

Gas separation by mixed matrix membranes with porous organic polymer inclusions within *o*-hydroxypolyamides containing *m*-terphenyl moieties.

Cenit Soto^{1,2}, Edwin S. Torres Cuevas³, Alfonso González-Ortega⁴, Laura Palacio^{1,2}, Ángel E. Lozano^{1,5,6}, Benny D. Freeman³, Pedro. Prádanos^{1,2,*}, Antonio. Hernandez^{1,2,*}.

¹ Surfaces and Porous Materials (SMAP), Associated Research Unit to CSIC. University of Valladolid, Facultad de Ciencias, Paseo Belén 7, E-47011 Valladolid, Spain.

² Institute of Sustainable Processes (ISP), Dr. Mergelina s/n, 47011, Valladolid, Spain.

³ McKetta Department of Chemical Engineering, Texas Materials Institute, The University of Texas at Austin

⁴ Department of Organic Chemistry, School of Sciences, University of Valladolid, Facultad de Ciencias, Paseo Belén 7, E-47011 Valladolid, Spain.

⁵ Institute for Polymer Science and Technology (ICTP-CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

⁶ IU CINQUIMA, University of Valladolid, Paseo Belén 5, E-47011 Valladolid, Spain.

*Correspondence: antonio.hernandez@uva.es (A.H.); ppradanos@uva.es (P.P.)

Supplementary materials

SI-1. Polymers and Membranes Manufactured

Table S1. Acronyms list for the polymers and membranes manufactured.

Polymers (polymeric matrix)	Acronym
5'-tertbutyl- <i>m</i> -terphenyl-4,4''-dichloride acid (tBTpCl) + 2,2-bis(3-amino-4-hydroxy phenyl)-hexafluoropropane (APAF). → tBTpCl-APAF	HPA
5'-tertbutyl- <i>m</i> -terphenyl-4,4''-dichloride acid (tBTpCl) + 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA). → tBTpCl-6FpDA	PA
5'-tertbutyl- <i>m</i> -terphenyl-4,4''-dichloride acid (tBTpCl) + 2,2-bis(3-amino-4-hydroxy phenyl)-hexafluoropropane (APAF) + 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA). → tBTpCl-APAF-6FpDA	HPA-PA
Mixed Matrix Membranes	
tBTpCl-APAF + 20% PPN-2	MMM-HPA
tBTpCl-6FpDA + 20% PPN-2	MMM-PA
tBTpCl-APAF-6FpDA + 20% PPN-2	MMM-HPA-PA

Thermal rearrangement tBTpCl-APAF + 20% PPN-2	TR-MMM-HPA
Thermal rearrangement tBTpCl-APAF-6FpDA + 20% PPN-2	TR-MMM-HPA-PA

SI-2. Preliminary gas separation properties

In a preliminary study, and to assess the influence of this filler on gas transport properties (especially for CO₂ separation), gas permeation measurements were performed at 35 °C and 3 bars. The comparative evaluation of gas permeabilities for MMMs and TR-MMMs with the two tested PPNs are shown in Table S2. These results denoted a pronounced difference of permeabilities between the fillers, in particular for TR-MMMs. Thus, an enhancement factor of at least 5-fold was recorded for the permeability of CO₂ for TR-MMMs from PPN-2, which reach ~394 Barrer but with a rather lower selectivity. Despite the fact that isatin-derived PPN-1 have narrower micropores, [24], this empirical findings showed that PPN-2 is much better for making high-performance MMMs, and consequently PPN-1 was discharged for additional characterization. A plausible explanation to this fact could explained by the different interactions of the filler with the polymer matrix [16].

Table S2. Permeability Coefficients (Barrer) at 3 bar (300 kPa) and 35 °C for HPA-MMMs and their corresponding TR-MMM-HPAs with loads of 20% of PPN-1 and PPN-2.

