Dynameric membranes for gas separation

Rubbery organic frameworks- ROFs

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http://nsa-systems-chemistry.fr/

Nanosystèmes Supramoléculaires Adaptatifs

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www.iemm.univ-montp2.fr

Tuning the gaz-diffusion through molecular networks in multicomponent functional membranes

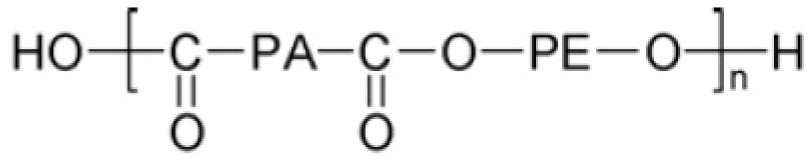
In general, the gas transport performances are controlled by the gas-diffusivity though glassy polymers and by solubility-selective behaviors of rubbery polymers.

The trade-off behaviour high selectivity/low permeability and vice versa is the most important challenge in developing membrane systems with high permeability whilst keeping a reasonable selectivity

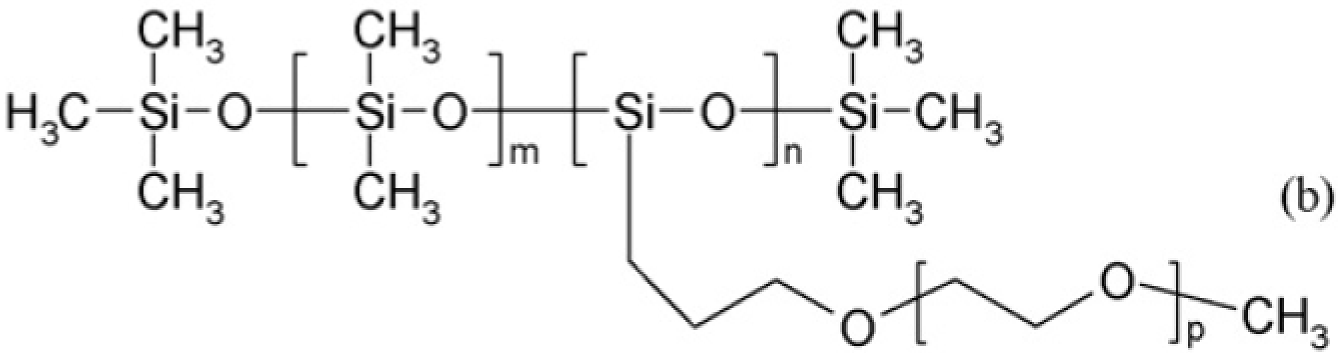
Polymer blending- molecular additives

Polymer blending is a versatile tool to combine the beneficial properties of polymers and molecular additives to increase the free volume of the polymer and the solubility.

A. Car, C. Stropnik, W. Yave, K.V. Peinemann, J. Membr. Sci. 307 (2008) 88–95.
A. Car, C. Stropnik, W. Yave, K.V. Peinemann, Sep. Purif. Technol. 62 (2008) 110–117.



(a) PEBAX®

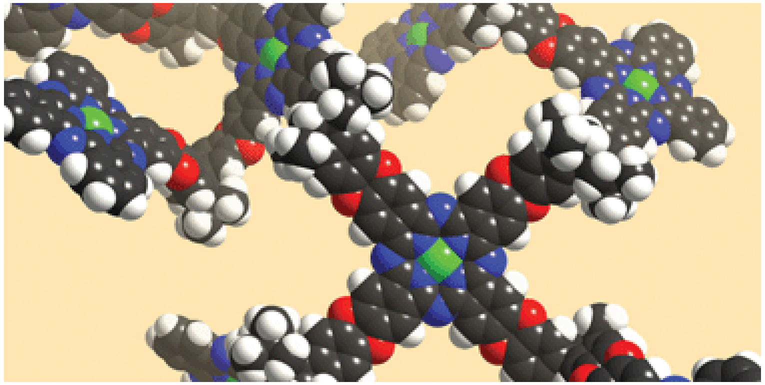


(b) PDMS-PEG

S. R. Reijerkerk, M. H. Knoef, K. Nijmeijer, M. Wessling J. Membr. Sci. 352 (2010) 126.

Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials

P. M. Budd , B. S. Ghanem , S. Makhseed , N. B. McKeown , K. J. Msayib, C. E. Tattershall
Chem. Commun., 2004, 230-231
P. M. Budd, N. B. McKeown, ***Polym. Chem.***, 2010,**1**, 63-68



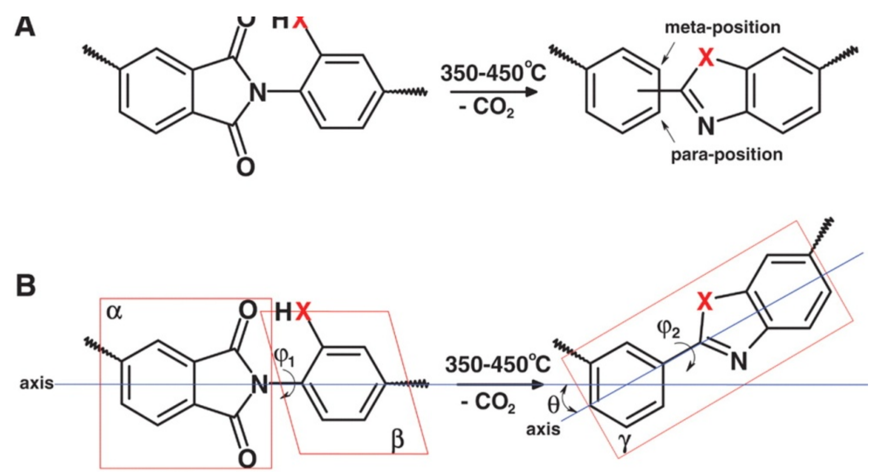
Soluble PIMs may be processed into thin films for use as highly selective gas separation membranes.

PIMs = potential heterogeneous catalysis and hydrogen storage systems.

Polymers with Cavities Tuned for Fast Selective Transport of Small Molecules and Ions

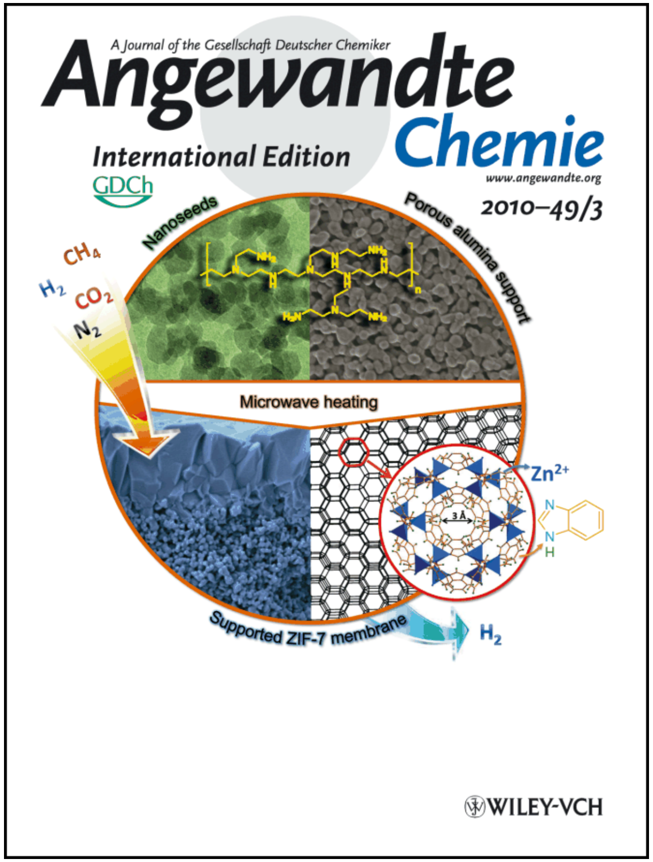
Ho Bum Park,[1,2] Chul Ho Jung,[1] Young Moo Lee,[1*] Anita J. Hill,[3] Steven J. Pas,[3] Stephen T. Mudie,[3] Elizabeth Van Wagner,[2] Benny D. Freeman,[2] David J. Cookson[4]

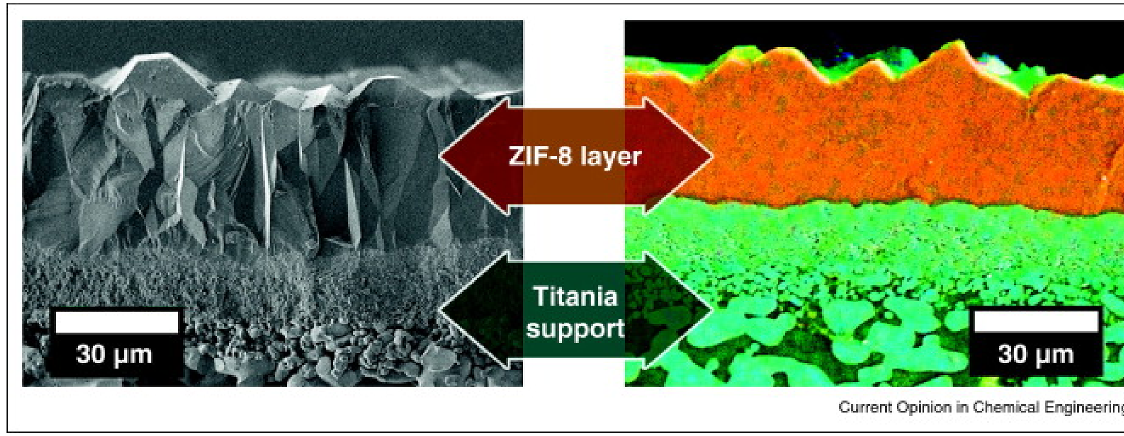
Within a polymer film, free-volume elements such as pores and channels typically have a wide range of sizes and topologies. This broad range of free-volume element sizes compromises a polymer's ability to perform molecular separations. We demonstrated free-volume structures in dense vitreous polymers that enable outstanding molecular and ionic transport and separation performance that surpasses the limits of conventional polymers. The unusual microstructure in these materials can be systematically tailored by thermally driven segment rearrangement. Free-volume topologies can be tailored by controlling the degree of rearrangement, flexibility of the original chain, and judicious inclusion of small templating molecules. This rational tailoring of free-volume element architecture provides a route for preparing high-performance polymers for molecular-scale separations.



Science 2007;318:254-258

Are MOF (ZIF) membranes better in gas separation than those made of zeolites?





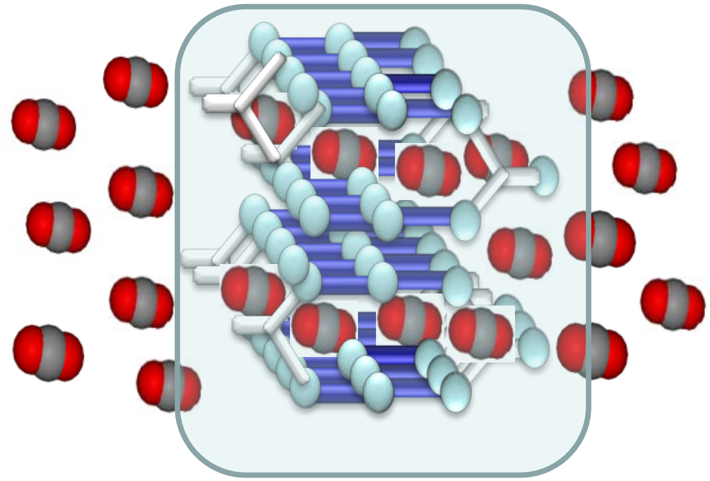
• the structural flexibility of MOFs apparently prevents a sharp molecular sieving with a pore size estimated from the 'rigid' crystallographic structure by size exclusion.

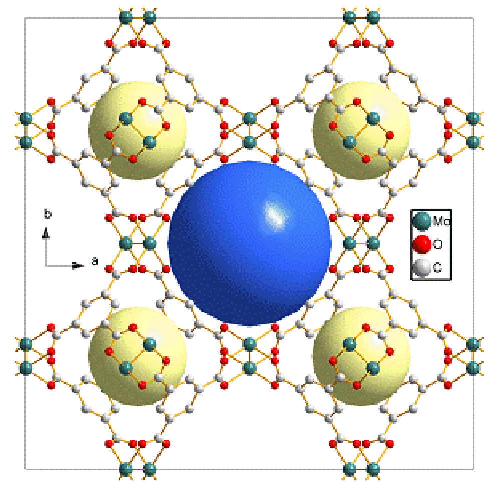
• mixed matrix MOFs membranes which show improved performance in comparison with the pure polymer membranes.

