Impact of MOF-5 on pyrrolidinium-based poly(ionic liquid)/ionic liquid membranes for biogas upgrading

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ABSTRACT

Bearing in mind that Metal Organic Frameworks (MOFs) have remarkable CO_2 adsorption selectivity and Mixed Matrix Membranes (MMMs) have been identified as potential solution for advancing the current state of the art of membrane separation technology, this work investigates the effect of combining a MOF, with high adsorption properties towards CO_2 when compared to CH_4 (MOF-5), with a blend of poly(ionic liquid)/ionic liquid (PIL/IL) for biogas upgrading. The blend system consisted of a pyrrolidinium-based PIL, poly([Pyr$_{11}$][Tf$_2$N]), and a free imidazolium-based IL, [C$_2$mim][BETI]. The MOF-5 was incorporated at different loadings (10, 20, 30 wt%), and MMMs were prepared by solvent evaporation and characterized by diverse techniques (FTIR, SEM, TGA, puncture tests and single gas transport). The results showed that the free IL is miscible with the PIL, while MOF-5 particles were uniformly dispersed into the PIL/IL matrix. The formed PIL/IL/MOF-5 membranes revealed suitable thermal stability (T_{onset} up to 656 K) for biogas upgrading processes, but a loss of mechanical stability was found after the incorporation of MOF-5, and thus more rigid and fragile membranes were obtained. At 30 wt% of MOF-5 loading the CO_2 permeability increased 133% when compared to that of the pristine PIL/IL membrane, mainly due to the adsorption capacity of the MOF, as well as its porous structure. The presence of a porous structure may also be the reason why the ideal selectivity decreases by 88% for the MMM with the highest loading. It was possible to demonstrate the relevance of studying different components within the polymeric matrix in order to assess not only thermal, mechanical and chemical properties, but also gas transport response.

KEYWORDS
Biogas upgrading, CO_2 removal, poly(ionic liquid)s, ionic liquids, metal organic frameworks, mixed matrix membranes.

1. INTRODUCTION

The rising environmental problems faced by our world has been prompting political debates and actions regarding sustainable energy strategies, including the use of bioenergy conversion routes for biofuels production as alternative to fossil fuels.[1, 2] Biogas is one of the foremost

bioenergy that has been attracting much attention since its production, not only results in a valuable renewable energy source to substitute natural gas or liquefied petroleum, but also reduce the volume of disposed solid wastes.[3]

Biogas is a mixture of gases produced from anaerobic digestion of biological wastes, where its composition is strongly dependent on the type of process and source.[4] Typically, biogas consists of 55–65% methane (CH_4), 35–40% carbon dioxide (CO_2), small amounts of hydrogen sulfide (H_2S) and water vapor (H_2O), and may also contain traces of other gases and volatile organic compounds.[5] Apart from CH_4, the presence of CO_2, H_2S and other impurities reduce the heating value and thus, their removal by upgrading technologies is crucial to improve gas quality. In view of the fact that biogas must be composed of more than 95 vol% of CH_4, in order to reach competitive calorific values and also meet the regulations,[6] biogas upgrading deals primarily with CO_2 removal.

Among the different gas separation techniques currently available, membrane technology is particularly attractive since it offers a number of benefits, namely lower energy consumption, small footprint and easily engineered modules.[7] Although several membrane-based processes have been proposed for biogas upgrading,[8-12] they still have not reached the commercial value and efficiency of other conventional techniques, such as water scrubbing, pressure swing adsorption, or chemical absorption with amines. This is mainly due to the low CO_2/CH_4 separation efficiency of the commercial polymeric membranes, in which the gas transport is based on the solution-diffusion mechanism and the main challenge remains in the trade-off between permeability and selectivity.[5] Therefore, the development of membrane materials, combining high CO_2 separation efficiency is of vital importance to advance membrane-based biogas upgrading processes.

Over the past two decades, ionic liquids (ILs) and poly(ionic liquid)s (PIL)s have raised great interest as highly tuneable materials to improve existing membrane-based CO_2 separation processes, delivering a wide range of membranes with different chemical structures, physical/chemical properties, morphologies and separation performances.[13-15]

Different strategies have been used towards the development of IL-based membranes, such as supported ionic liquid membranes (SILMs),[16, 17] polymer/IL composite membranes,[18, 19] ion gel membranes,[20-22] or the fabrication of PIL/IL composite membranes.[23-25] In particular, the incorporation of ILs into PILs is an attractive strategy to obtain membranes with liquid-like gas transport properties, while maintaining a good mechanical stability.[26] A variety of PIL and IL chemical structures has been explored,[27-31] and the potential of PIL/IL membranes to outperform conventional polymer membranes has been shown, in particular for CO_2/N_2 and CO_2/H_2 separations.[32-34]

With the intent of improving the CO_2 separation efficiency, as well as the thermal and mechanical properties of PIL/IL composites, three-component mixed matrix membranes (MMMs) consisting of PILs, ILs and nanoporous fillers, such as zeolites and MOFs, have also been developed. The first example was published in 2010 by Hudiono *et al.*,[35] who prepared a MMM, composed of styrene-based imidazolium PIL, free IL [C_2mim][Tf_2N] and zeolite SAPO-34 particles, by UV-initiated polymerization. The results demonstrated that the presence of free IL improved the interfacial inorganic-organic adhesion. Hudiono *et al.*[36] have also performed a more detailed study focused on the effect of varying the contents of both SAPO-34 and free IL, providing valuable insights into how this system can be tuned. Later on, Singh *et al.*[37] varied other parameters, such as zeolite type, PIL structure and polymer cross-linking density. The authors reported an optimized and mechanically robust MMM, composed of 50 wt% poly([smim][Tf_2N]), 20 wt% IL [C_2mim][Tf_2N] and 30wt% SAPO-34, outperforming the 2008 Roberson upper bound limit, with CO_2 permeability of 260 Barrer and CO_2/CH_4 selectivity of 90. What is more, Dunn *et al.*[38] showed that the use of curable IL prepolymers, instead of a (IL monomer + cross-linker) mixture, to prepare cross-linked PIL/IL/zeolite, afforded MMMs with faster gelation times and improved resistance to support penetration when casting on ultrafiltration membranes.