Membrane	Permeability (Barrer*)			
	N ₂	O ₂	CH ₄	CO ₂
PPN-1				
tBTpCl-APAF-20%, MMM-HPA-PPN-1	1.03	5.98	0.67	24.85
TR-tBTpCl-APAF-20% TR-MMM-HPA-PPN-1	13.38	55.10	11.99	243.4
PPN-2				
tBTpCl-APAF-20% MMM-HPA-PPN-2	3.48	18.46	2.65	79.0
TR-tBTpCl-APAF-20% TR-MMM-HPA-PPN-2	20.65	87.97	20.80	394.1

Figure S1 shows the correlation for O₂/N₂ and CO₂/CH₄ and in the Robeson's limit for the tested MMMs with PPN-1 and PPN-2 and their corresponding TR-MMM. Note

that, despite PPN-1 synthesized from triptycene-isatin exhibited a higher CO₂ capture (207 mg g⁻¹) than PPN-2 synthesized from triptycene-TFAP (83 mg g⁻¹) [24] the permeabilities of all measured gases were lower for the MMMs derived from PPN-1. This could be attributed to a low interaction between the filler and the polymer matrix, which consequently would result in a poor adhesion and the formation of interfacial voids that were not fixed during thermal rearrangement this should explain as well the lower selectivity for the MMMs containing PPN-2. In any case the different behavior of both PPNs lead to a better permeability-selectivity compromise as seen in Figure S1.

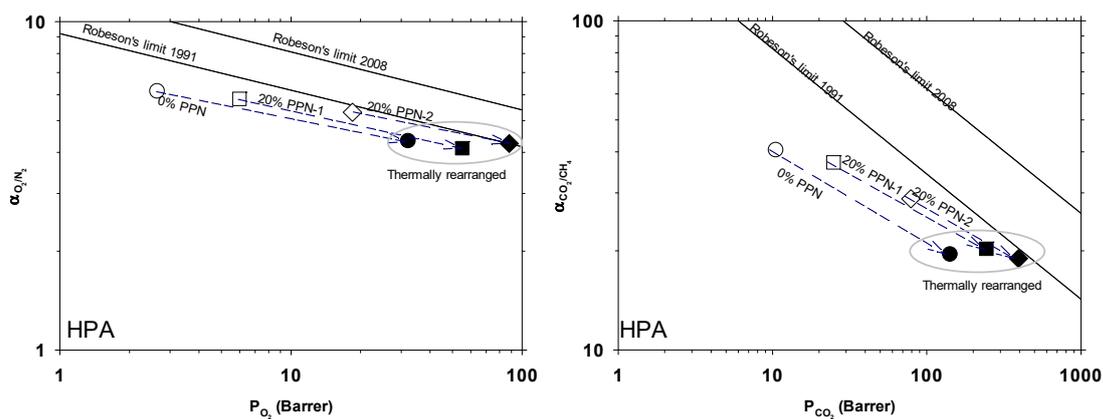
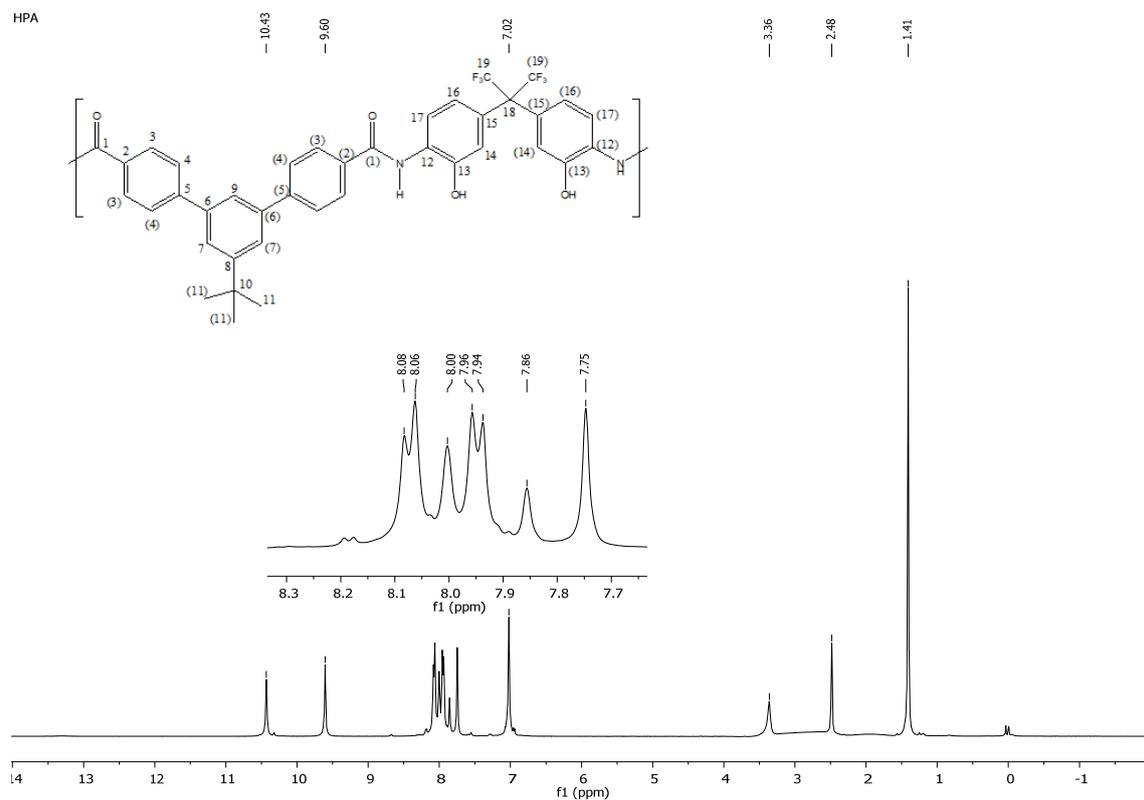


