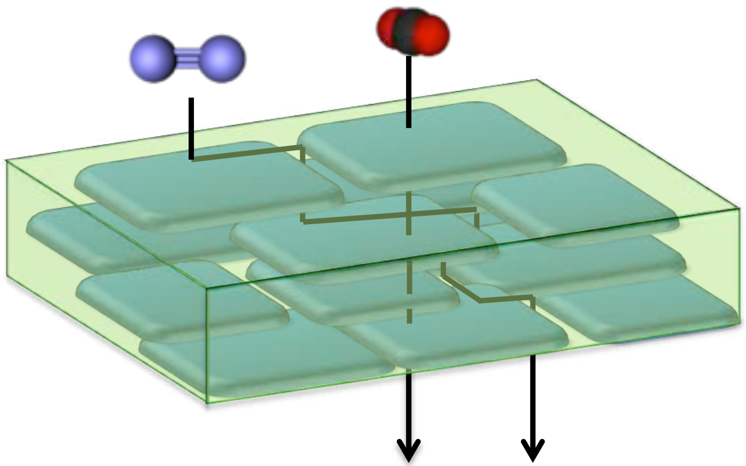
Proof of principle – lab scale
'Pull-through coater'

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

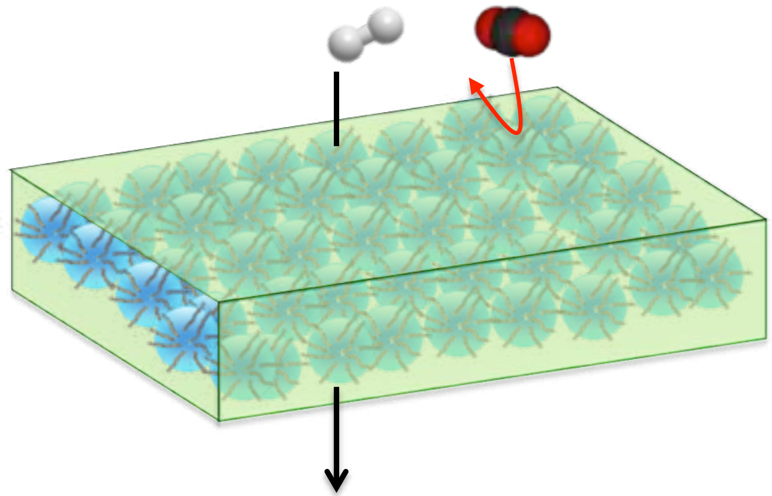
- fibers with a length even larger than 50 cm, or continuously
- working at a speed that can be varied in a quite large range (e.g., 1 - 500 mm/min).

Flux - Selectivity improvements



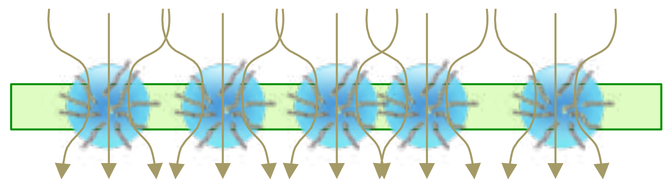
High flux polymers:

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



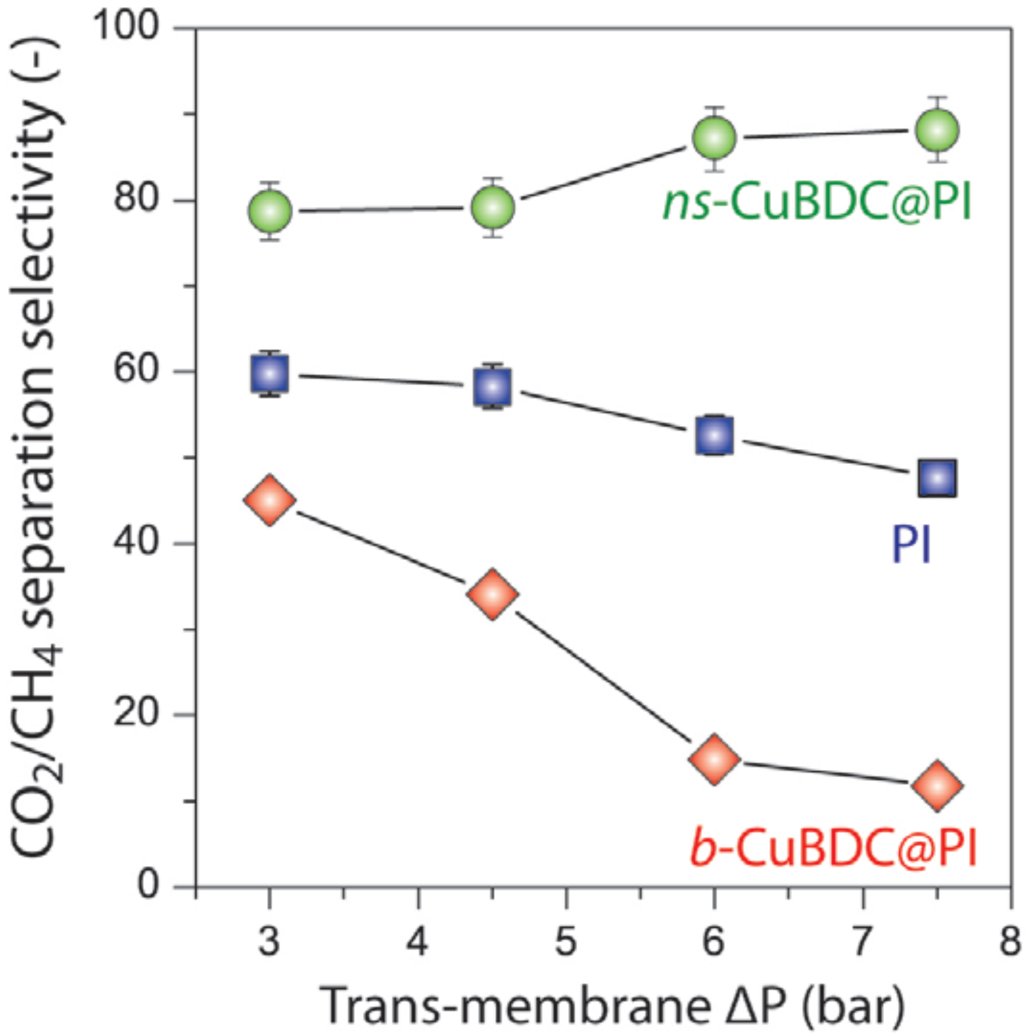
Selective polymers:

