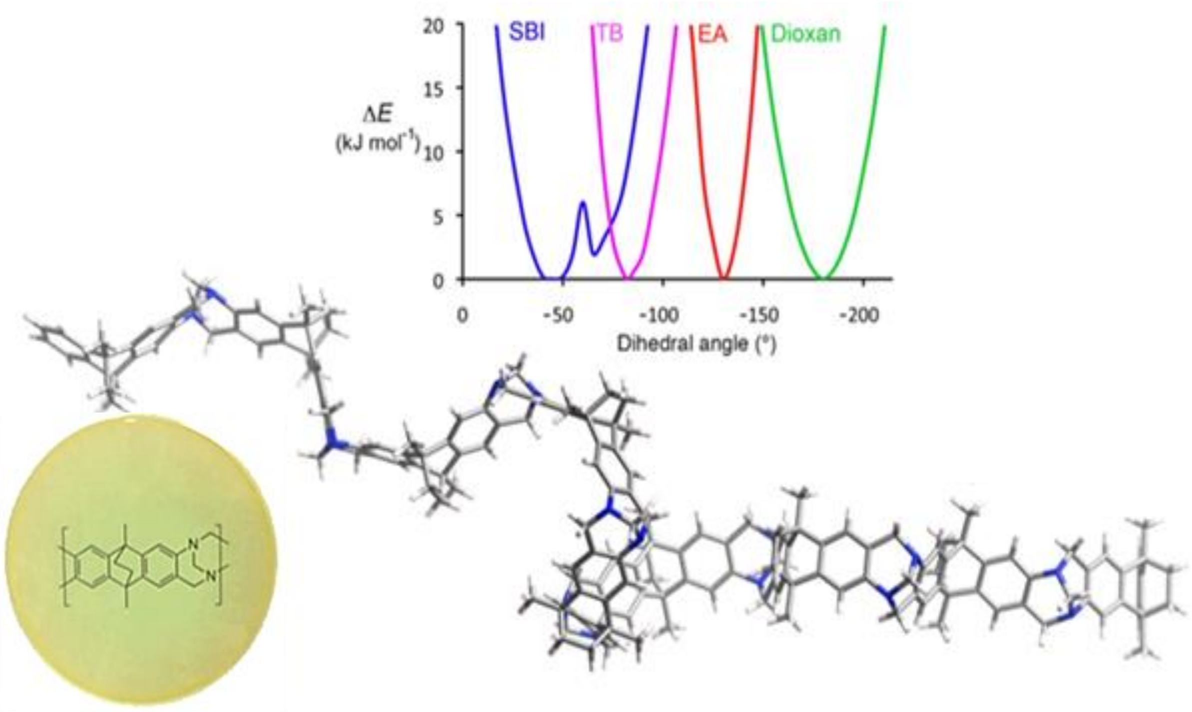
Polymers of Intrinsic Microporosity for Gas Separation Membranes

100
1920~2020

Swansea University
Prifysgol Abertawe



Dr Mariolino Carta

Swansea University (UK)

NATIONAL NATURAL SCIENCE FOUNDATION OF CHINA
国家自然科学基金委员会
1986

BRITISH COUNCIL
英国文化教育协会
英国大使馆文化教育处

BRITISH COUNCIL
RESEARCHER LINKS

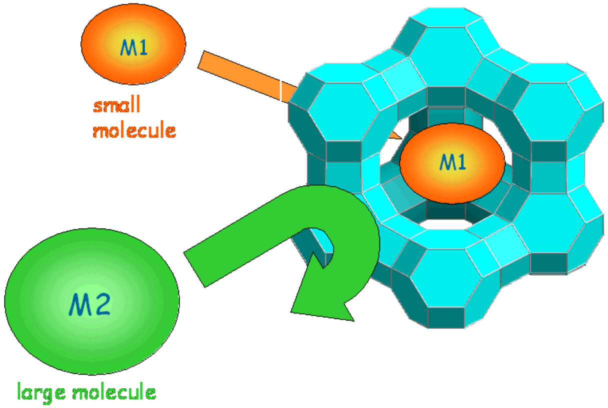
Newton Fund

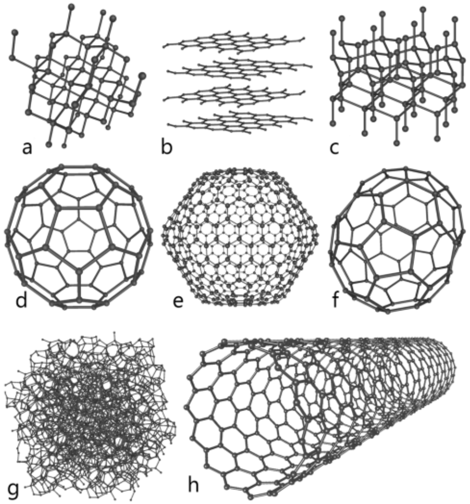
Nanjing 15th October 2018

Microporous materials

Porous materials can be classified depending upon the dimension of their pores.
According to the IUPAC definition (International Union of Pure and Applied Chemistry) :

- Pores < 2 nm are defined as **microporous**
- Between 2-50 nm **mesoporous**
- > 50 nm **macroporous**





Zeolites

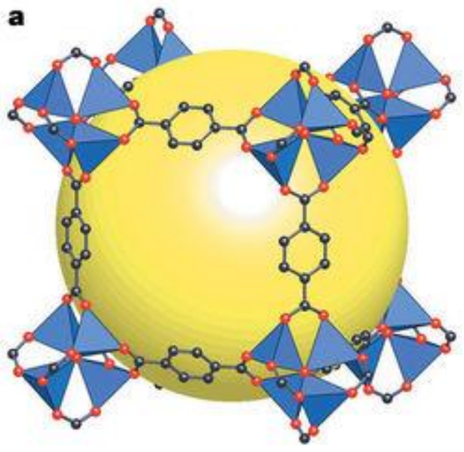
- Natural occurring aluminum silicates
- BET surface areas = 400-700 $m^2\ g^{-1}$

Activated carbons

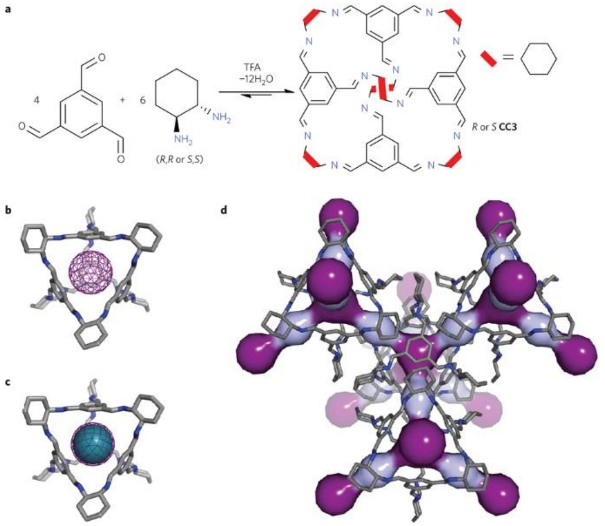
- Derived from the combustion of organics
- BET surface areas = 400-3000 $m^2\ g^{-1}$

D. A. Rouquerol, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing and K. K. Unger, ***Pure Appl. Chem***, 1994, 66, 1739