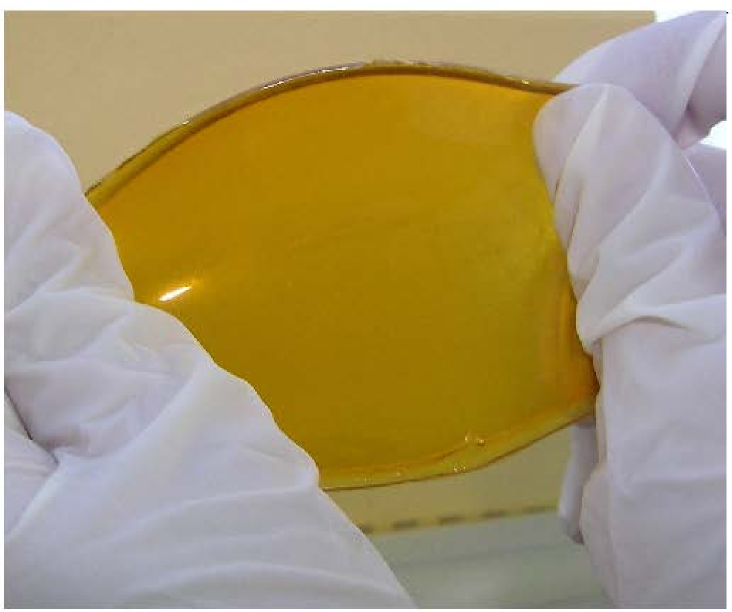
• Different from zeolites as organic–inorganic material, the MOF nanoparticles can be easily embedded into organic polymers, and standard shaping technologies to hollow fibers or spiral wound geometries can be applied

Yan-Shuo Li, Fang-Yi Liang, Helge Bux, Armin Feldhoff, Wei-Shen Yang, and Jürgen Caro Angew. Chem. Int. Ed. 2010, 49, 548 –551

Rubbery Organic Frameworks (ROFs)





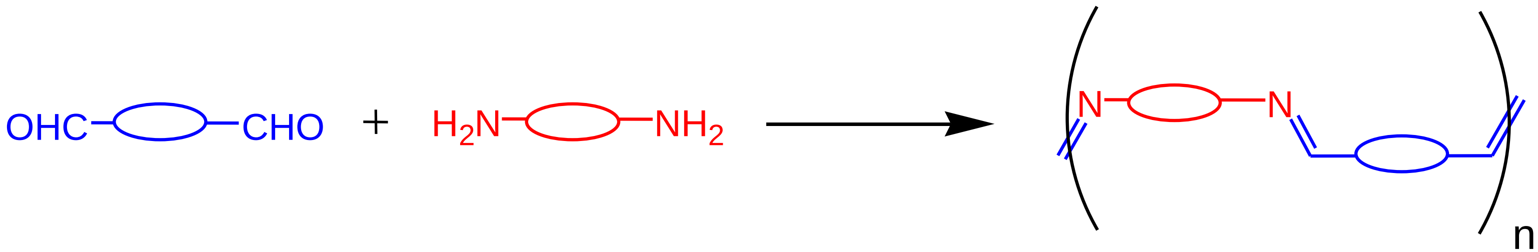


DYNAMERS

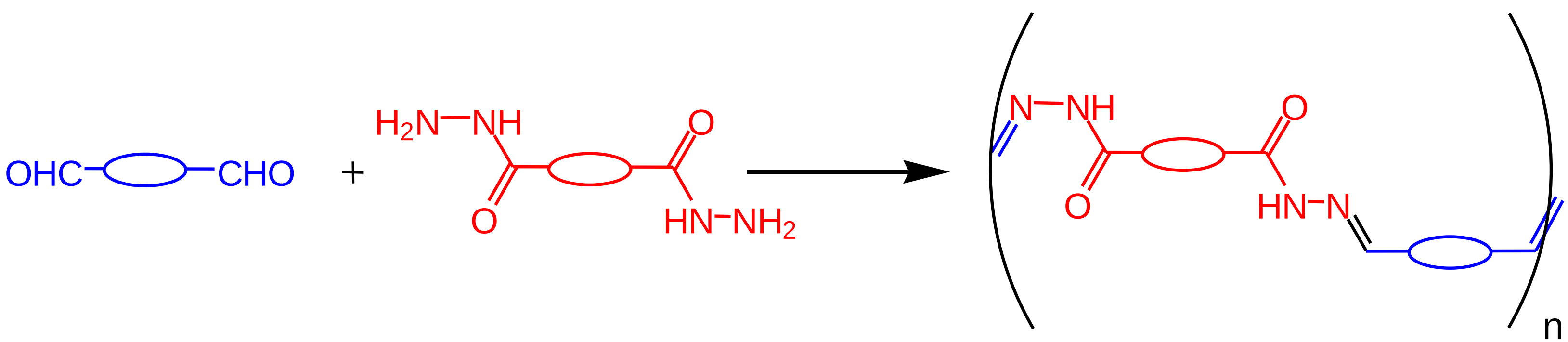
Proc. Natl. Acad. Sci. **2004**, *101*, 8270-8275.

DYNAMIC POLYMERS generated via

REVERSIBLE COVALENT CONNECTIONS



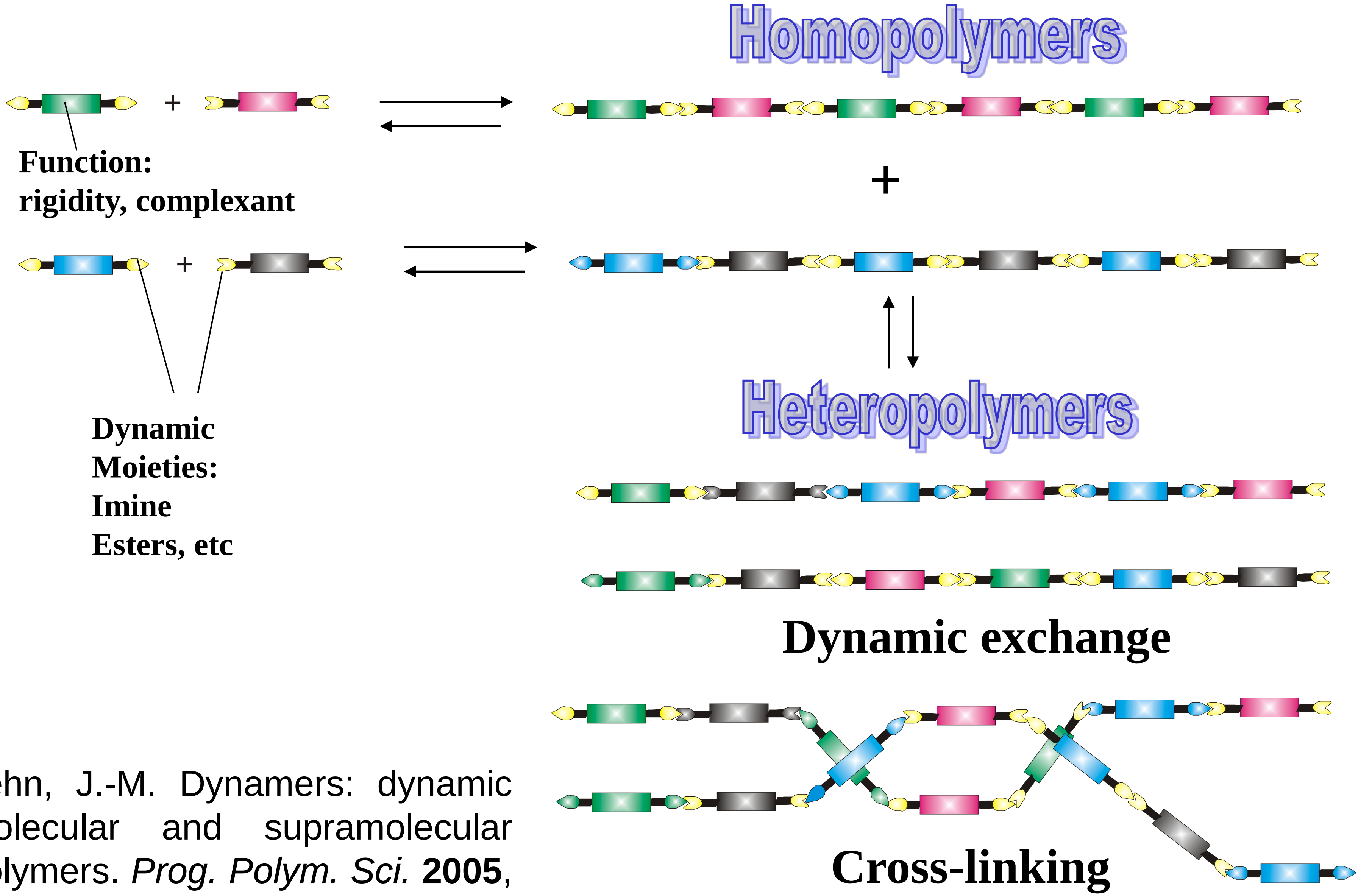
dialdehyde diamine **polyimines**



dialdehyde dihydrazide **polyacylhydrazones**

courtesy of Jean-Marie LEHN

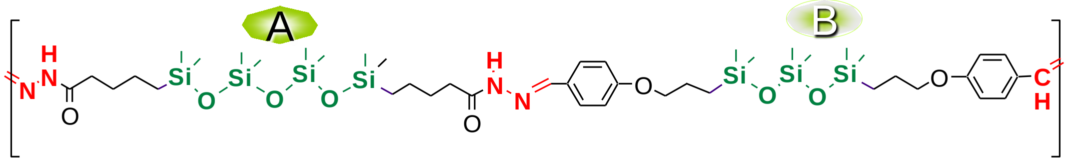
COMPONENT RECOMBINATION between DYNAMIC POLYMER CHAINS



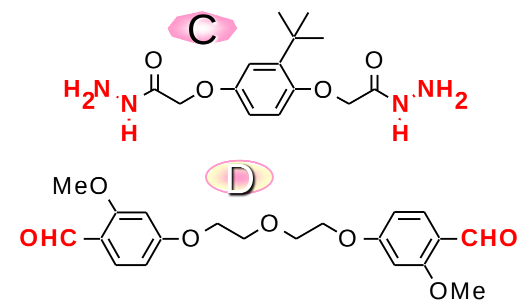
Lehn, J.-M. Dynamers: dynamic molecular and supramolecular polymers. *Prog. Polym. Sci.* **2005**, *30*, 814-831.

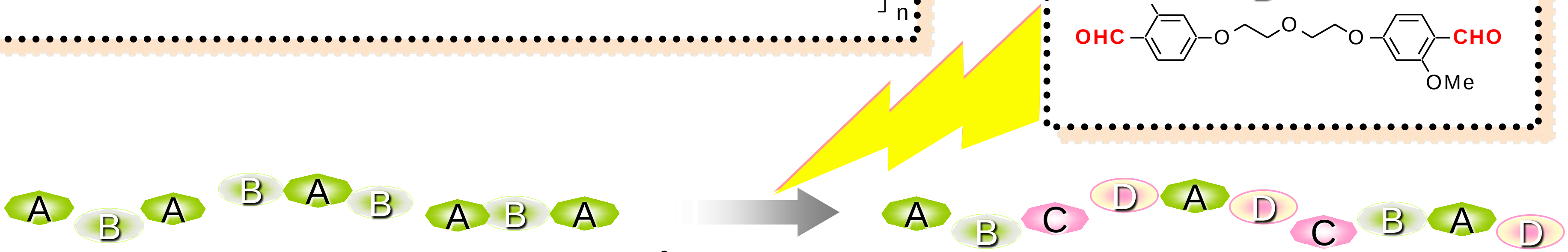
Soft-to-Hard Transformation of Dynamers

Very Soft Stretchy Film



Hard Monomers





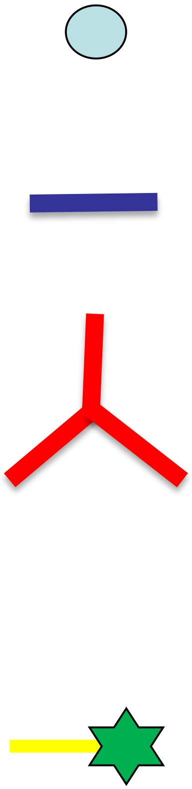
60°, 24h, in $CHCl_3$

Soft Stretchy Film | 25mol% | 50mol% | 75mol%

➡ Conversion of a Soft Stretchy Film into a Hard Tough Film by Dynamic Modification