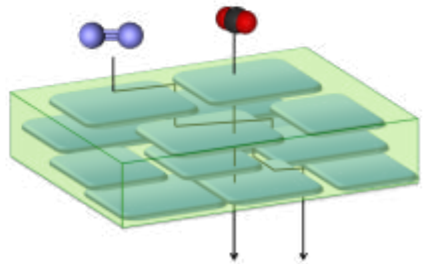
- Flux improvements
  - Hollow spheres
  - Mesoporous, good adsorption
- Shorter effective path-lengths

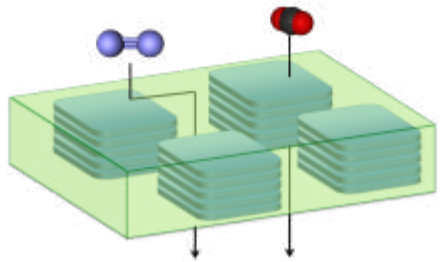


- Percolation membranes

Separation performance







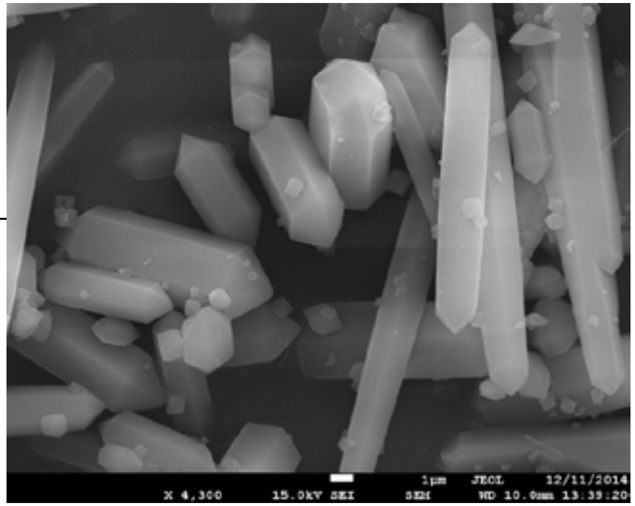
Rodenas *et al.* Nature Materials 14, 48–55 (2015)

MIL-96(Al)