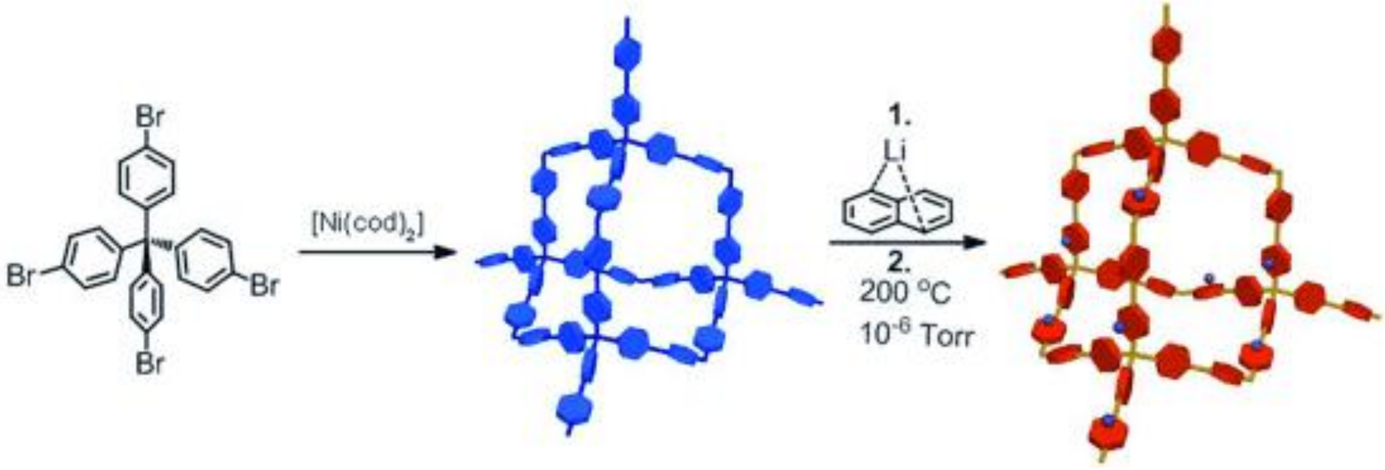
Synthetic microporous materials



M. Eddaoudi,, O. M. Yaghi, *et al.* 1999. ***Nature***, *402*(6759), 276

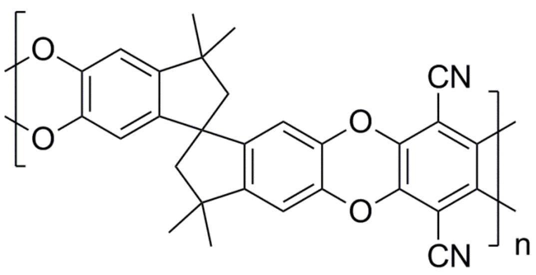


A. I. Cooper *et al*, ***Nat. Mater.*** 2014, 13, 954



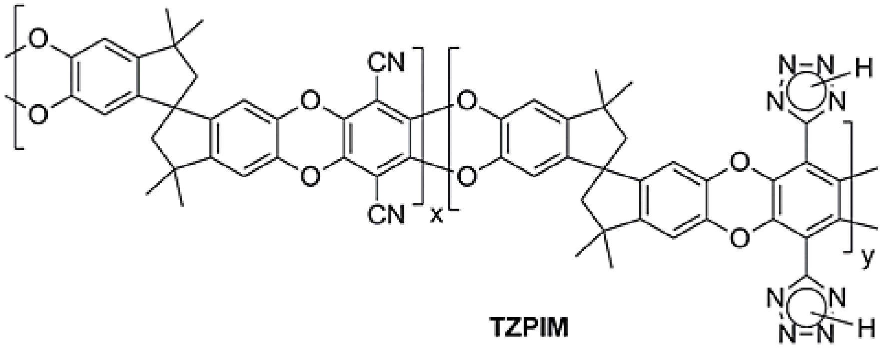
K. Konstas, *et al*, ***Angew. Chem. Int. Ed.,*** 2012, 51, 6639

Polymers of Intrinsic Microporosity (PIMs)



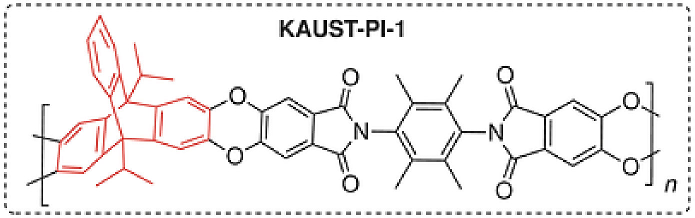
PIM-1

N. B. McKeown, *et al.* ***Chem. Commun***. *2004, 230*

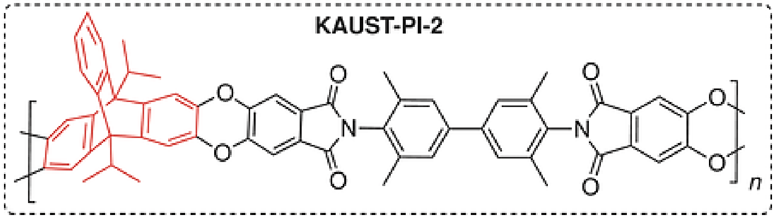


TZPIM

M. D. Guiver *et al.* ***Nat. Mater.*** *2011, 10(5):372*

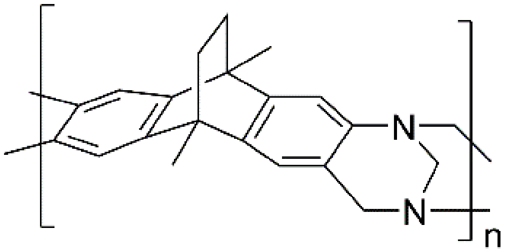


KAUST-PI-1



KAUST-PI-2

I. Pinnau, *et al*,. ***Adv. Mater.***, 2014 *26*(22), 3688

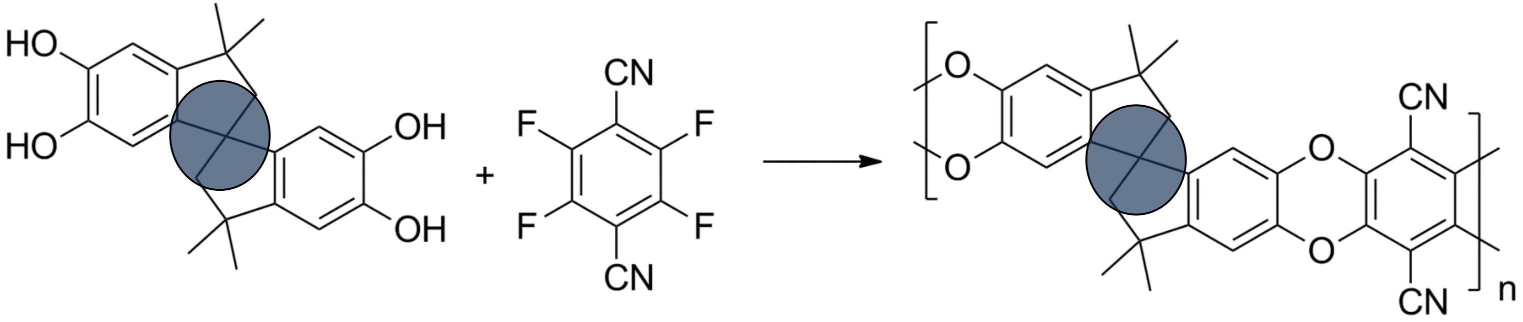


PIM-EA-TB

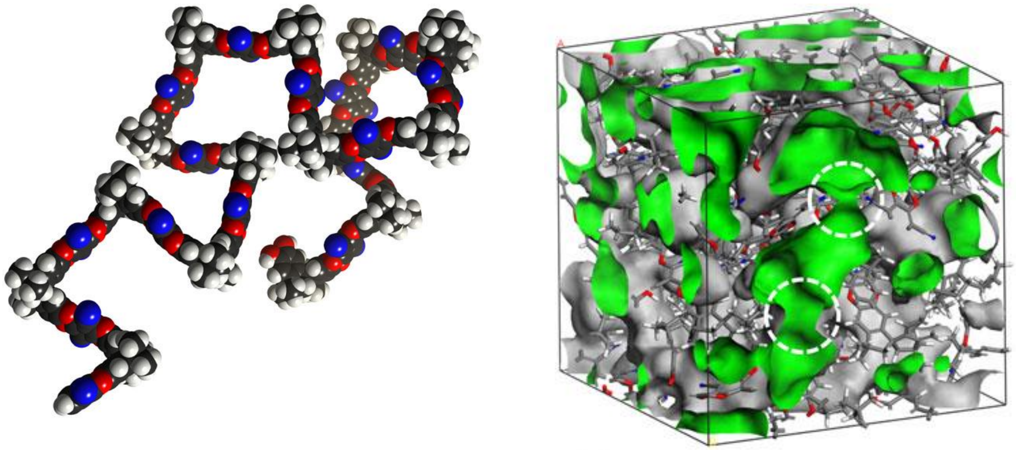
M. Carta *et al.* ***Science***, 2013, *339*, 230

A Polymer of Intrinsic Microporosity : (PIM-1)

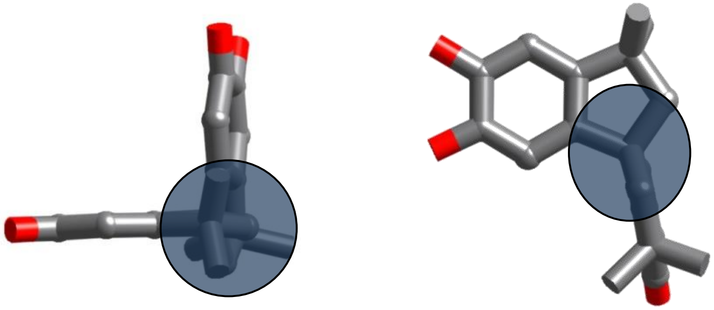
***f av* = 2**



M_w = >200 x 10^3 (GPC)
T_g > 350 °C
Fluorescent (yellow)
Soluble!
BET surface area = 760 m^2/g