courtesy of Jean-Marie LEHN

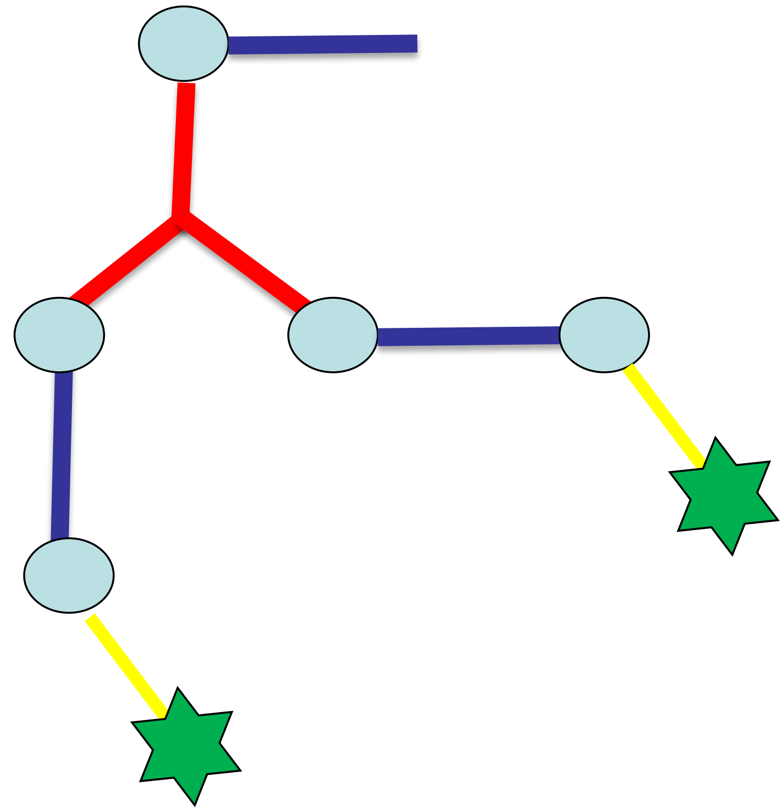
Rubbery Organic Frameworks (ROFs)
Systems Membranes
Libraries of components in reversible exchanges



Core centres

Connectors

Functional heads



Israel J. Chem. 2013, **53(1-2), 97-101**

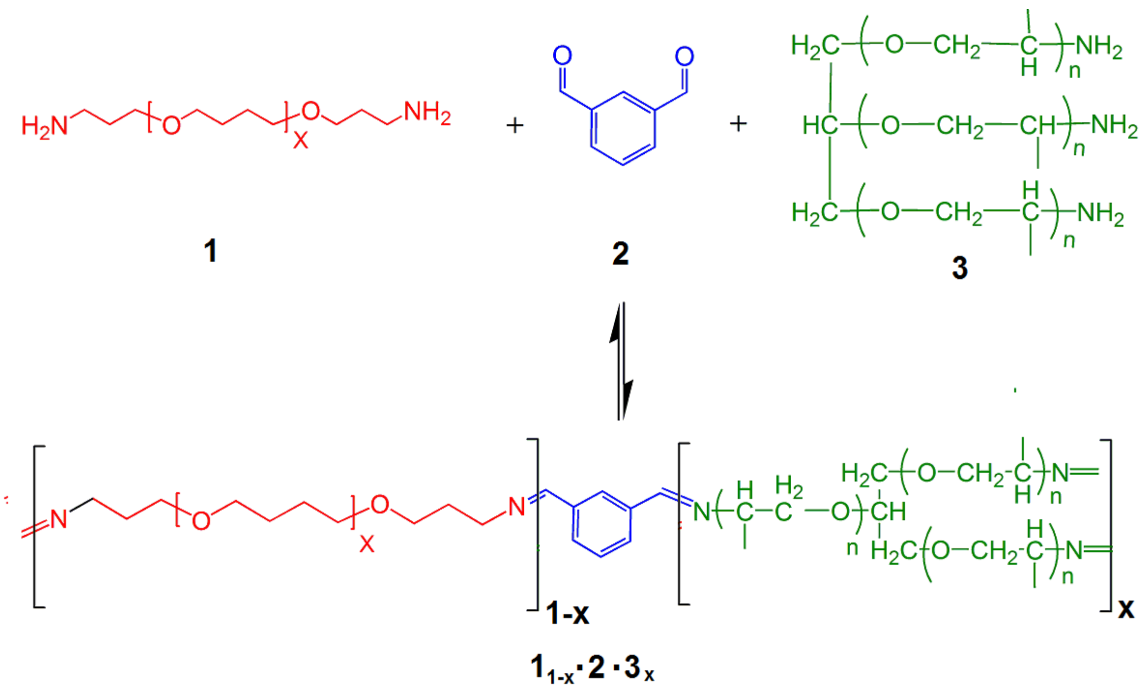
Rubbery Organic Frameworks (ROFs) for gas separation Ist generation

1. the hydrophobic polyTHF **linear macromonomers** have been used to generate the crystalline phases considered as low-permeable for the gas transport;

2) the polyMe(PEG) **star-type macromonomers** allowinga high solubility for the CO_2 contribute to the cross-linking behaviour of the dynameric network.

3) The connection between the macromonomeric units is based on thereversible covalent isophthaldiminecore **connectors**.

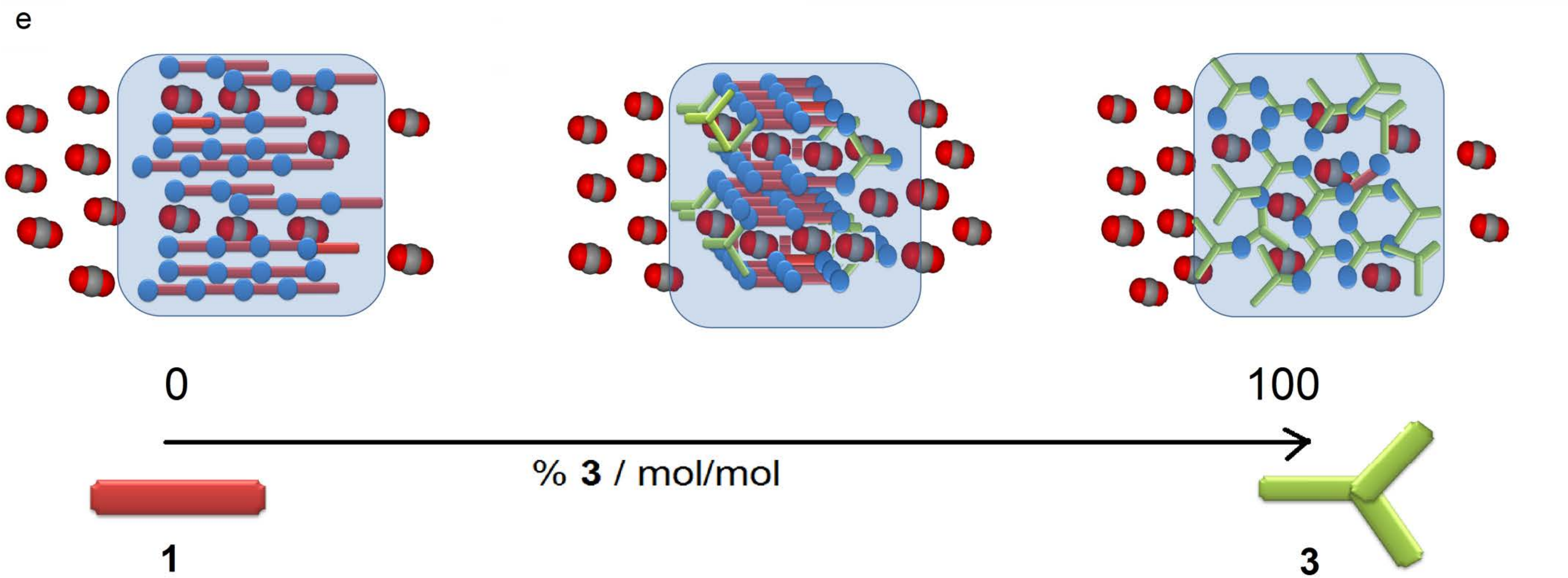
a)



Israel J. Chem. 2013, **53(1-2), 97-101**

Dynameric Membranes for gas separation

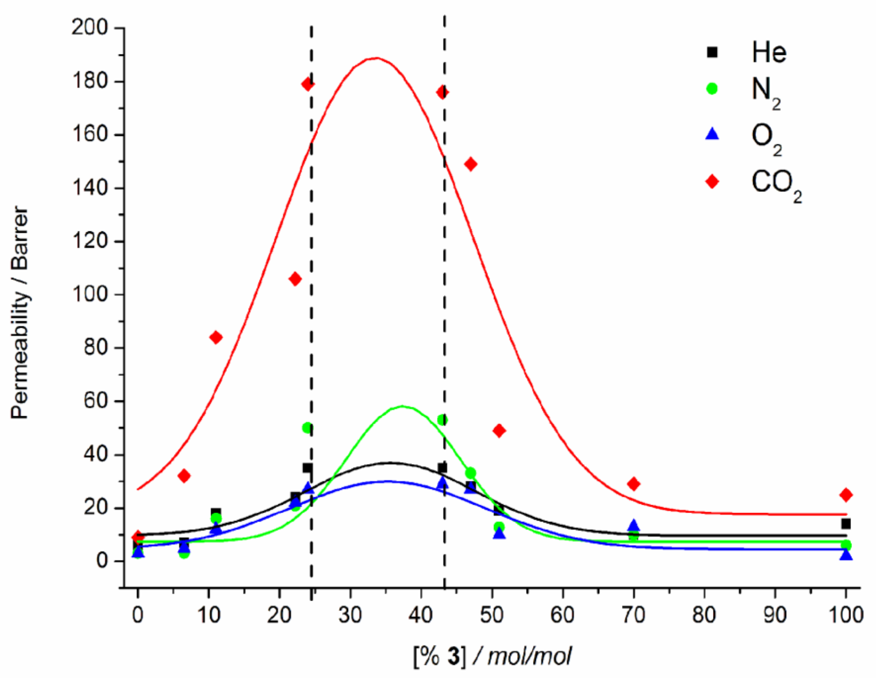
The increase of the free volume is most likely caused by the incorporation of **3**, acting as separator of linear PolyTHF compact matrix