Figure S1. Permeability vs permselectivity for tBTpCl-APAF, HPA, membranes and MMMs containing PPN-1 and PPN-2 fillers before and after thermal rearrangement for the O₂/N₂ (left) and CO₂/CH₄ (right) gas pairs.

SI-3. NMR characterization of polymers

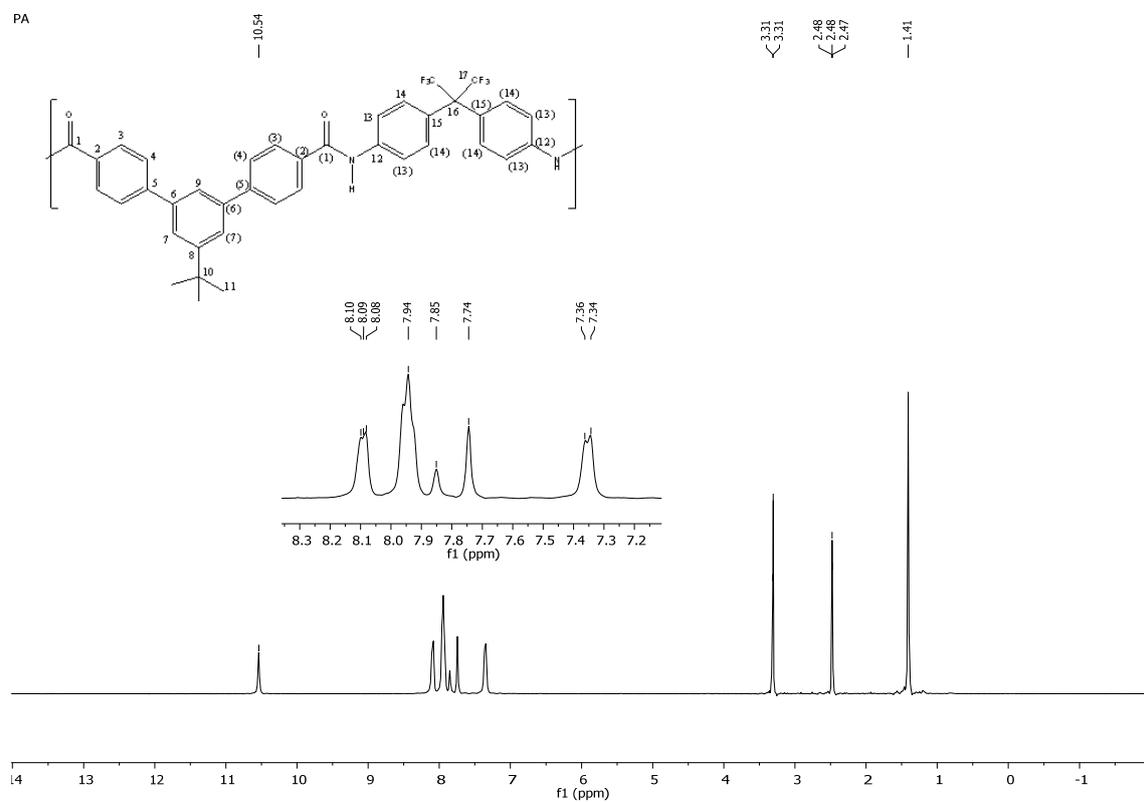
tBTpCl-APAF (HPA) \rightarrow 5'-terbutyl-*m*-terphenyl-4,4'' acid dichloride + 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane