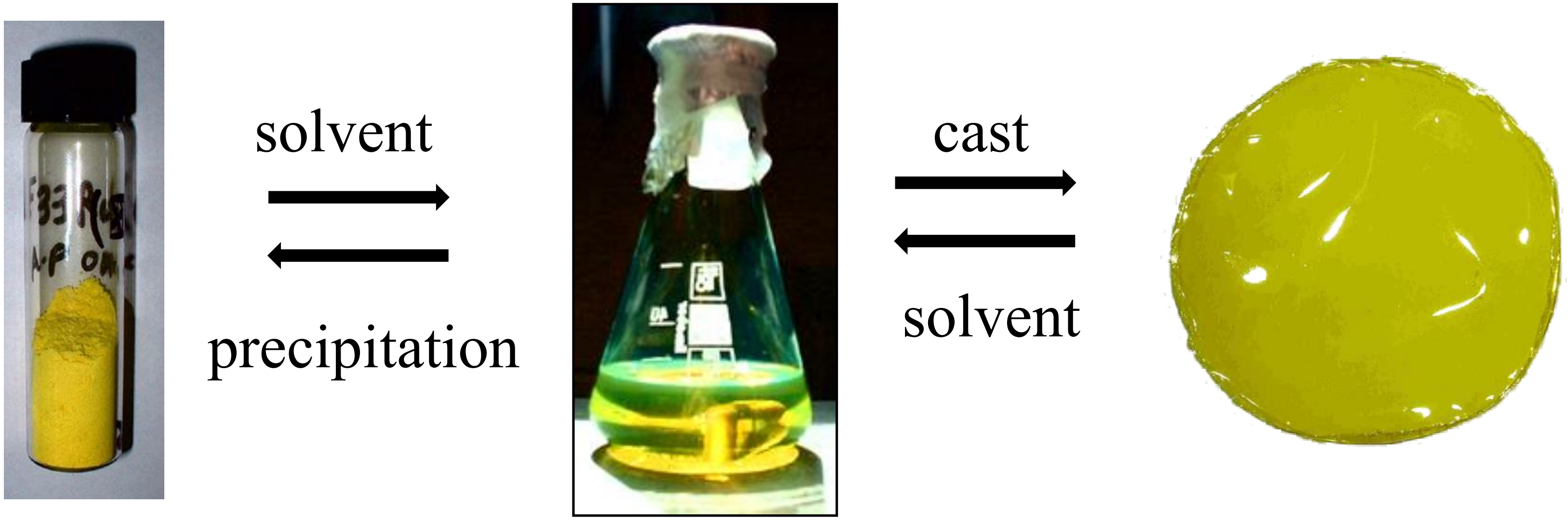
High Internal Free Volume



Spiro-centre = site of contortion

N. B. McKeown, *et al.* ***Chem. Commun***. *2004, 230*

PIMs : soluble microporous materials


solvent

precipitation

cast

solvent

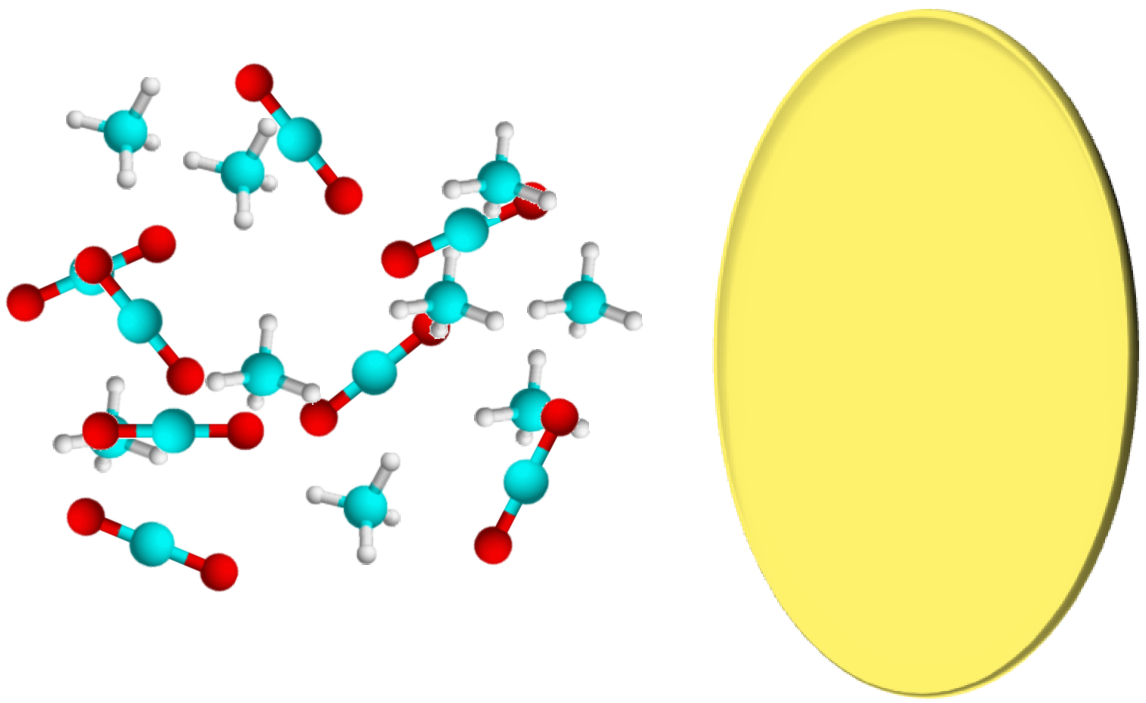
SA = 760 m^2 g^{-1}

PIM-1 (THF, $CHCl_3$)

SA = 690 m^2 g^{-1}

N. B. McKeown, *et al.* ***Chem. Commun***. *2004, 230*

PIMs for Gas Separation Membranes



Feed mixture

e.g. CO_2/CH_4

Membrane

(selective barrier)

Retentate

Enriched in methane

$CH_4 > CO_2$

(not 100% selective)

Permeate

Enriched in CO_2

$CO_2 > CH_4$

Solution-diffusion model: $P = SD$

P **= permeability coefficient;** ***S*** **= solubility coefficient;** ***D*** **= diffusion coefficient**

Courtesy of John Jansen (ITM, Italy)

Robeson plots: how to beat the upper bound

"…the upper bound correlation is an empirical relationship demonstrating the state-of-the-art for approaching true molecular sieving structures."

L. M. Robeson, ***J. Membrane Sci.***, **1991**, 62, 165.

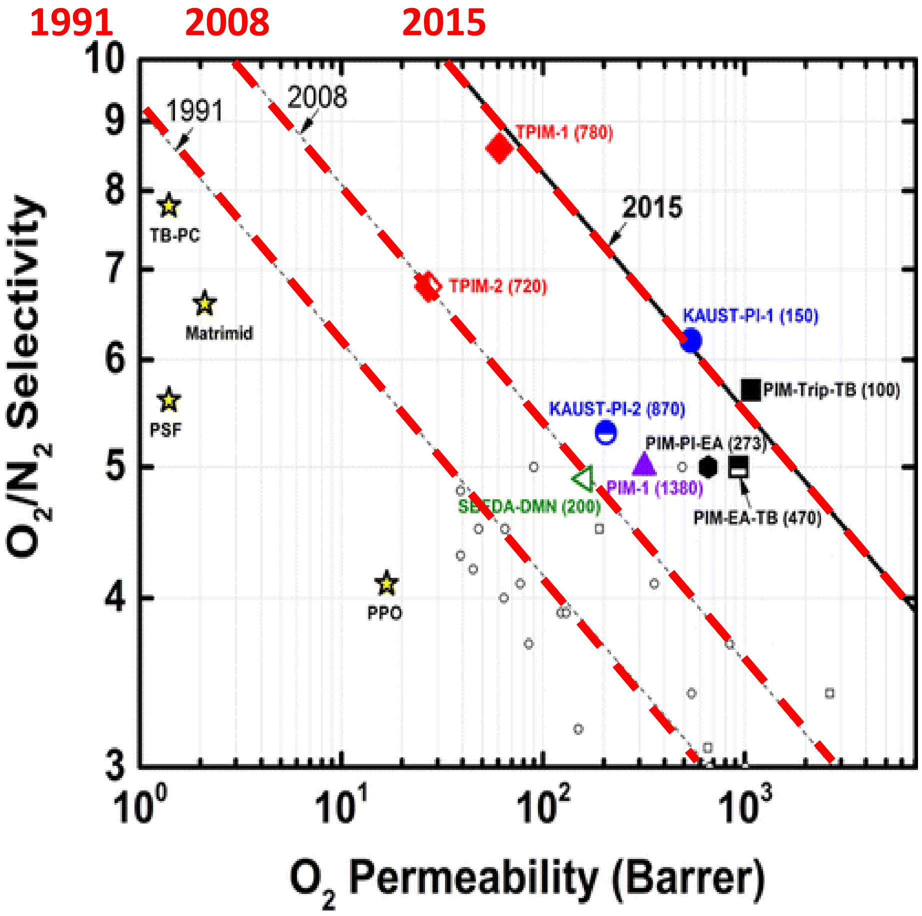
1991: "high T_g polymers"
(e.g. polyimides).

L. M. Robeson, ***J. Membrane Sci.***, **2008**, 32, 375.

2008: "ladder-type rigid polymers"
(i.e. PIM or PIM-like polymers with conformational restriction).