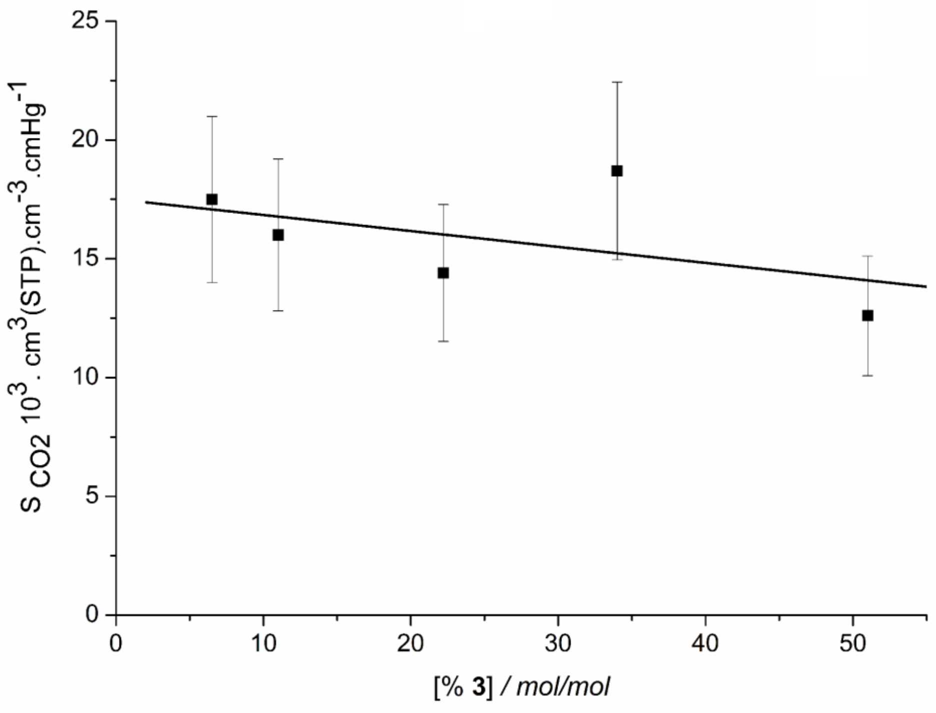


***Israel J. Chem*.** 2013**, 53(1-2), 97-101**

Dynameric Membranes for gas separation

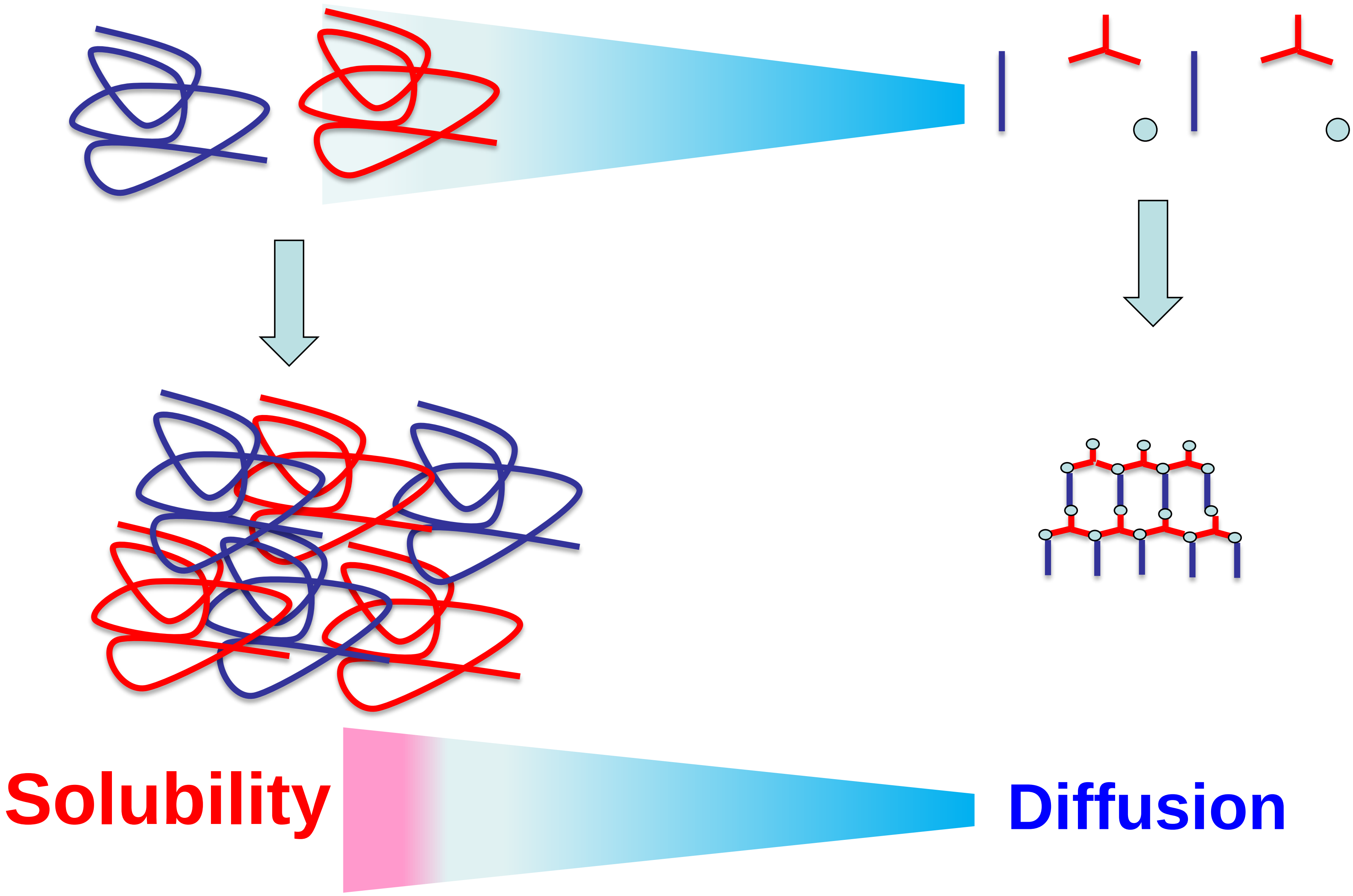
ROFs allow high permeabilities for the CO_2 and interesting CO_2/light gas selectivities



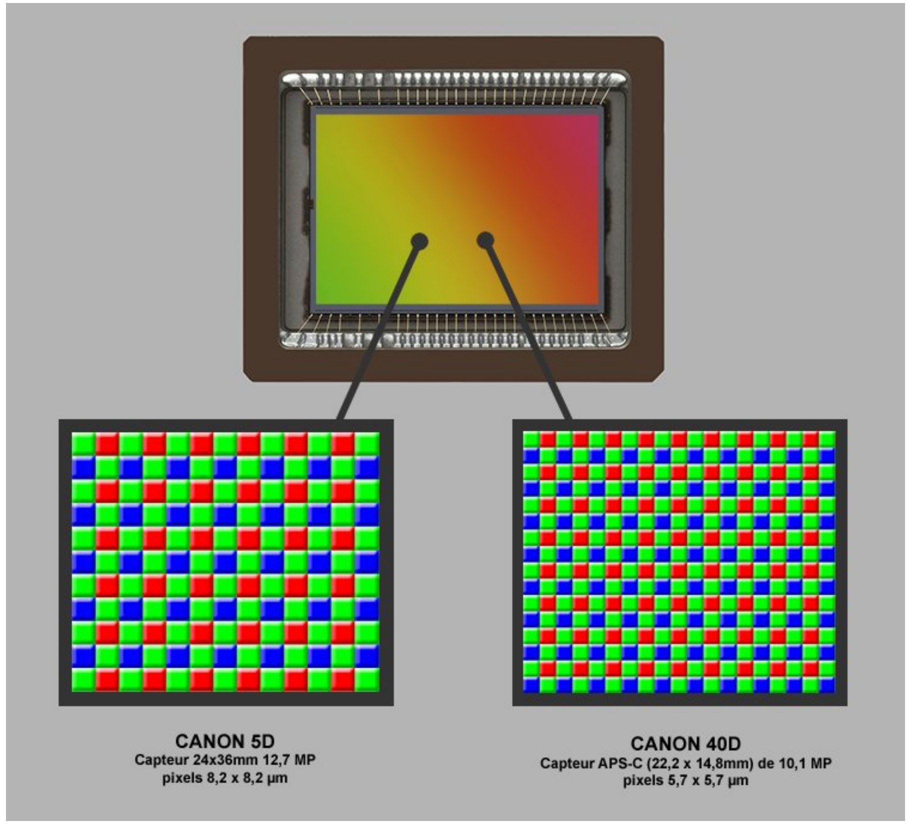


Israel J. Chem. 2013**, 53(1-2), 97-101**

Minimizing the size of elastomeric segments would allow to achieve the molecular limit for highly organized domains

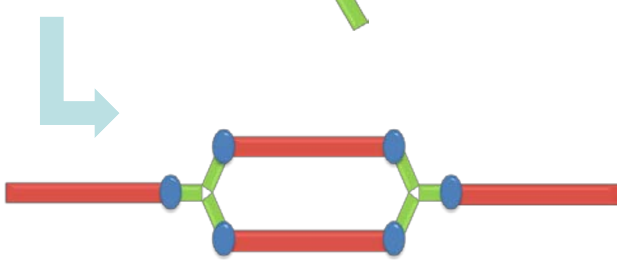


Dynameric Membranes- controlling “the metrics” of membrane material

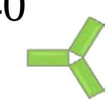


PolyTHF 1100 + Triamine T-440

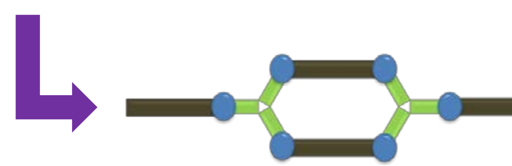
+ Core center



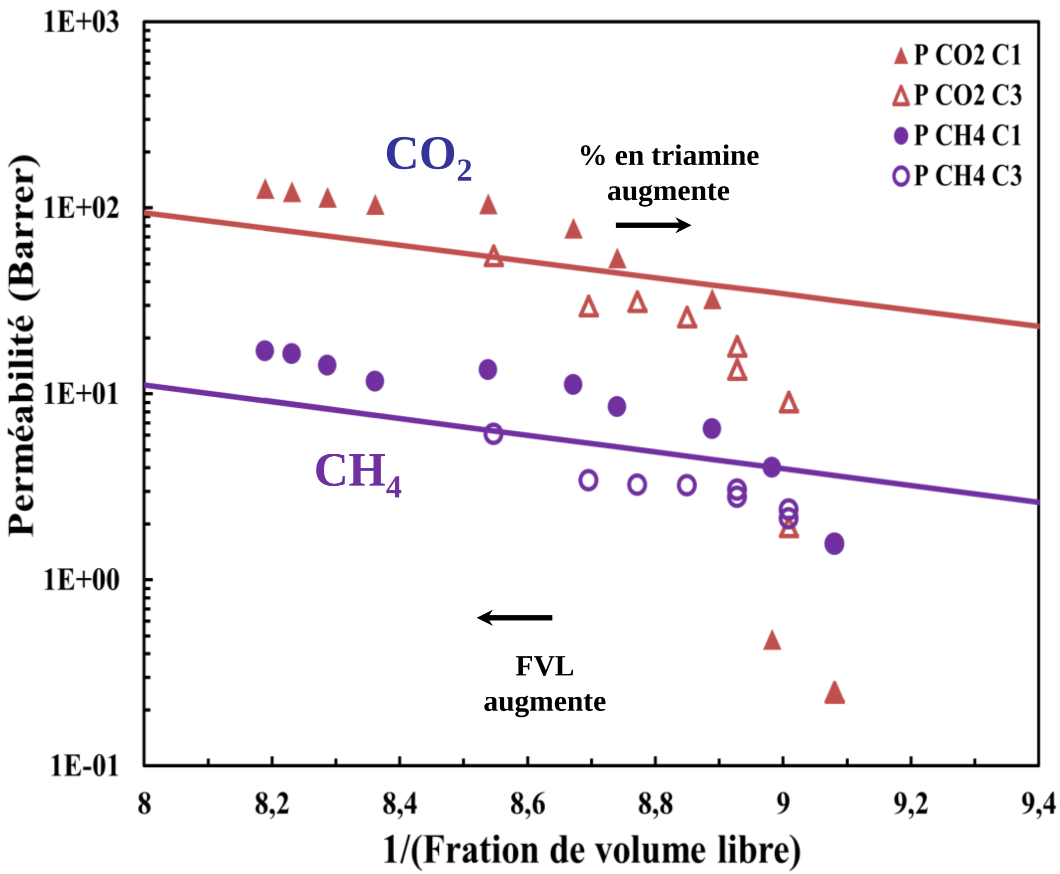
PolyTHF 350 + Triamine T-440



+ Core center



Free volume model: Permeability
Fick diffusion



Fugita Model:

$$P = A_P \exp(-B/FFV)$$

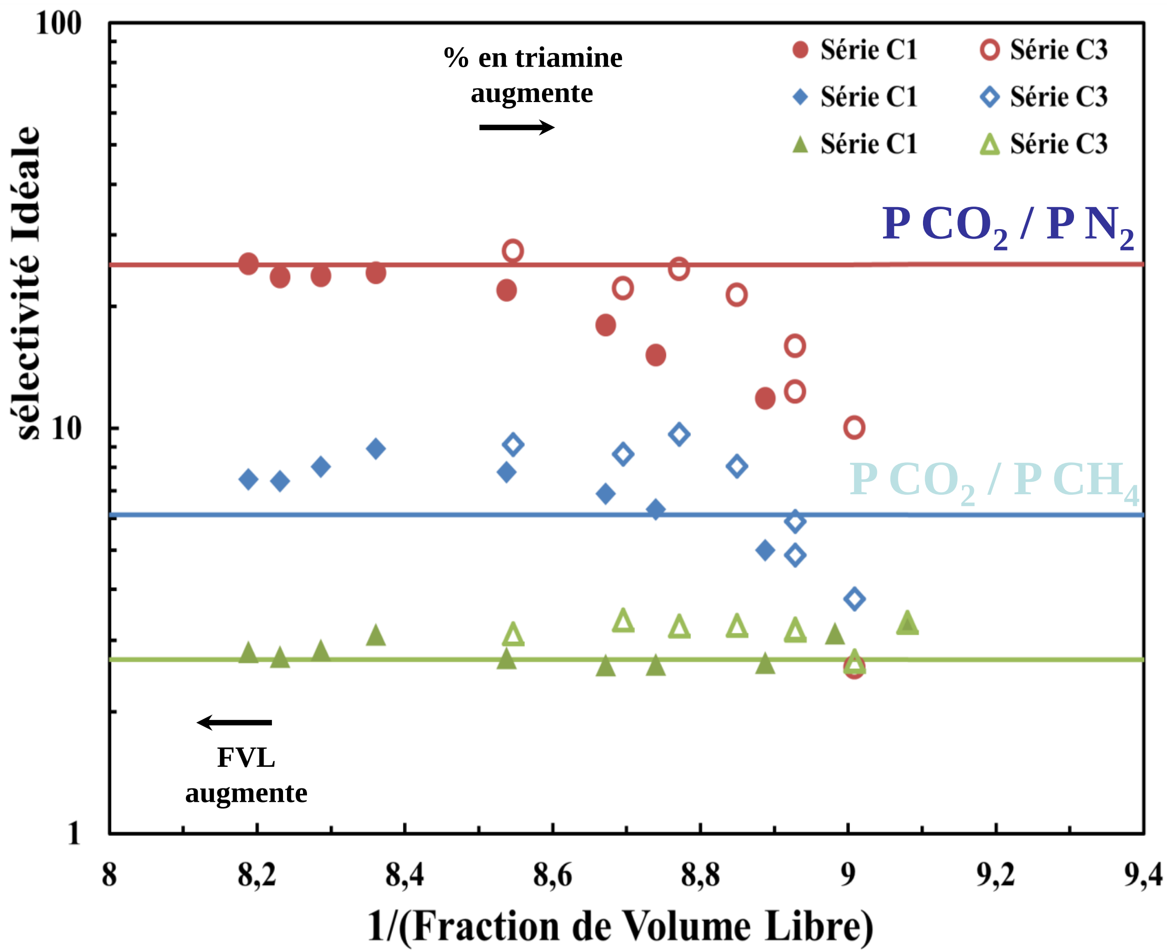
	A_D	B
CH_4	4,60E+04	1,04
CO_2	2,80E+05	1
N_2	1,10E+04	0,96
O_2	2,95E+04	0,94