$^1\text{H-NMR}$ (400 MHz, DMS d_6 : δ (ppm); 10.43 (2 NH), 9.60 (2 OH), 8.07 (4 H(3)), 8.0 (2 H(14)), 7.95 (4 H(4)), 7.86 (1 H(9)), 7.75 (2 H(7)), 7.02 (2 H(17)), 2 H(16), 3.36 (H₂O), 2.48 (DMS), 1.41 (9 H(11)).

Figure S2. NMR results for membrane HPA.

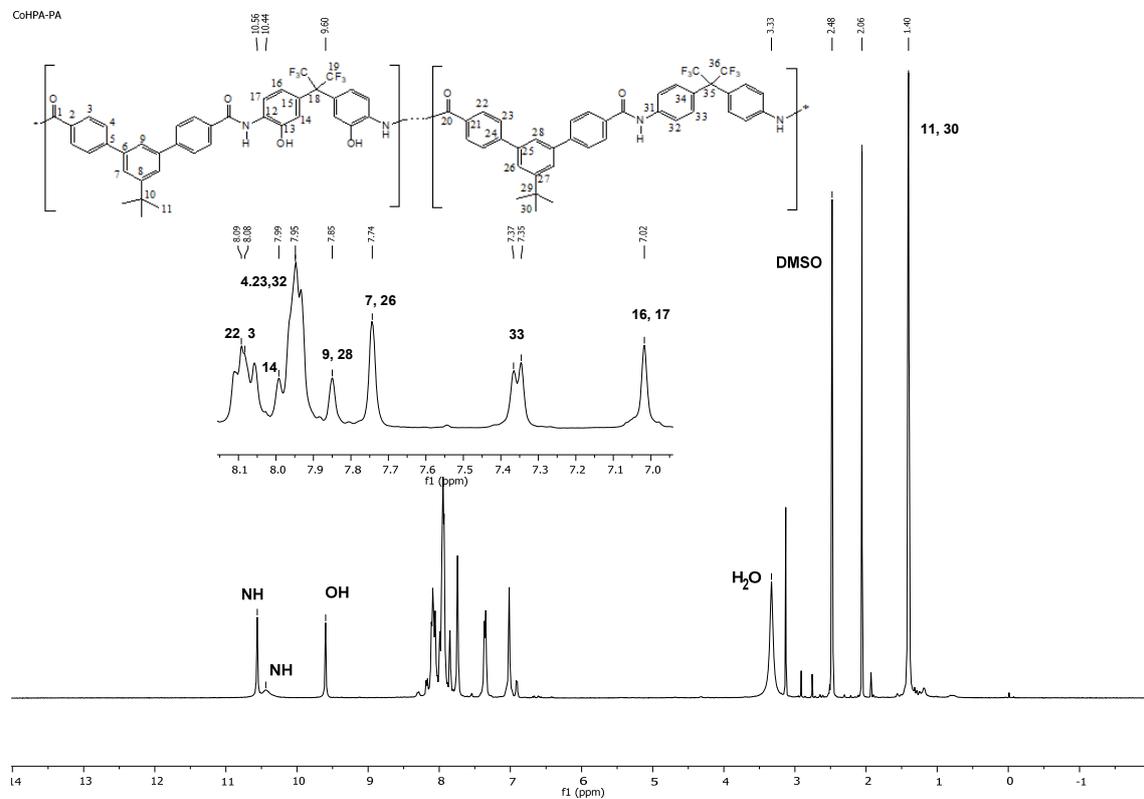
tBTpCl-6FpDA (PA) \rightarrow 5'-terbutyl-*m*-terphenyl-4,4'' acid dichloride + 2,2-bis(4-aminophenyl)hexafluoropropane.