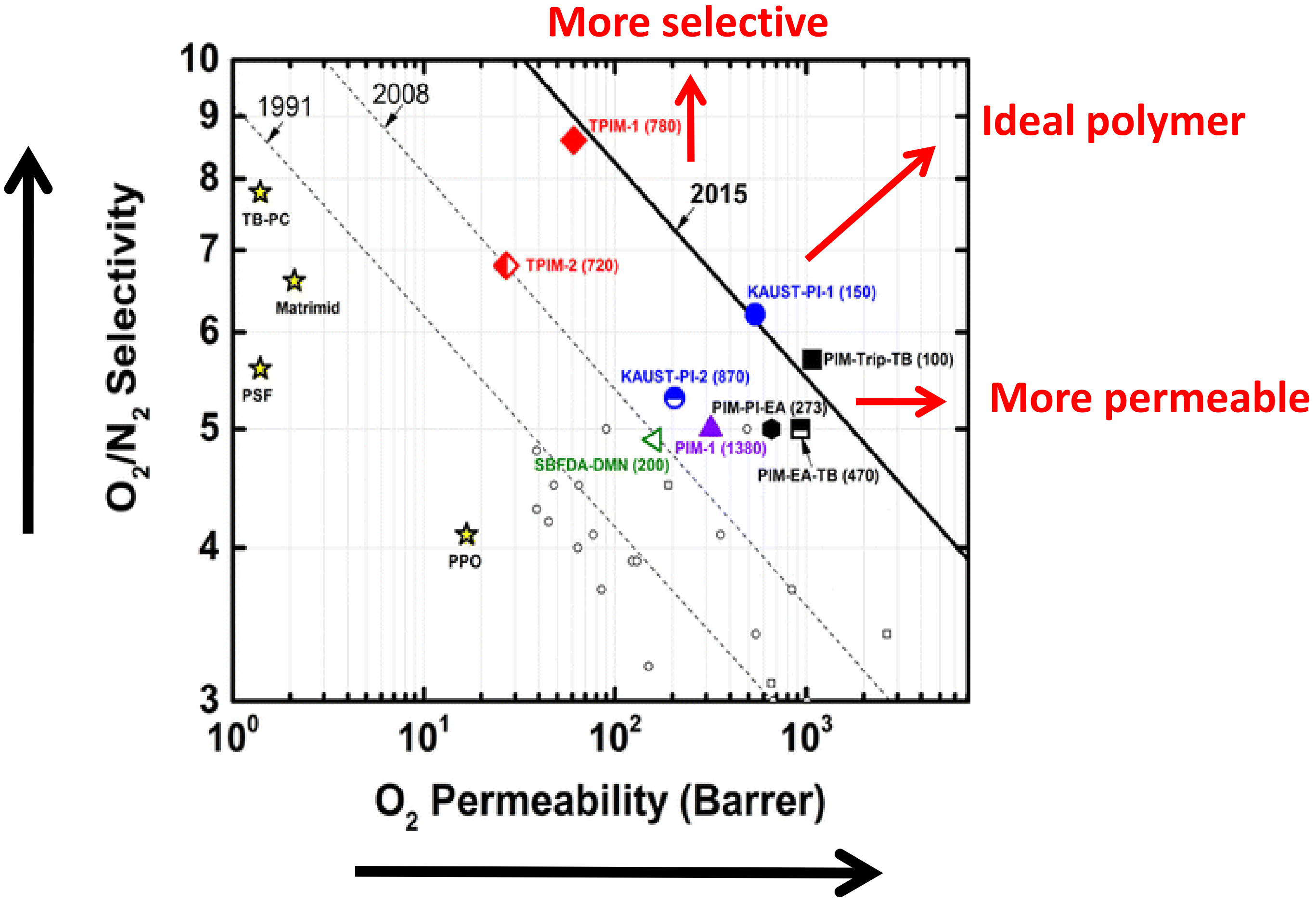
I. Pinnau *et al*. ***ACS Macro Lett.,*** **2015**, 4 (9), 947

2015: "A subtle balance between intrachain rigidity and interchain spacing has been achieved in the amorphous microstructures of PIMs"



Gas permeability and selectivity trade-off

Important gas pairs: O_2/N_2, H_2/N_2, CO_2/N_2, CO_2/CH_4, H_2/CO_2



More selective

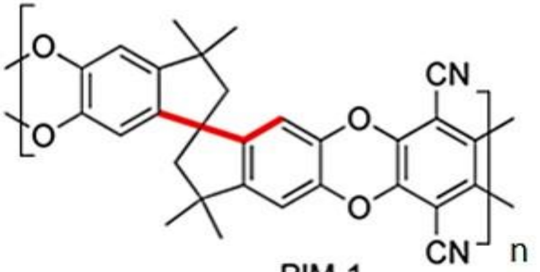
Ideal polymer

More permeable

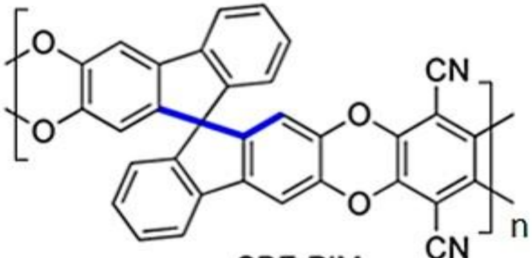
Solution-diffusion model: ***P* = *SD***

***P* = permeability coefficient; *S* = solubility coefficient; *D* = diffusion coefficient**

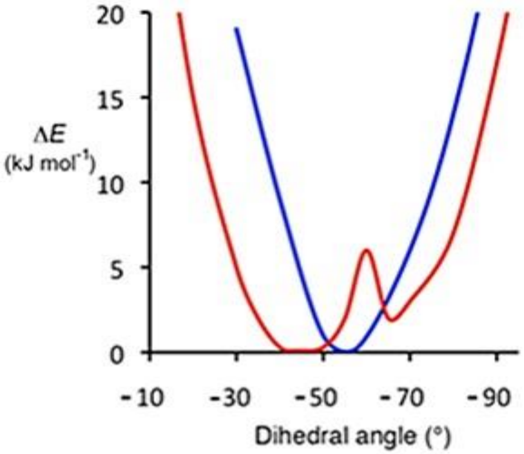
Modifications and improvements of PIM-1



PIM-1



SBF-PIM



The molecular structures of PIM-1 and PIM-SBF. A plot showing the increase in energy associated with the deviation in dihedral angle about the spiro-centre for PIM-1 (red) and PIM-SBF (blue) to illustrate the greater rigidity of the PIM-SBF polymer chains.

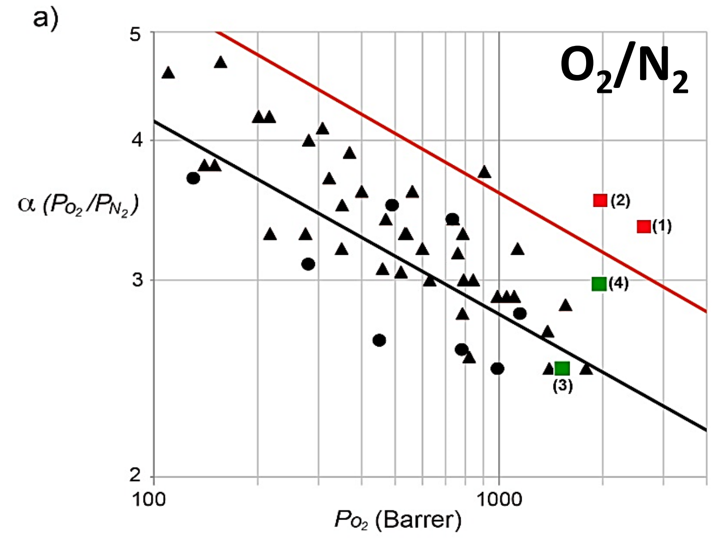
Very good solubility in $CHCl_3$

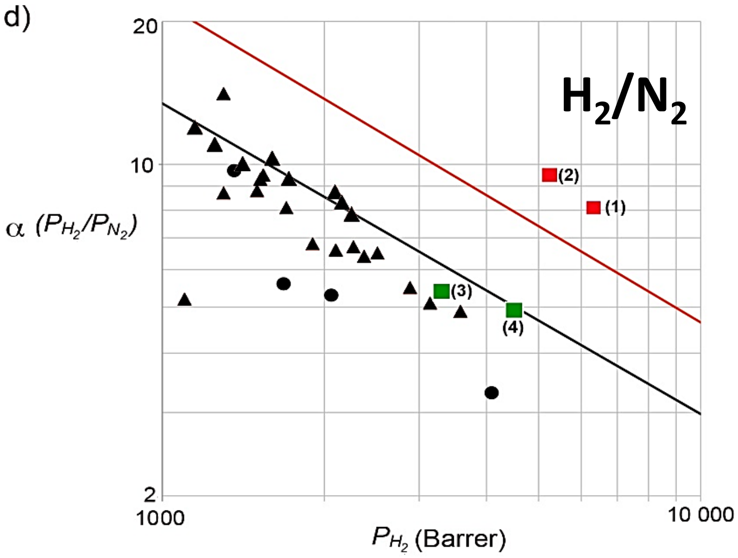
Surface Area: 803 m^2g^{-1}

Good molecular mass: MW 89 x 10^3

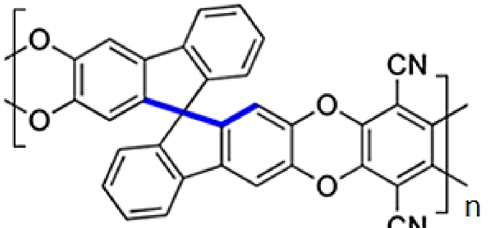
C. G. Bezzu, M. Carta, A. Tonkins, J. C. Jansen, P. Bernardo, F. Bazzarelli, N. B. McKeown, ***Adv. Mater.*** *2012,* 24, 5930