B CH_4 > B CO_2 > B N_2 > B O_2

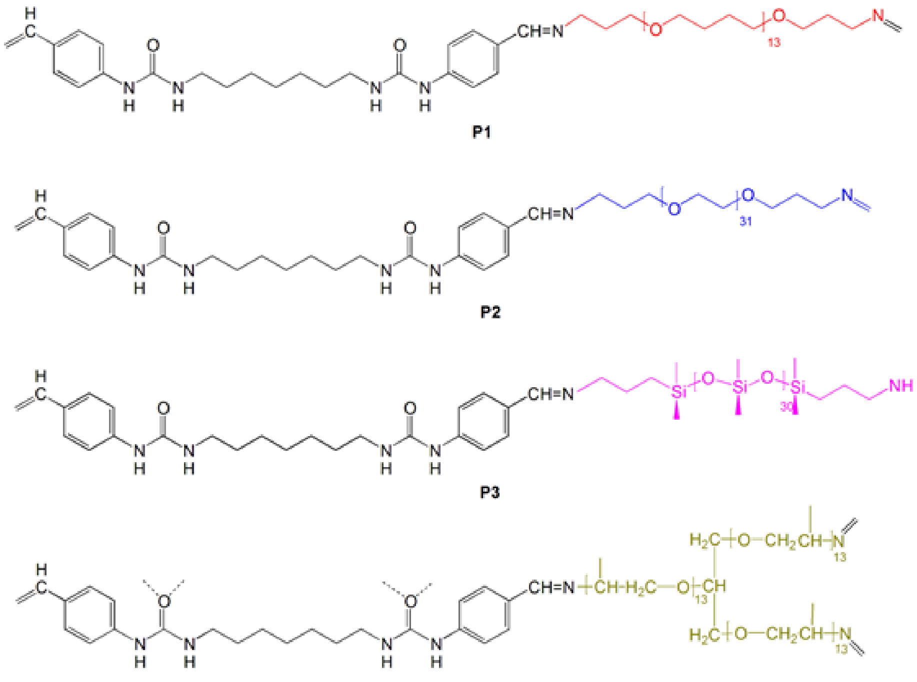
Vc CH_4 > Vc CO_2 > Vc N_2 > Vc O_2

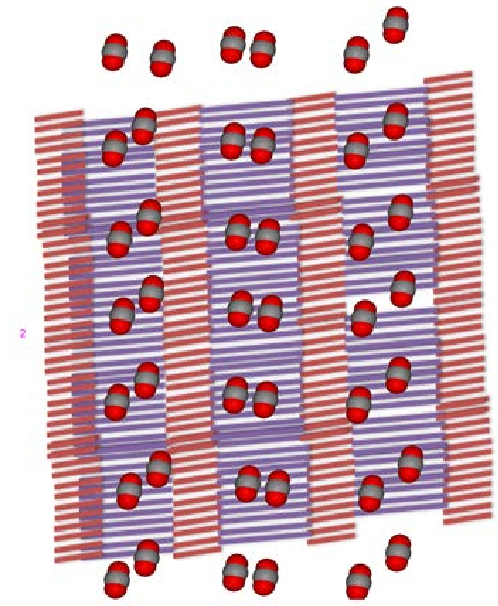
H. Fugita, *Fortshritte Hochpolymere Forschung*, **1961**, 3, 1-15

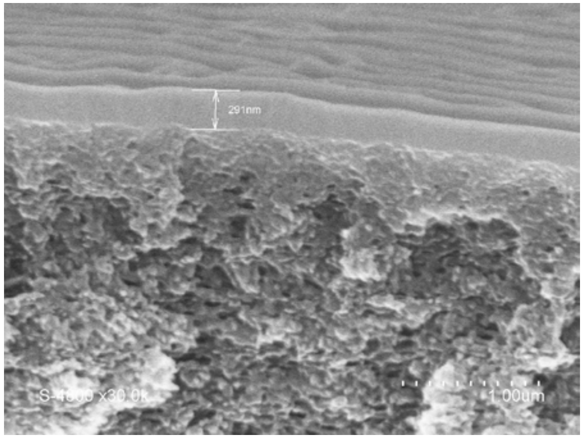
Ideal selectivity –free volume model



Double dynameric membranes: supramolecular hard and macromolecular permeable soft domains



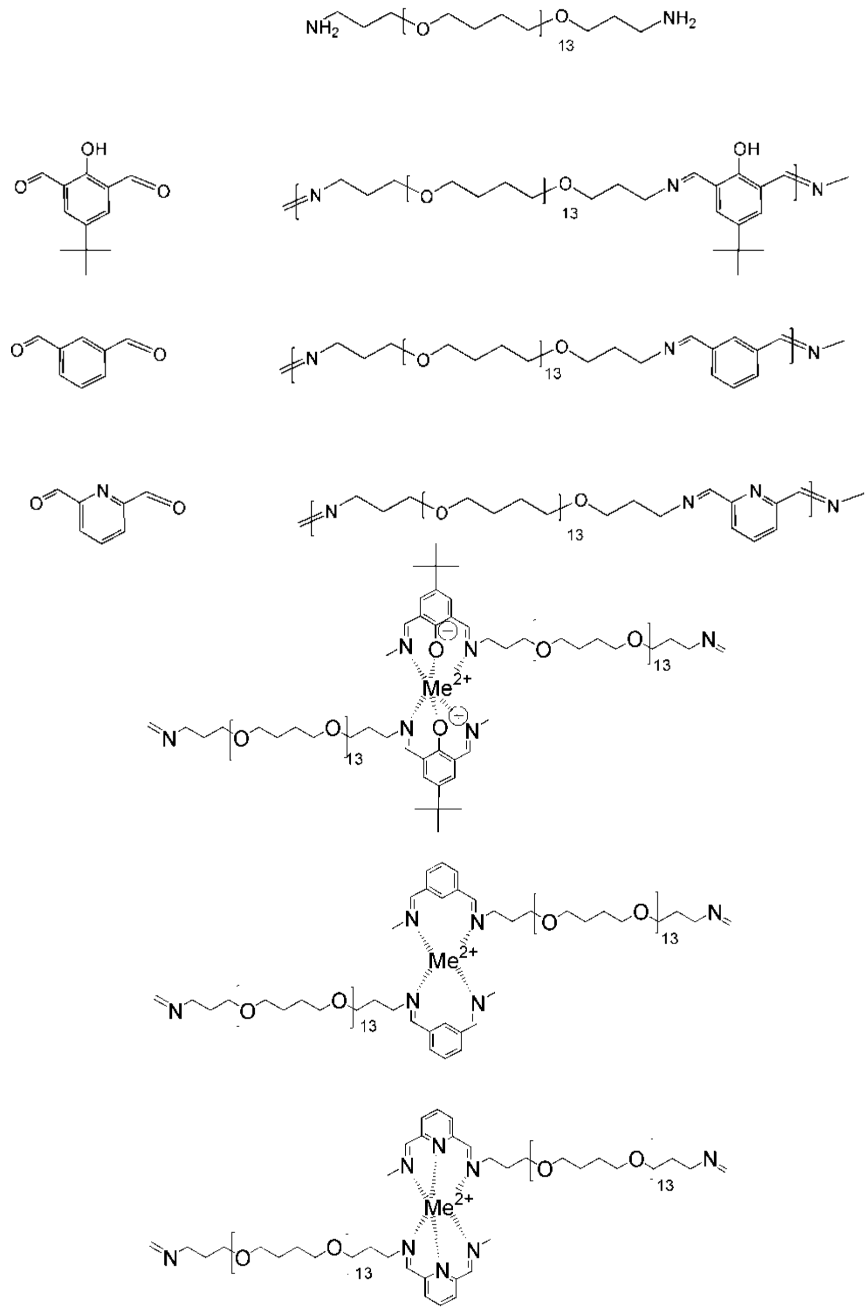


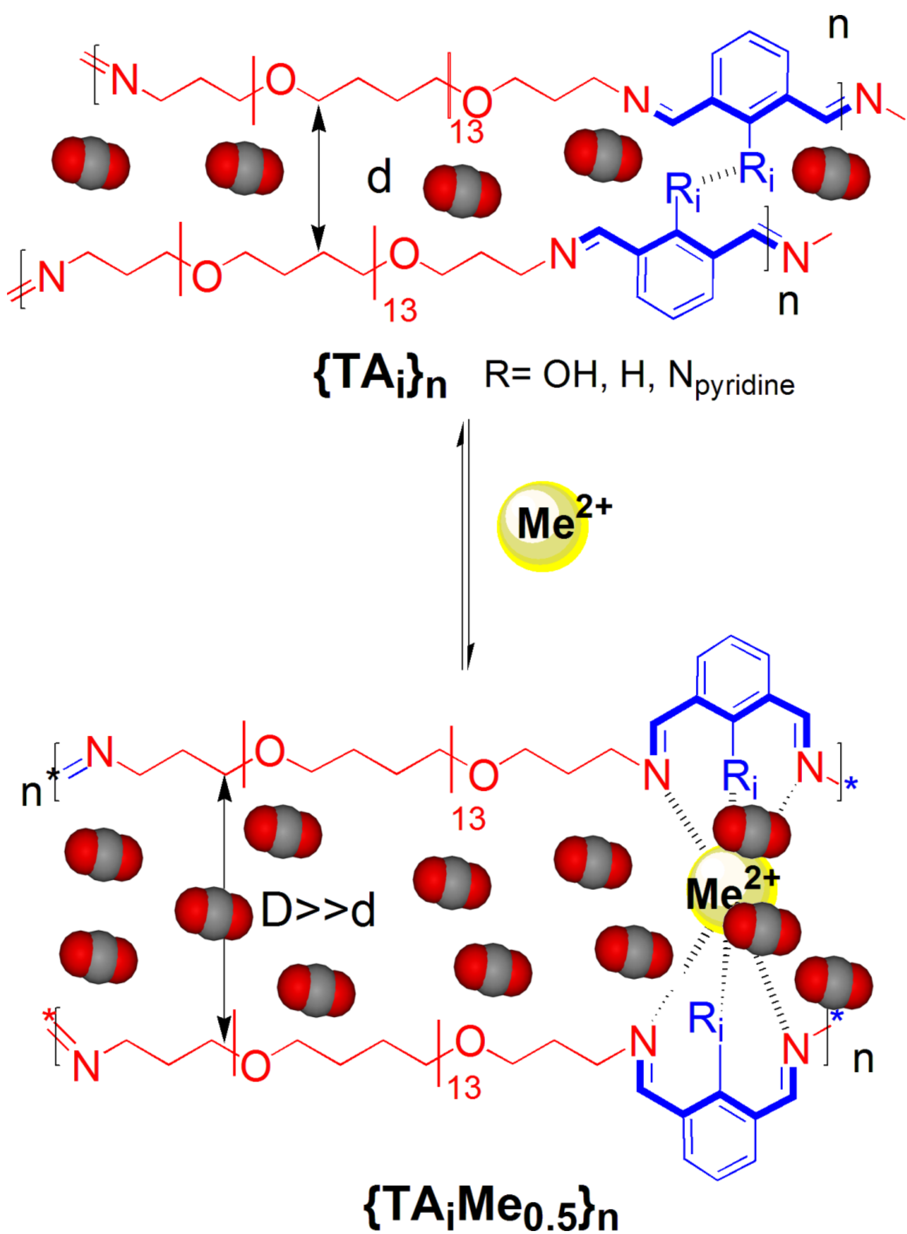


Membrane	P_{O2} Barrer	P_{N2} Barrer	P_{CO2} Barrer	$S_{CO2/N2}$	$S_{O2/N2}$
P1	6.2	2.2	80.2	36.7	2.8
P2	0.33	0.2	3.00	1.7	14.9
P3	474.7	204.8	2685.3	13.1	2.2
P4	3.5	1.6	43.0	28	2.3
P5	3.0	3.0	9.0	3	1
P6	6.0	2.0	25.0	14	3