M^4CO_2

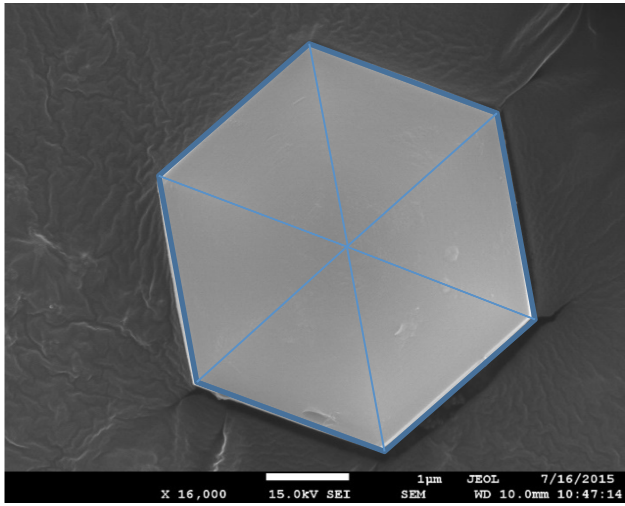
3^{rd} generation nanoMOFs

Hydrothermal
Hexagonal rods

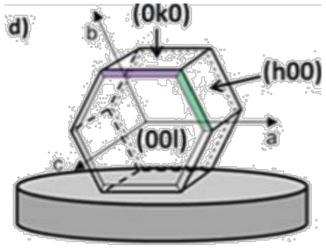


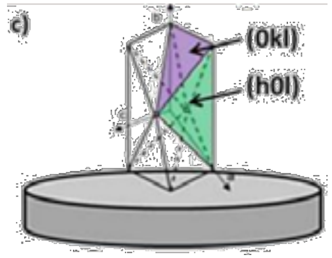
Up to 20μm long

Microwave
Hexagonal platelets

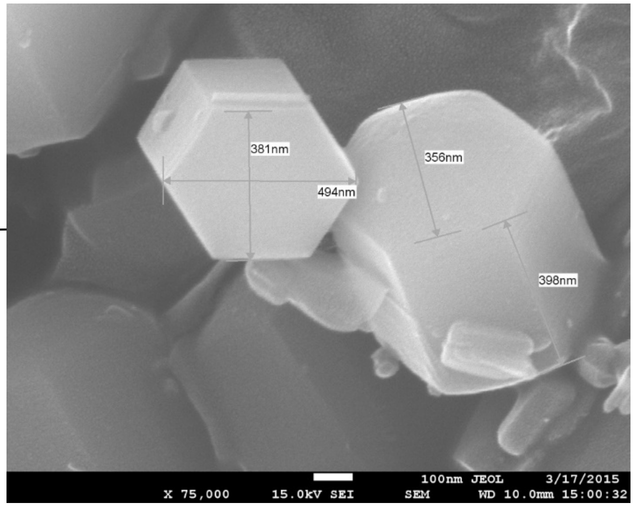


Up to 300nm thick



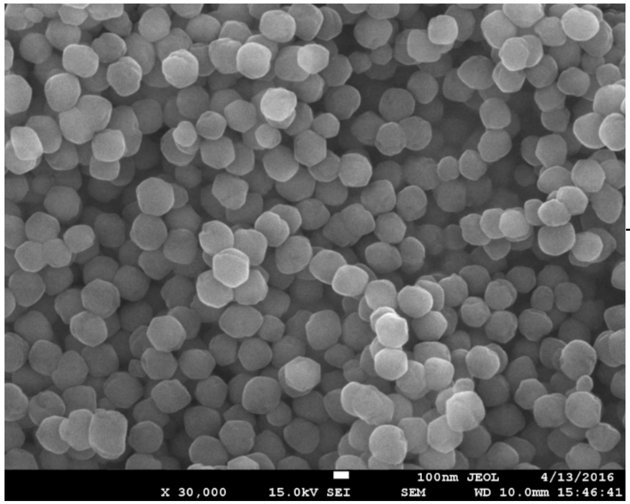


Reflux H_2O
nano rods



Intermediate shape

Reflux H_2O/DMF
nano spheres



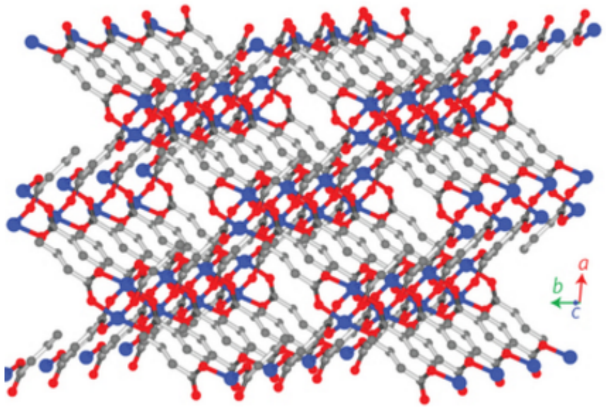
150nm

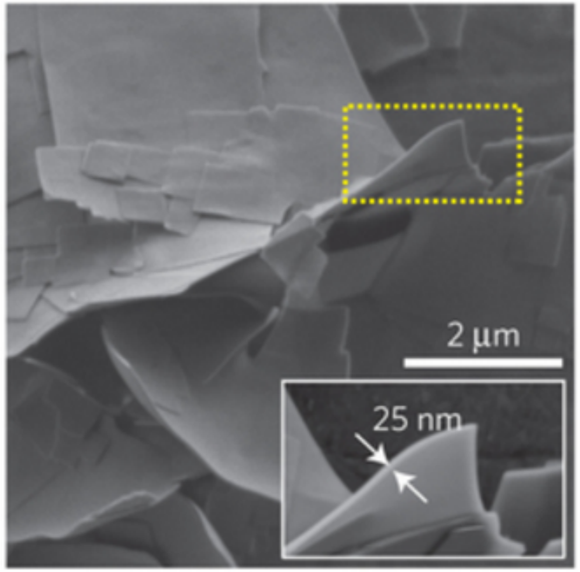
Control of morphology influencing diffusion properties

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

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
- Stable system

Rodenas et al, Nat. Mater. 2015

M^4CO_2 status – June 2016

- Project runs in-line with planning
- Process designs guide development direction
  - Selectivity strongest sensitivity
- 1st and 2nd generation materials identified
  - Development lamellar and layered 3rd generation materials
  - MOF stabilizes M4's (3 year)?
- Membrane testing uniform
- 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
  - New experimental and modeling techniques in-situ performance studies