Performance of Spirobifluorene-based PIM





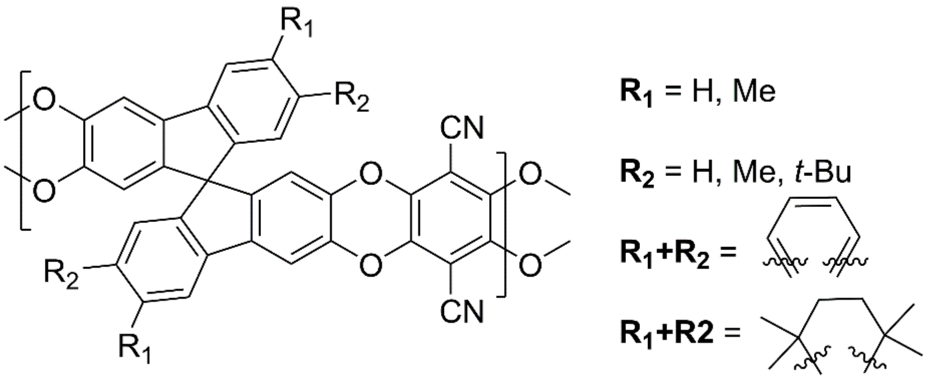
Sample	Transport parameters	O_2	CO_2	CH_4	H_2
PIM-SBF	P_x [Barrer]	2635	13914	1102	6324
	$\alpha(P_x/PN_2)$	3.35	17.7	1.4	8.1
	D_x	420	181	42	6800
	S_x	4.70	53.2	19.6	<0.7
PIM-1	P_x [Barrer]	1530	11200	1160	3300
	$\alpha(P_x/PN_2)$	2.5	18.4	1.9	5.4
	D_x	390	160	71	5000
	S_x	3.0	53.2	12.4	0.5



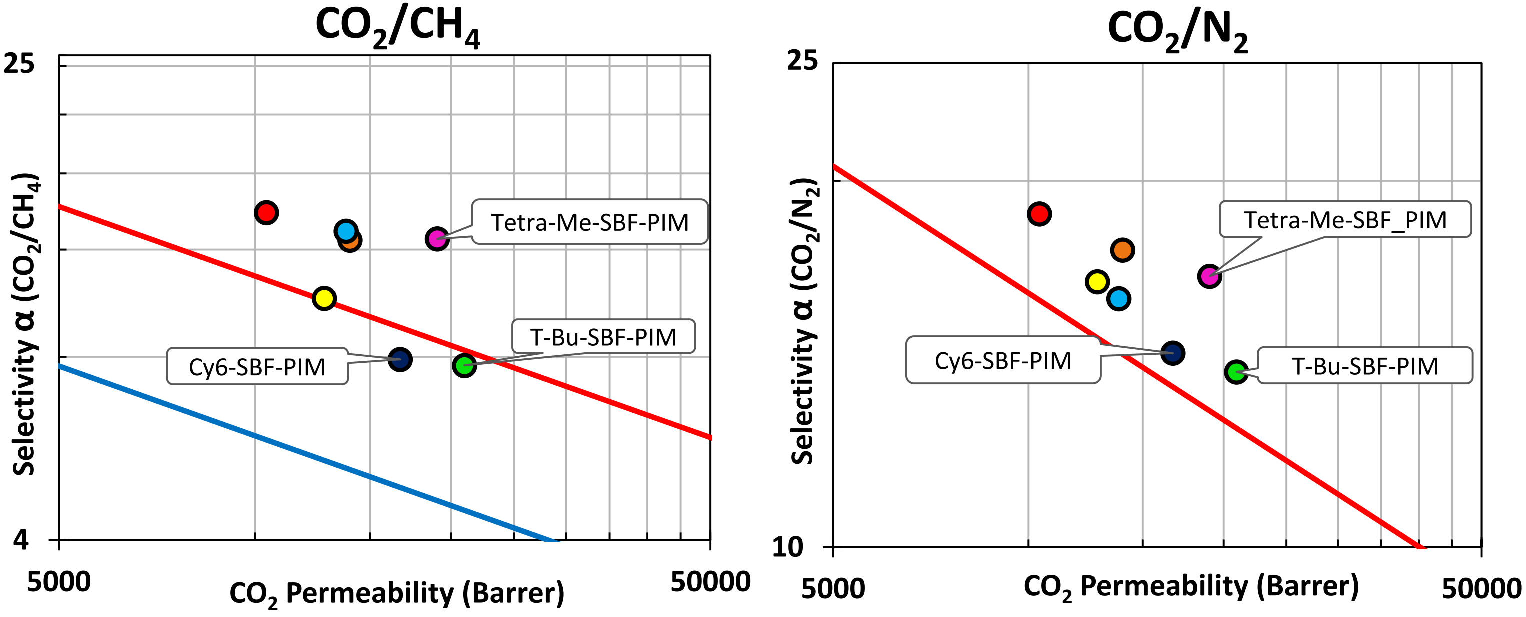
SBF-PIM

C. G. Bezzu, M. Carta, A. Tonkins, J. C. Jansen, P. Bernardo, F. Bazzarelli, N. B. McKeown, ***Adv. Mater.*** *2012,* 24, 5930

Permselectivities performance of substituted SBF-PIMs

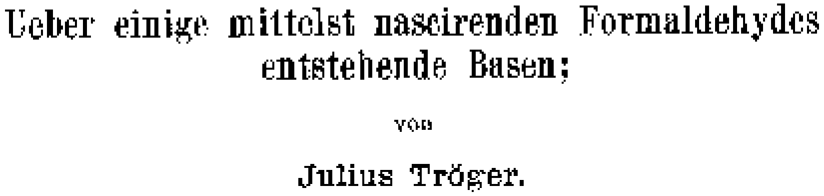


- ● PIM-1
- ● SBF-PIM-1
- ● Tetra-Me-SBF-PIM
- ● Di-Me-SBF-PIM
- ● Me-Me-SBF-PIM
- ● t-Bu-SBF-PIM
- ● Cy6-SBF-PIM



C. G. Bezzu, M. Carta, M.-C. Ferrari, J. Jansen, M. Monteleone E. Esposito, A. Fuoco, K. Hart, T. P. Liyana-Arachchi, C. M. Colina and N. B. McKeown J. Mater. Chem. A, **2018**, 6, 10507

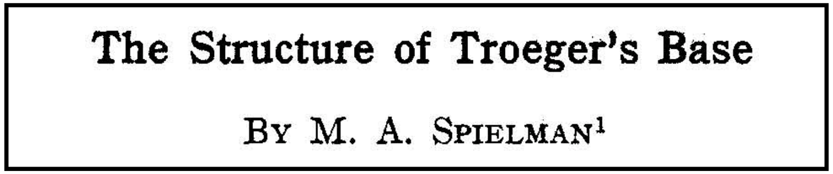
PIMs via Tröger’s base formation


Ueber einige mittelſt naſcirenden Formaldehyds
entſtehende Baſen;

von

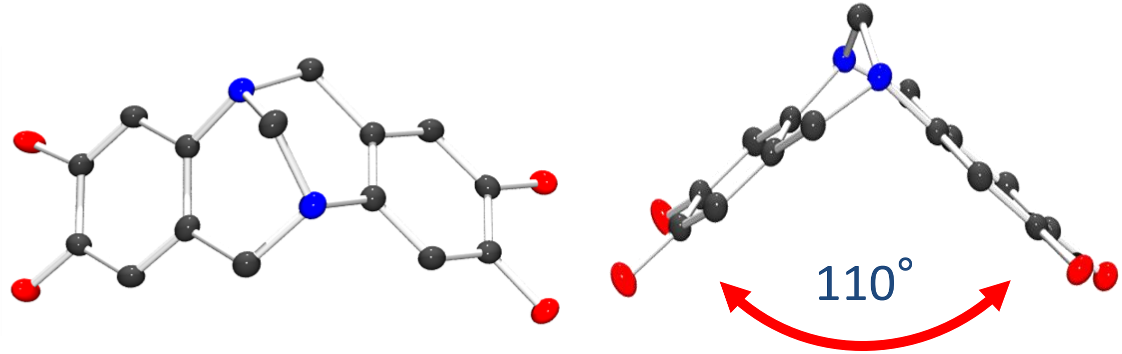
Julius Tröger.