Chem. Commun., 2012, *48*, 7398-7400

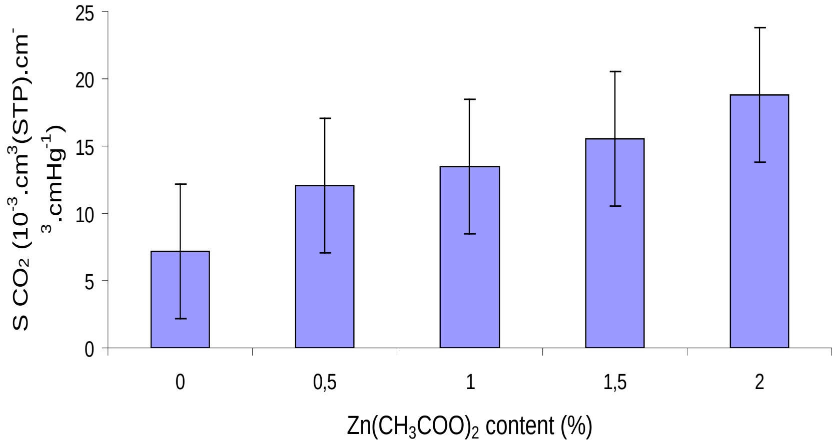
Metallodynameric membranes

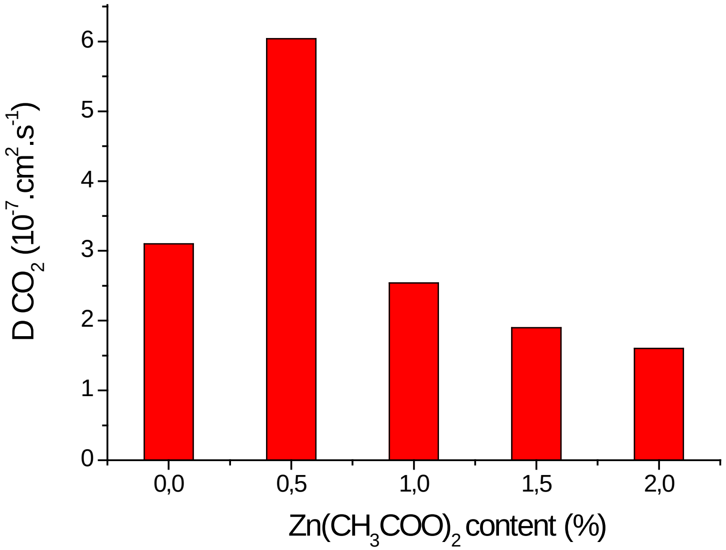




Chem. Commun., 2012, *48*, 6827-6829

Gas transport solubility and diffussion





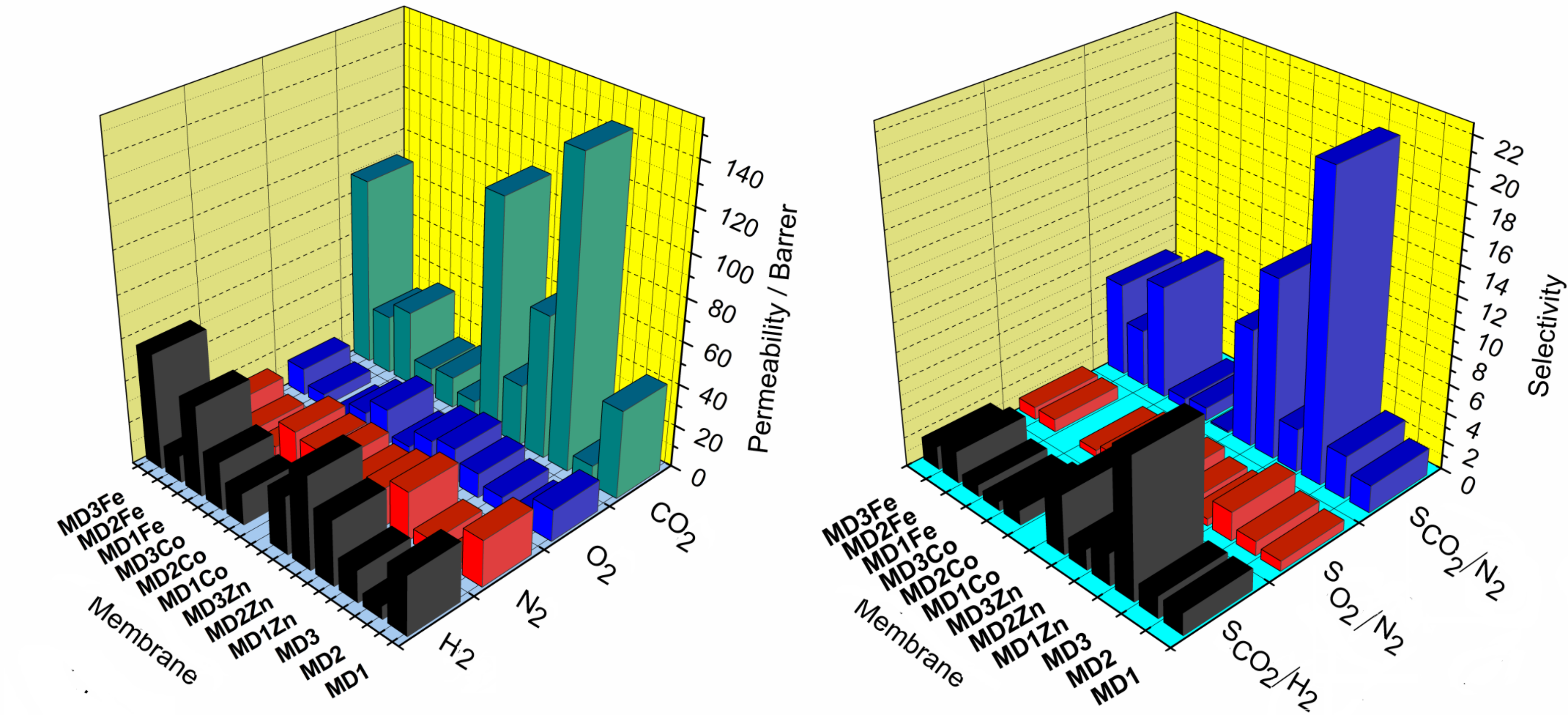
Increasing S with Zn^{2+} content ⇒ Interaction Zn^{2+}--H_2O - CO_2

Zn^{2+}	$S_{time-lag}$ 10^{-3} (cm^3(STP)$cm^{-3}cm^{-1}{}_{Hg}$)	S' 10^{-3} (cm^3(STP)$cm^{-3}cm^{-1}{}_{Hg}$)
g_1d	13.5	7.2
g_1d 0.5	13.1	12.1
g_1d 1	13.9	-
g_1d 2	20.0	18.8

Even if the process seems to be controlled by CO_2 sorption, the diffusion becomes more influent under decomplexation reaction effect which restricts the diffusion process

Good agreement between calculated and experimental solubility coefficient

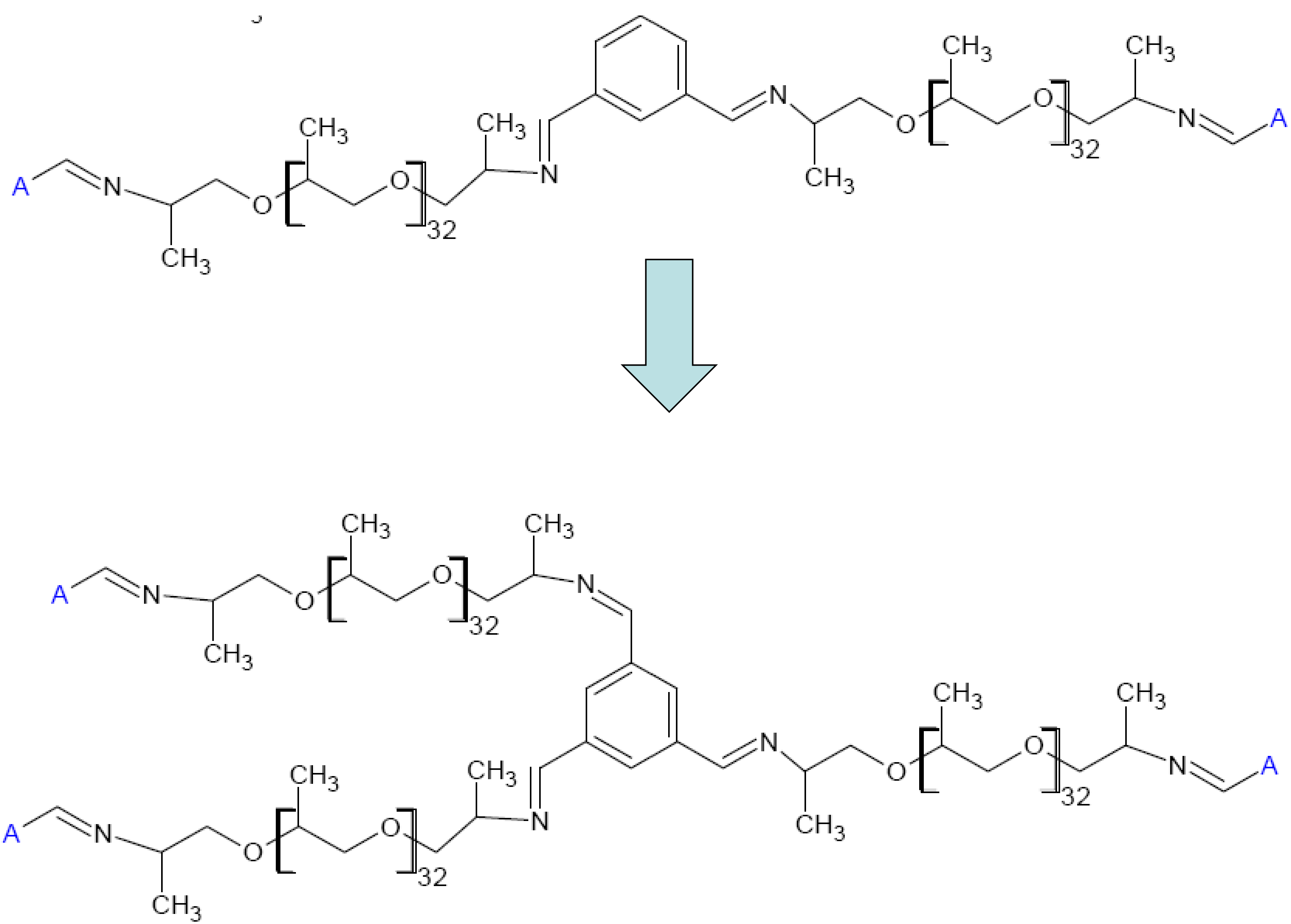
Efficient screening for optimal performances



Pure gas permeabilities and b) pure CO_2/N_2, O_2/N_2 CO_2/H_2 selectivities at 298 K and 1.0×10^{-5} Pa,

Chem. Commun., 2012, *48*, 6827-6829

Rubbery Organic Frameworks (ROFs) IInd generation



Rubbery Organic Frameworks (ROFs) for gas separation IInd generation

Table 1 Permeation results for single gas at 5 bars

Membrane	Permeability (Barrer)			Selectivity (CO_2/N_2)	Selectivity (CO_2/CH_4)
	N_2	CO_2	CH_4		
T3	8	250	27	31	9
T2	43	711	126	17	6
T5	0,81	34	2,24	42	15
T6	27	895	104	33	9