¹H-RMN (400 MHz, DMSO *d*₆: δ (ppm); 10.54 (2 NH), 8.09 (4 H(3)), 7.94 (4 H(4), 4 H(13)), 7.85 (1 H(9)), 7.74 (2 H(7)), 7.75 (2 H(7)), 7.35 (2 H(17), 4 H(14)), 3.31 (H₂O), 2.48 (DMSO), 1.41 (9 H(11)).

Figure S3.- NMR results for membrane PA.

tBTpCl-APAF-6FpDA (HPA-PA) \rightarrow 5'-terbutyl-*m*-terphenyl-4,4'' acid dichloride + 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane + 2,2-bis(4-aminophenyl)hexafluoropropane.



$^1\text{H-NMR}$ (400 MHz, DMS d_6 : δ (ppm) 10.56 (NH), 10.44 (NH), 9.60 (OH), 8.09 (H₍₂₂₎), 8.08 (H₍₃₎), 7.99 (H₍₁₄₎), 7.95 (H_(4,23,32)), 7.85 (H_(9,28)), 7.74 (H_(7,26)), 7.36 (H₍₃₃₎), 7.02 (H_(16,17)), 3.33 (H₂O), 2.48 (DMSO), 1.40 (H_(11,30)).

Figure S4. NMR results for membrane HPA-PA.

SI-4. TGA results.

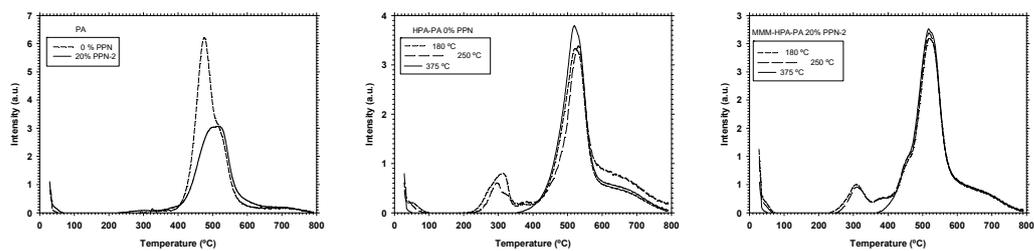


Figure S5. TGA thermograms for: PA and MMM-PA (A), HPA-PA (B) and MMM-HPA-PA (C). Samples were heated from 50 to 800 °C at 5 °C/min under a N₂ atmosphere.