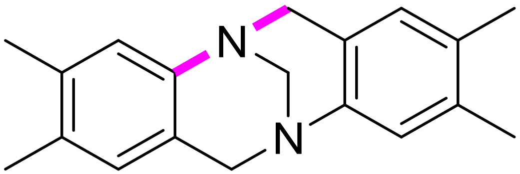
J. Prak. Chem., 1887, 36, 225


The Structure of Troeger's Base

By M. A. Spielman[1]

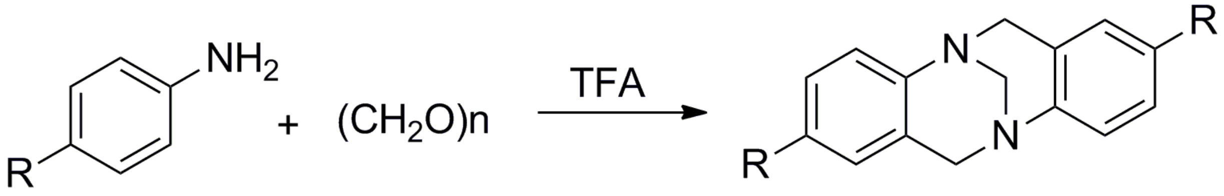
J. Am. Chem. Soc., 1935, 57, 583





Bridged bicyclic ring structure (rigidity); non-linear shape, basic

PIMs via Tröger's base formation



R = Me, Et, Pr, *i*-Pr; isolated yields in range 79-96 %

D. Didier, ***Tetrahedron***, 2008, 64, 6252

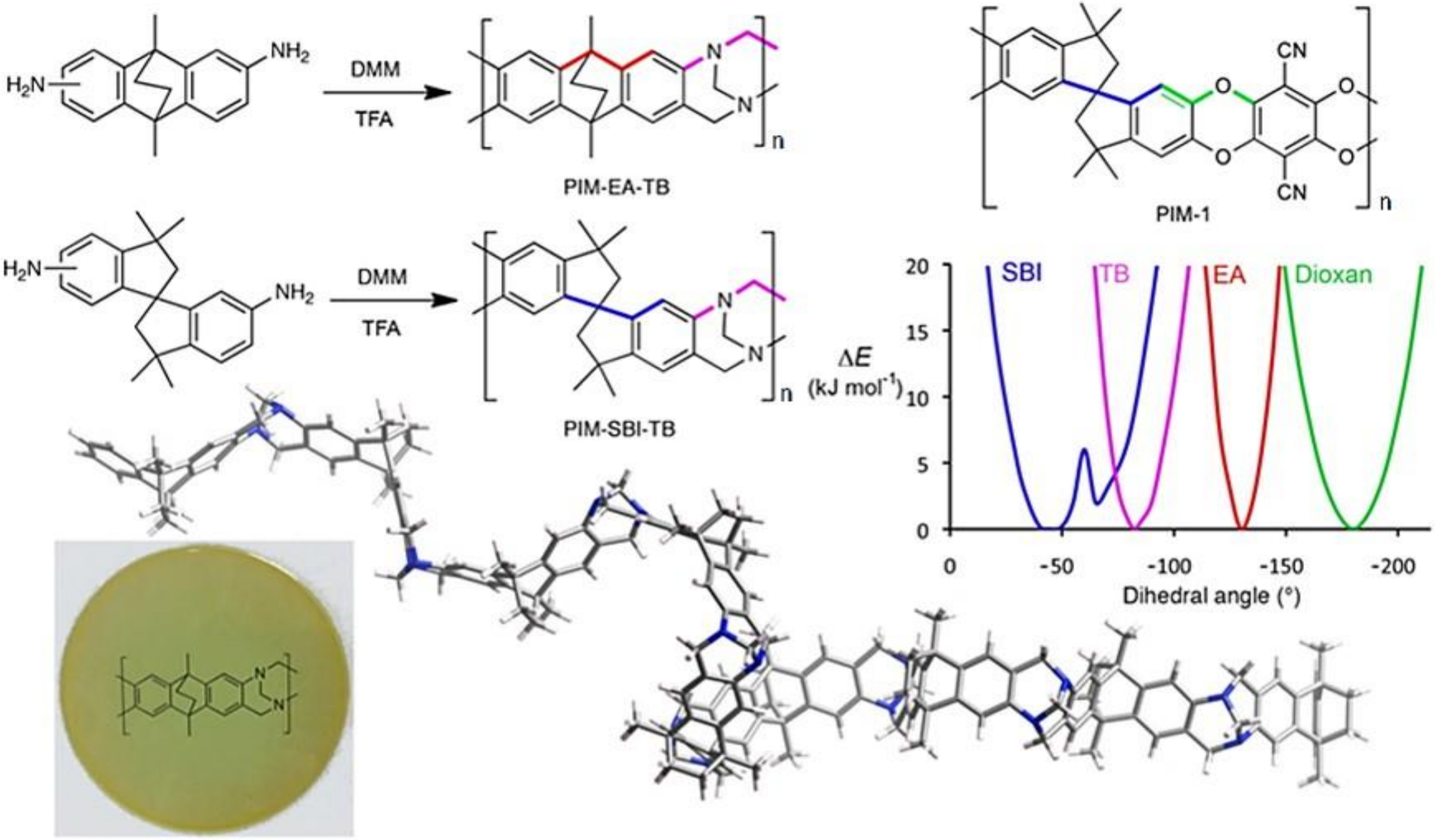
Any bis-aniline

Step-growth polymerisation

N. B. McKeown, M. Carta, M. J. Croad, **PCT Int. Appl.** WO 2012035327 A1 20120322, (*2012*)

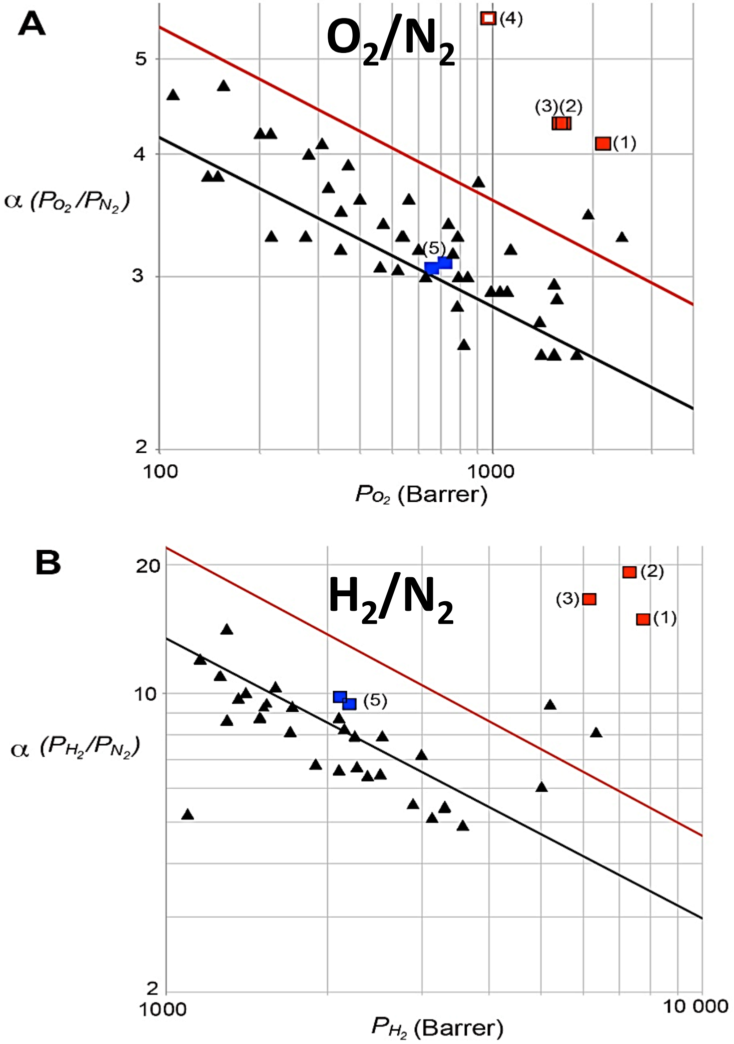
M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, M. Lee, I. Rose, N. B. McKeown, ***Polym. Chem.**, 2014,* 5(18), 5255

PIMs via Tröger's base formation

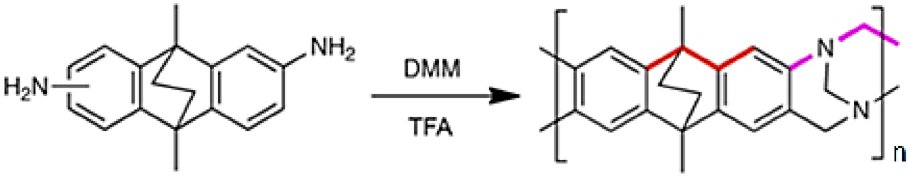


M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli, N. B. McKeown,
Science, *2013, 339* (6117), 303

Performance of Tröger's base-PIMs



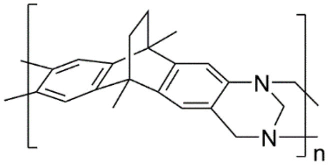
Sample	Transport parameters	O_2	CO_2	CH_4	H_2
PIM-EA-TB	P_x [Barrer]	2150	7140	699	7760
	$\alpha(P_x/PN_2)$	4.1	13.6	1.3	14.8
	D_x	318	87	36	>7000
	S_x	6.0	57.0	14.8	<0.8
PIM-1	P_x [Barrer]	1530	11200	1160	3300
	$\alpha(P_x/PN_2)$	2.5	18.4	1.9	5.4
	D_x	390	160	71	5000
	S_x	3.0	53.2	12.4	0.5