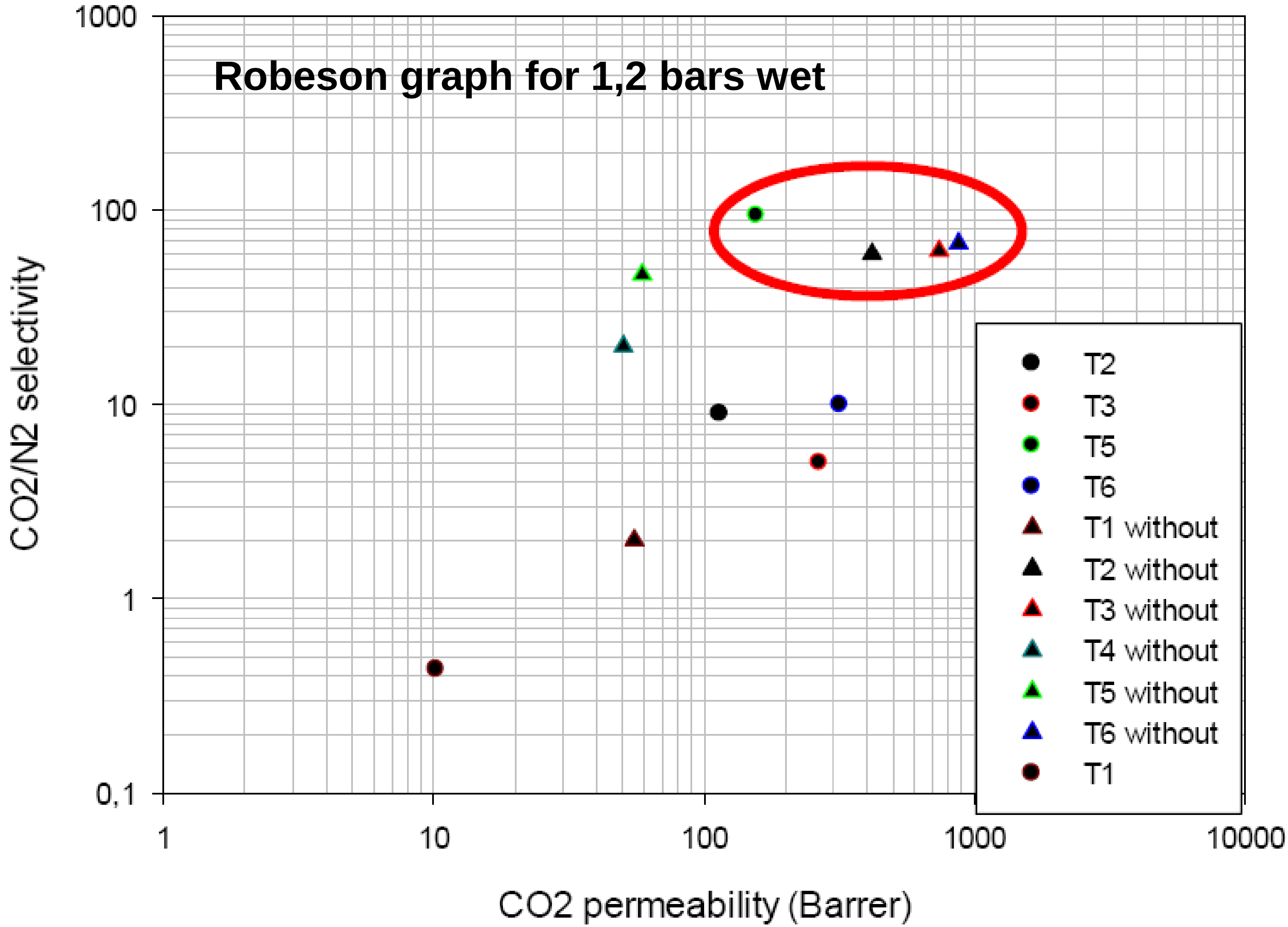
Table 2 CO_2 and N_2 permeability results mix gas experiments

Membrane	CO2 Permeability (Barrer)			
	1,2 bar dry	5 bar dry	1,2 bar wet	5 bar wet
T3	372	272	418	408
T2	786	1128	741	726
T5	59	32	59	40
T6	1086	898	876	658

Membrane	N2 Permeability (Barrer)			
	1,2 bar dry	5 bar dry	1,2 bar wet	5 bar wet
T3	25	5	5	6
T2	5	24	12	13
T5	5	2	1	1
T6	36	23	13	14