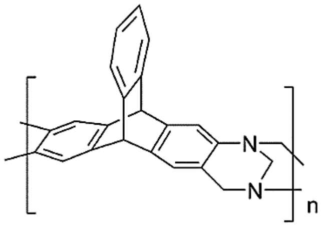
PIM-EA-TB

M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli, N. B. McKeown, ***Science***, *2013, 339* (6117), 303

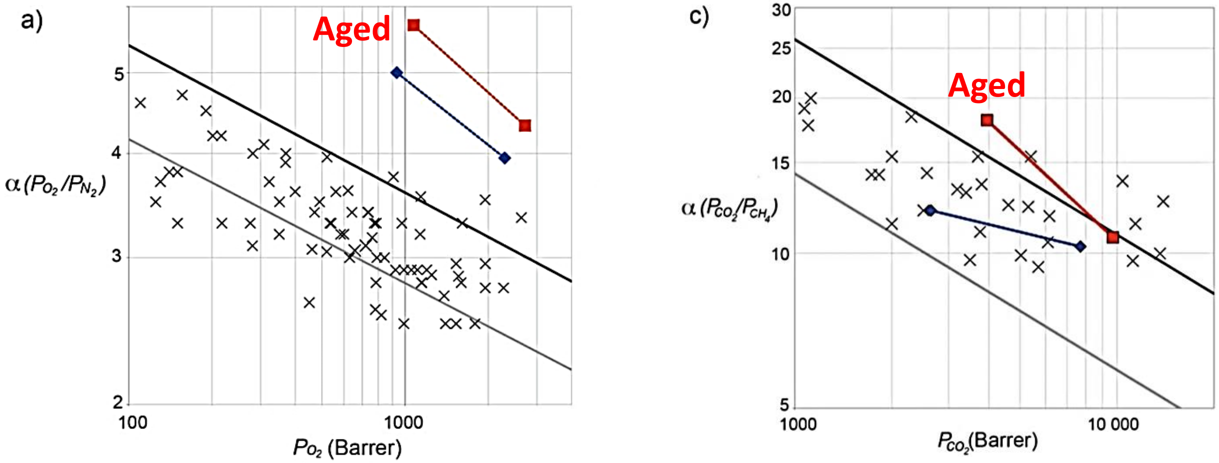
Triptycene-TB Ladder Polymers



vs



	N_2	O_2	CO_2	CH_4	H_2	He
P_x (PIM-Trip-TB)	629	2718	9709	905	8039	2500
[Barrer]	(189)	(1073)	(3951)	(218)	(4740)	(1585)
α (P_x/PN_2)	–	4.3	15.9	1.4	12.8	4.0
(PIM-Trip-TB)	(–)	(5.7)	(21.0)	(1.4)	(25.1)	(8.4)
P_x (PIM-EA-TB)	580	2294	7696	774	8114	2685
[Barrer]	(188)	(933)	(2644)	(219)	(4442)	(1630)
α (P_x/PN_2)	–	3.95	13.3	1.3	14.0	4.6
(PIM-EA-TB)	(–)	(4.95)	(14.1)	(1.2)	(23.6)	(8.7)

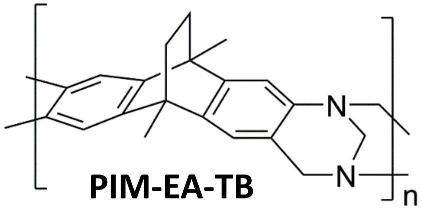


Trip-TB

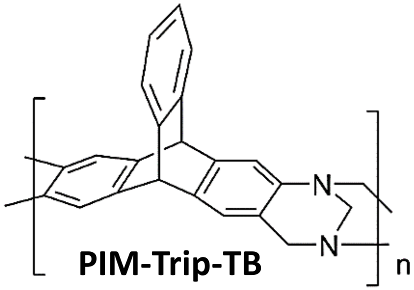
EA-TB

M. Carta, M. Croad, R. Malpass-Evans, J. C. Jansen, P. Bernardo, G. Clarizia, K. Friess, M. Lanc, N. B. McKeown, ***Adv. Mater.*** *2014*, 26,(21), 3256

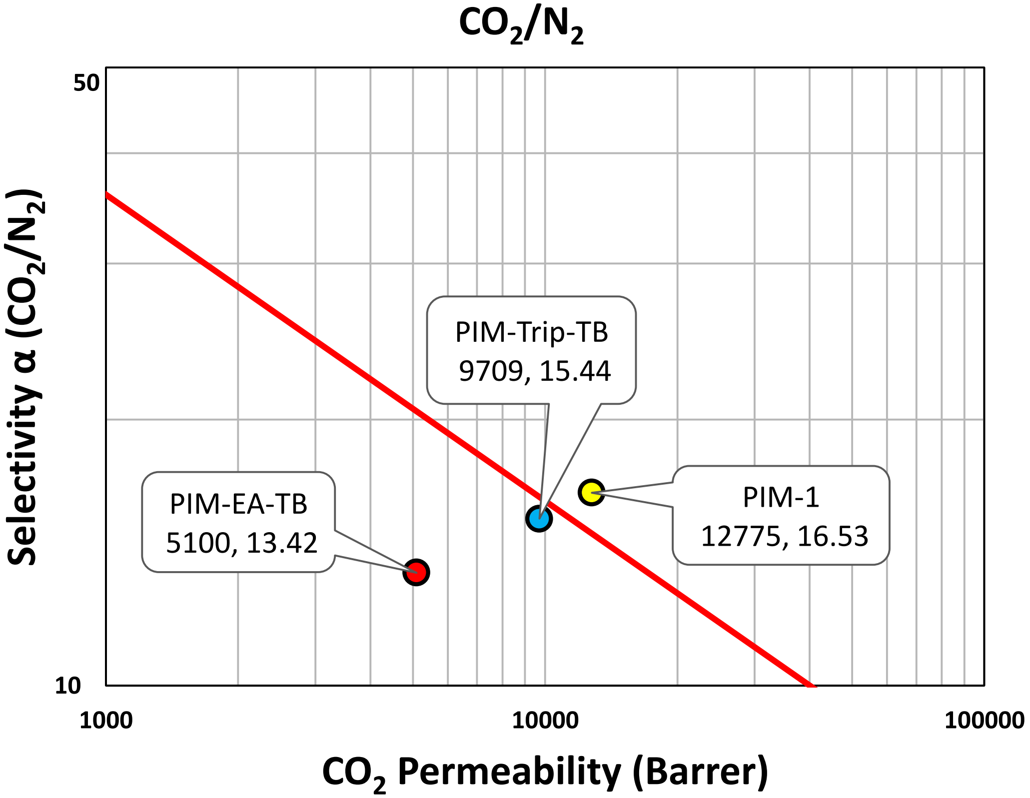
CO_2 Permeability enhancement



PIM-EA-TB

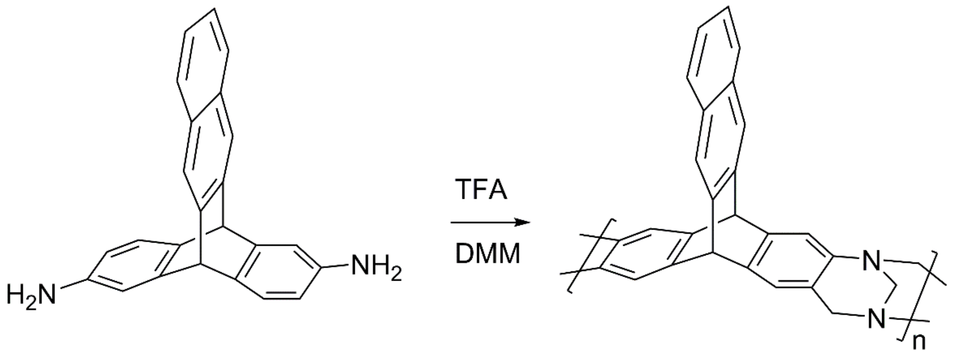


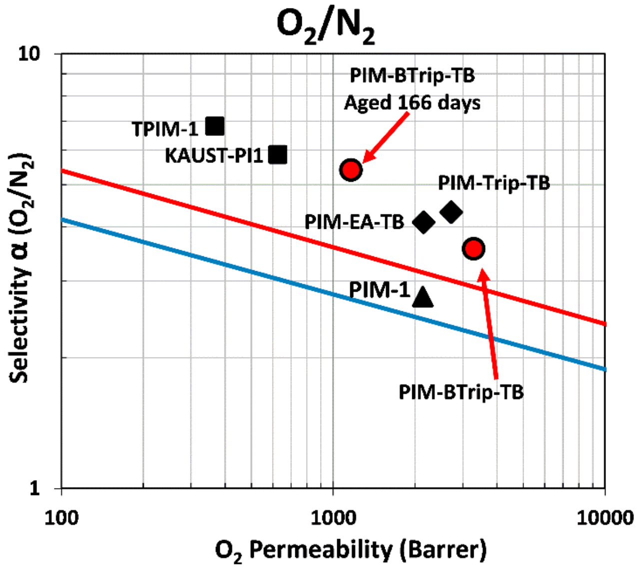
PIM-Trip-TB

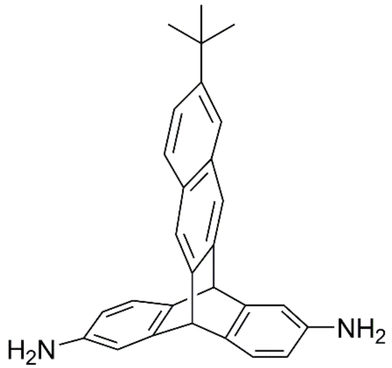


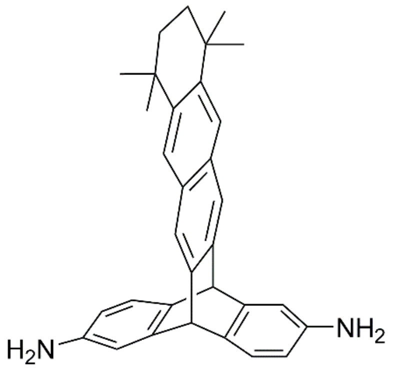
M. Carta, M. Croad, R. Malpass-Evans, J. C. Jansen, P. Bernardo, G. Clarizia, K. Friess, M. Lanc, N. B. McKeown, ***Adv. Mater.*** *2014,* 26,(21), 3256