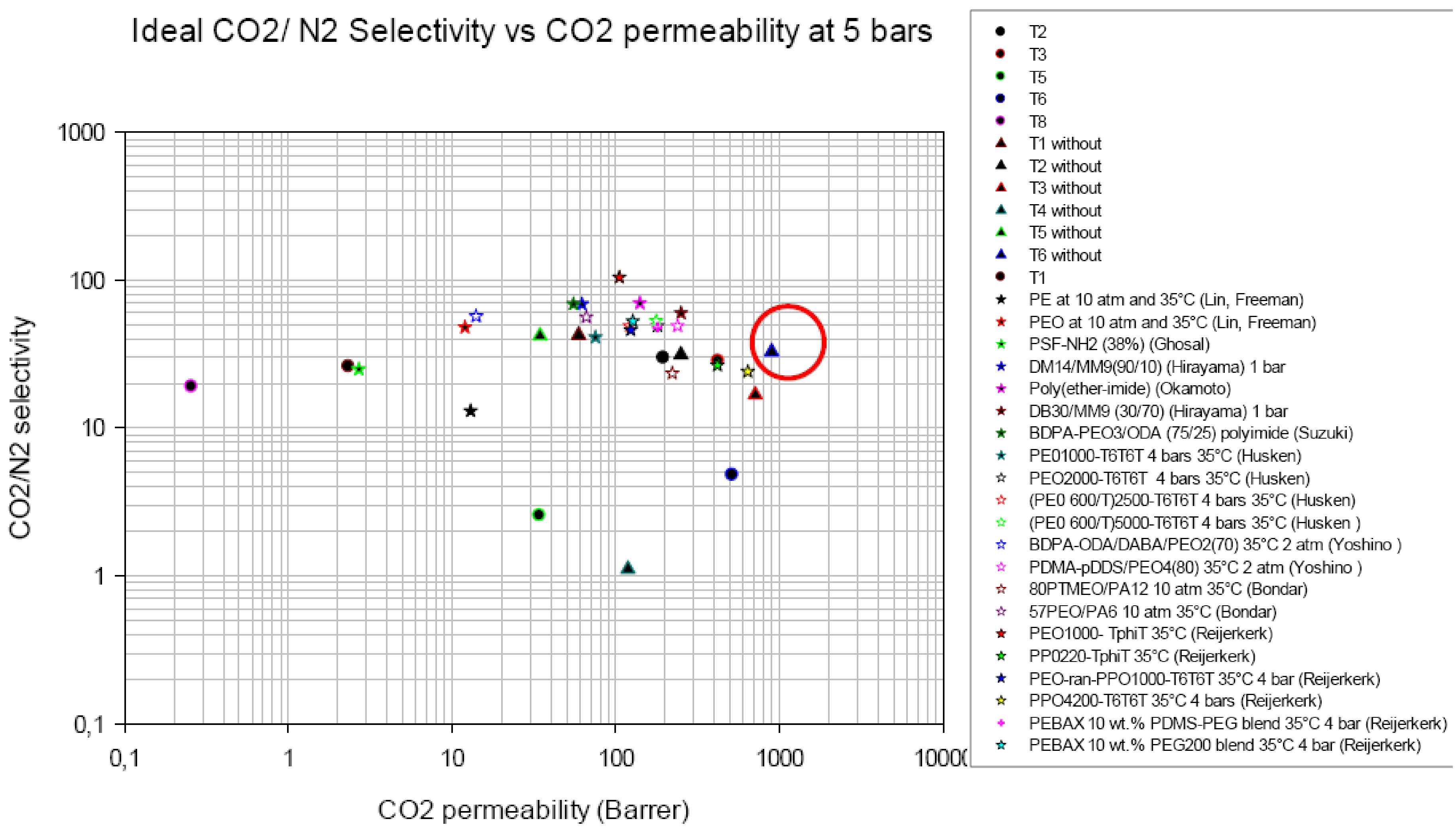
Collab. with M. Sandru and M. Britt Hag

Rubbery Organic Frameworks (ROFs) for gas separation IInd generation



Collab. with M. Sandru and M. Britt Hag

Rubbery Organic Frameworks (ROFs) for gas separation IInd generation



Collab. with M. Sandru and M. Britt Hag

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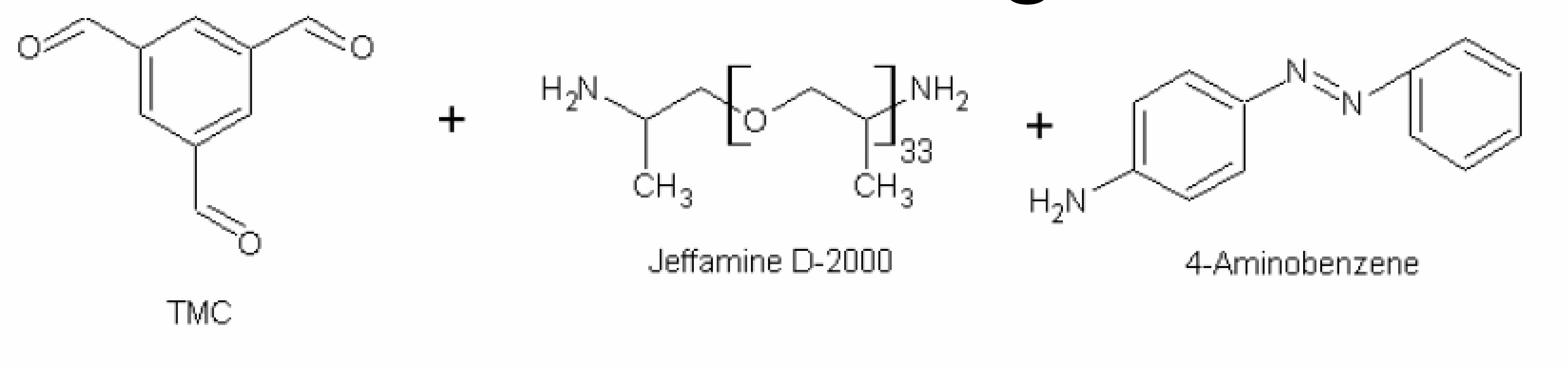
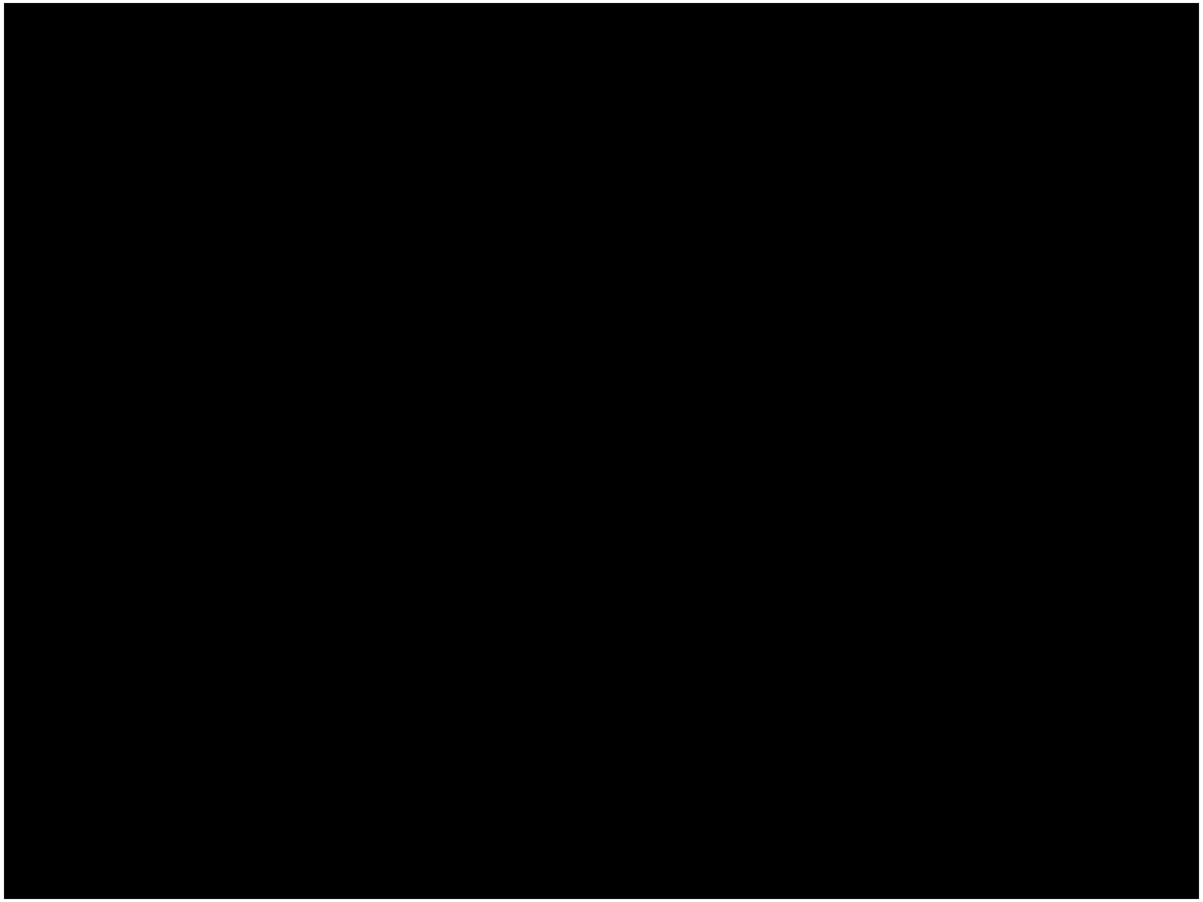
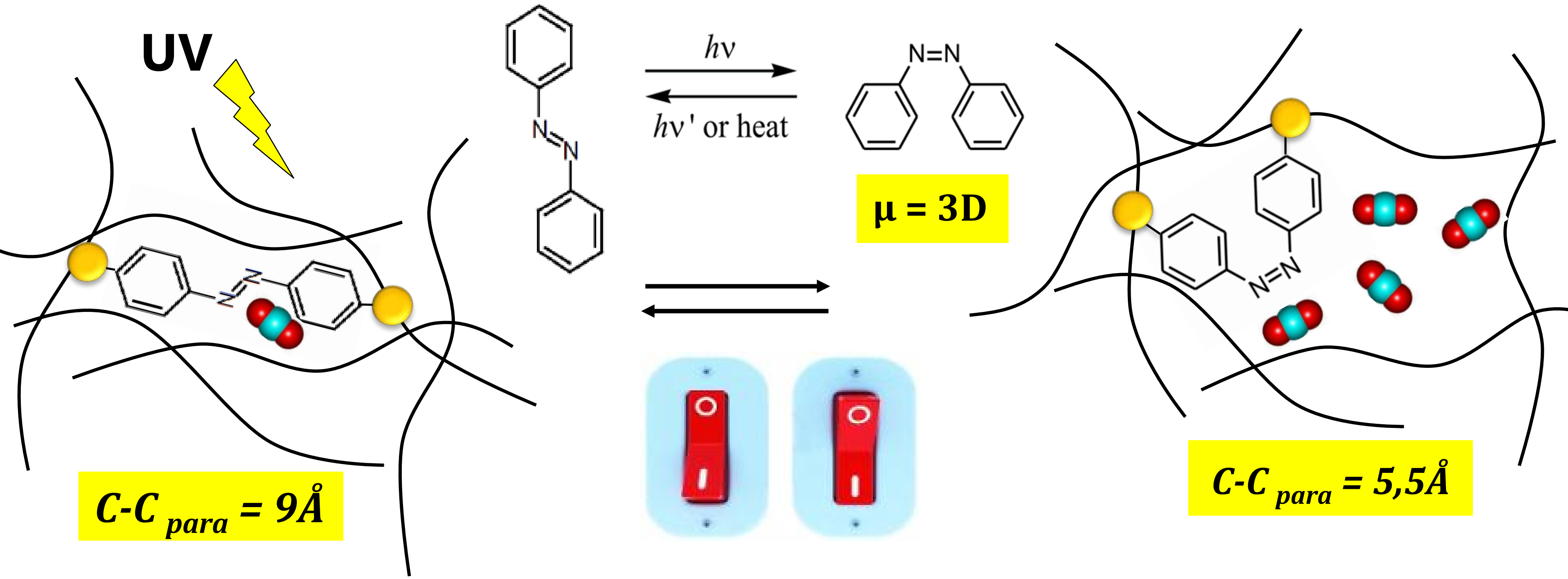
Self-healing membranes

ROFs and light





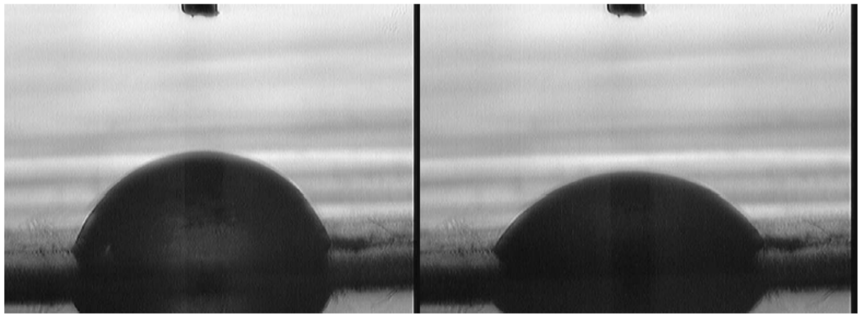
ROFs and light



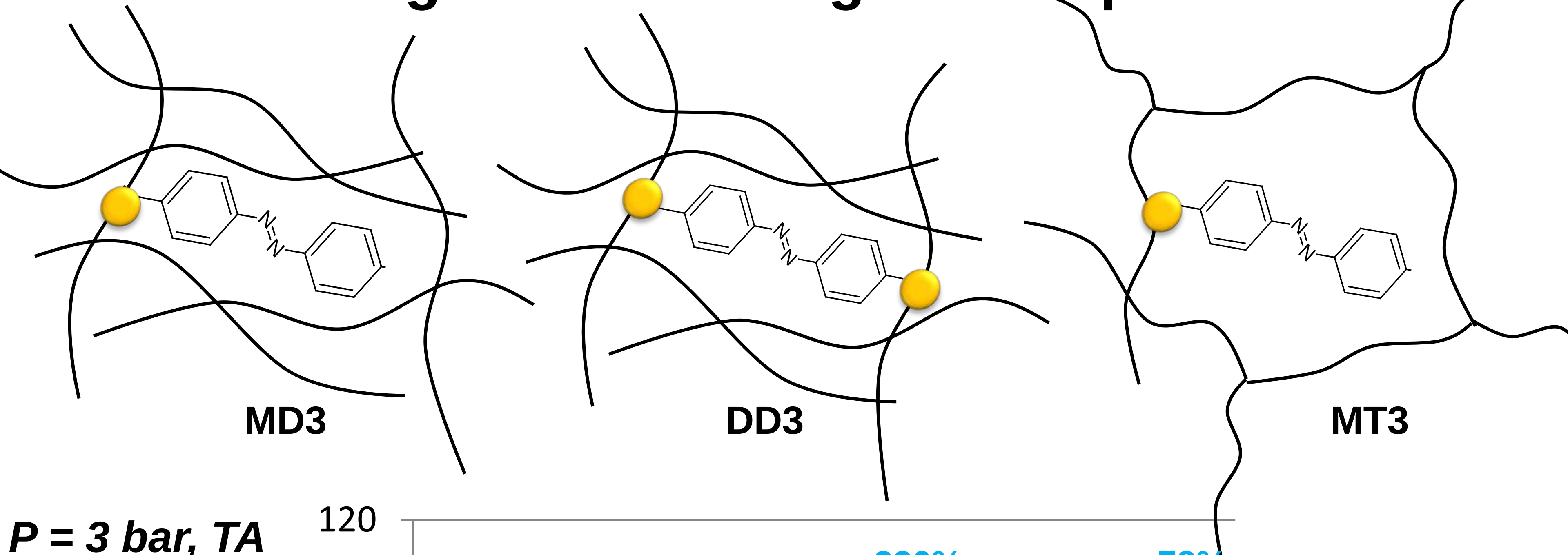
Molecular switches- molecular stirrers

- **Solubility** +
- **Free volume** +

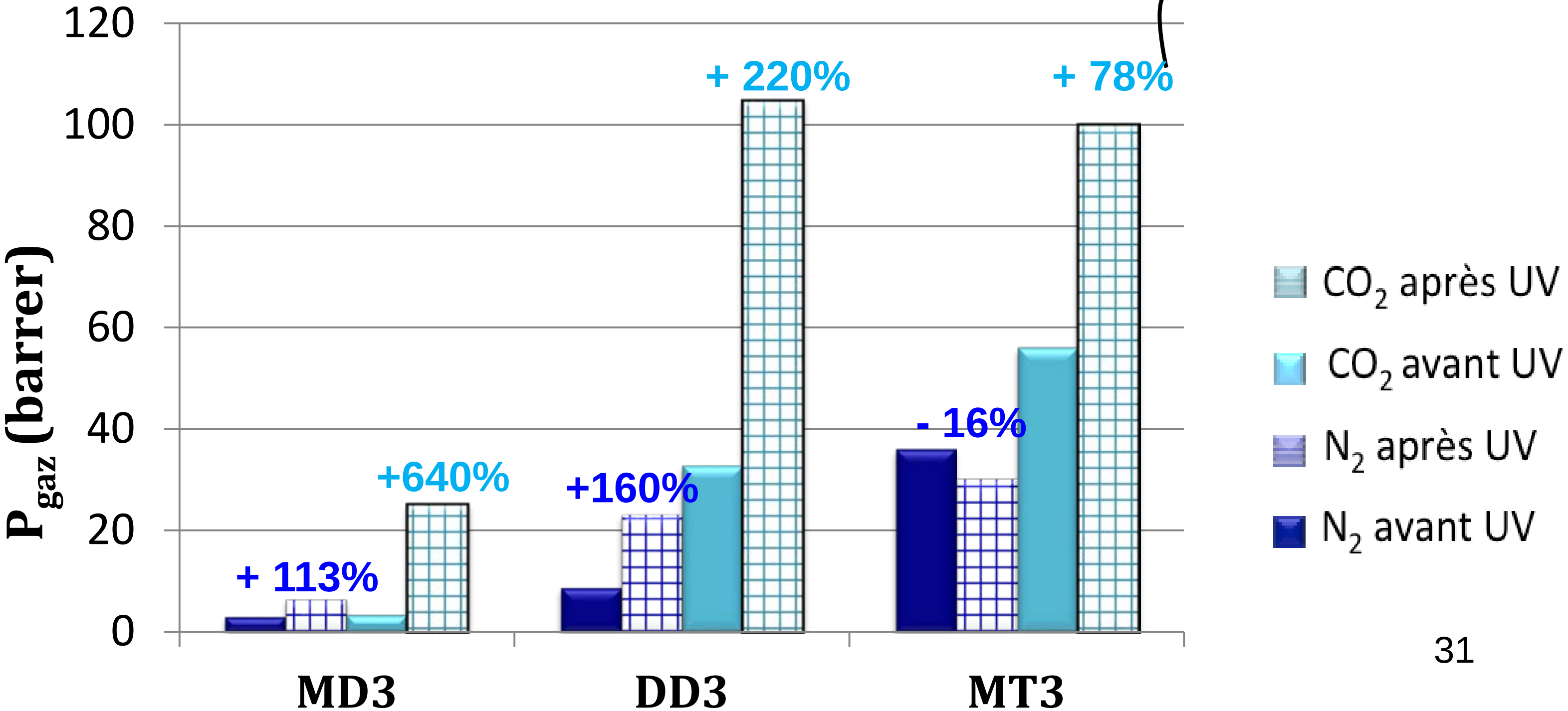
Before after irradiation



Light controlled gas transport



P = 3 bar, TA
UV (280-560 nm)
Time600s



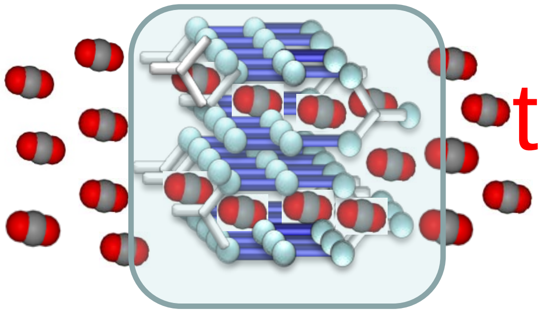
Rubbery Organic Frameworks

•Variability, versatility, easy screening for best performances.

•Diffussion-controlled transport

•Self healing, stability

•Adaptability-commutable



the rubbery version of MOFs, ZIFs or PIMs