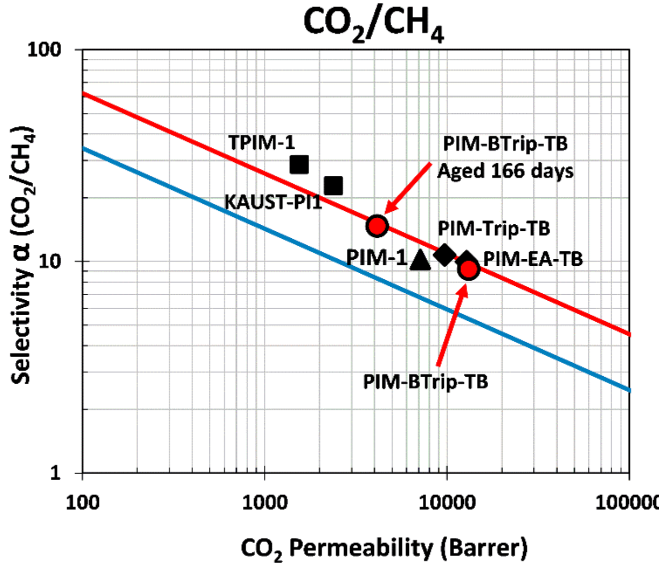
CO_2 Permeability enhancement







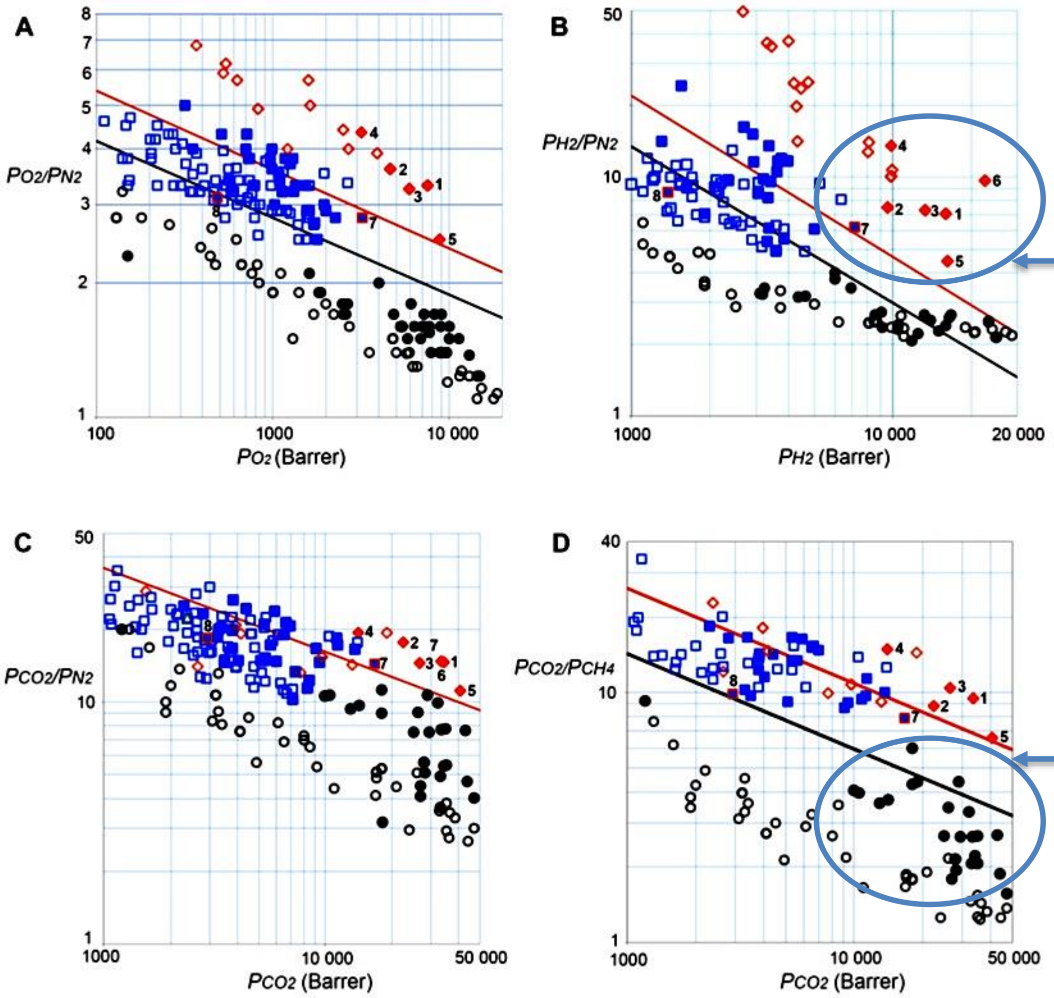


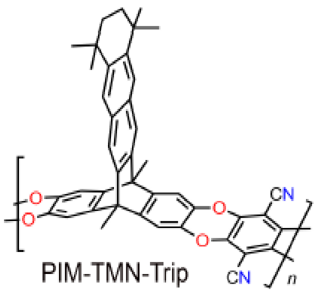


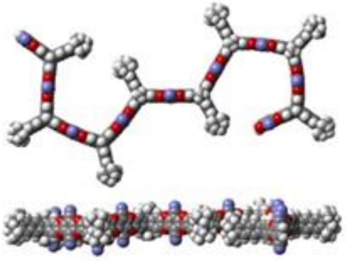
I. Rose, M. Carta, R. Malpass-Evans, M.C. Ferrari, P. Bernardo, G. Clarizia, J. C. Jansen, N. B. McKeown, ***ACS Macro Letters,*** *2015,* 912-915

CO_2 Permeability enhancement

Polybenzodioxane benzotriptycene polymers

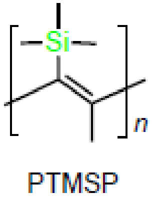






PIM-TMN-Trip

P_{CO2} = 35000 Barrer



P_{CO2} = 40000 Barrer

PTMSPs *

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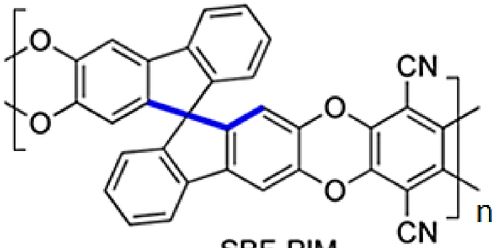
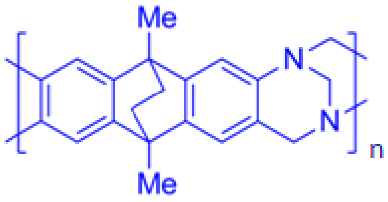
Conclusions

- We succeeded in the difficult task of improving the performance of PIM-1 synthesizing polymers such as SBF-PIM and PIM-TB
- We succeeded in modifying the rigidity of monomers obtaining ultra permeable polymers

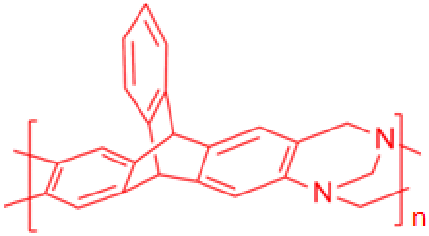


SBF-PIM

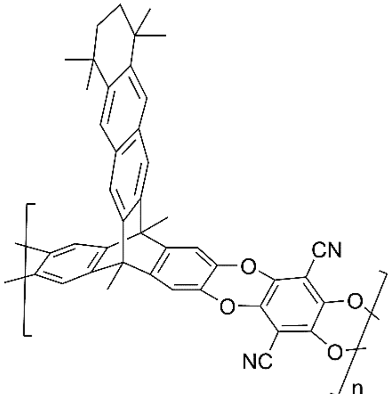


PIM-EA(Me)-TB

- Tröger's base (TB) chemistry demonstrated great potential for the synthesis of new PIMs for selective gas separations
- We succeed in tuning the properties of monomers to selective improve gas separation of important gas pairs



PIM-Trip-TB



PIM-TMN-Trip

Acknowledgments

100
1920~2020

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