Despite the remarkable features of MOFs for CO_2 capture,[39] and the knowledge on MOF combination with polymers to build MMMs,[40] only two studies concerning PIL/IL/MOF

membranes have been published in the literature. Hao *et al.*[41] studied MMMs of poly([vbim][Tf$_2$N), three different ILs ([C$_2$mim][BF$_4$], [C$_2$mim][Tf$_2$N], [C$_2$mim][B(CN)$_4$]) and ZIF-8 nanoparticles. These membranes displayed a continuous increase in gas permeability with increasing ZIF-8 content, but the CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivities remained nearly constant. Recently, we investigated MMMs comprising poly([Pyr$_{11}$][Tf$_2$N]), IL [C$_4$mpyr][Tf$_2$N] and three different MOFs (ZIF-8, MIL-53(Al) and Cu$_3$(BTC)$_2$).[42] Besides simultaneous improvements in both CO$_2$ permeability and CO$_2$/H$_2$ selectivity were observed as the MOF content increased, the prepared MMMs remarkably surpassed the CO$_2$/H$_2$ upper bound limit. These promising results not only revealed an opportunity for further improvements behind pyrrolidinium-based PIL/IL/MOF membranes, as varying PIL and IL structures or MOF type, but also encouraged us to re-examine the potential of using this design strategy for CO$_2$ removal from other gas streams, in particular for biogas upgrading (CO$_2$/CH$_4$ separation).

In this work, MMMs based on poly([Pyr$_{11}$][Tf$_2$N]) and [C$_2$mim][BETI] IL were prepared with different loadings of MOF-5 (between 10 and 30 wt%) and characterized in terms of their thermal and mechanical stability, as well as CO$_2$/CH$_4$ separation performance. It is expected that the presence of a highly fluorinated IL, such as [C$_2$mim][BETI], will significantly improve the properties of the prepared membranes, particularly in terms of thermal stability and gas transport. MOF-5, also known as IRMOF-1, is one of the most widely studied MOFs, for different gas separations. Particularly in the case of CO$_2$/CH$_4$ separation, MOF-5 presents an overall higher ideal selectivity, compared to other well-known MOFs, such as Cu(BTC), MIL-53, ZIF-8 and ZIF-90, according to what has been published in the literature.[43-46] Moreover, MOF-5 presents a high BET surface area (3000 m^2 g^{-1}), leading to a high gas adsorption capacity,[43, 47] which makes MOF-5 a potential candidate for CO$_2$/CH$_4$ separation applications.

2. EXPERIMENTAL SECTION

2.1. Materials. The poly[Pyr$_{11}$][Tf$_2$N] was synthesized by anion metathesis reaction from the poly(diallyldimethylammonium) chloride precursor (average M$_w$ 400,000 – 500,000, 20 wt% in

water), following an established procedure.[29] MOF-5 was synthesized according to a procedure described elsewhere.[48] Zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.99 wt% pure), terephtalic acid (H_2BDC, 98 wt% pure), dimethylformamide (DMF, 99.8 wt% pure) and acetone (>99.5 wt% pure) were purchased from Sigma Aldrich (Portugal). IoLiTec GmbH (Germany) provided the 1-ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide ([C_2mim][BETI], 98 wt% pure). The chemical structure of the PIL, IL and MOF are illustrated in Figure 1. CO_2 (high purity grade, 99.998%) and CH_4 (>99.99% purity) were supplied by Praxair (Portugal).
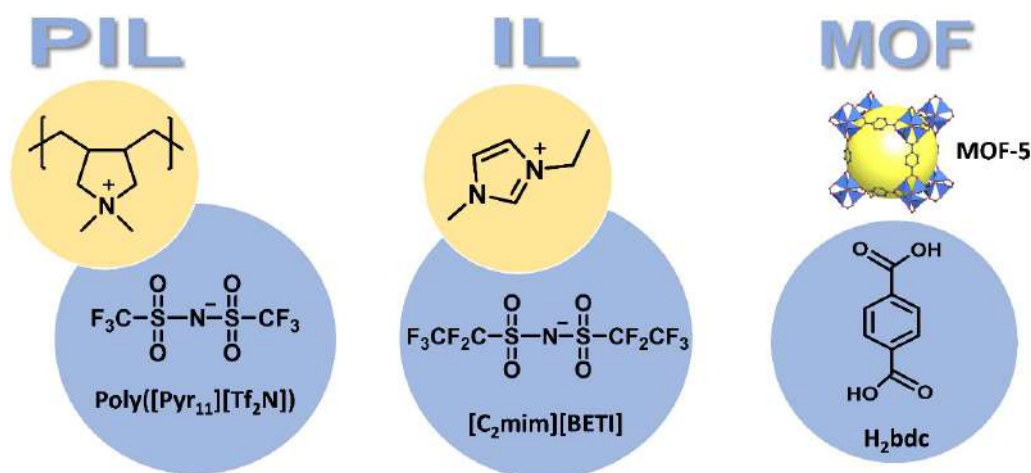

Figure 1. Chemical structure of the PIL, IL and MOF used in this work to prepare the PIL/IL and PIL/IL/MOF membranes.

2.2. Membranes Preparation. PIL/IL and PIL/IL/MOF membranes, composed by 40 wt% of [C_2mim][BETI] IL and different MOF-5 loadings (10, 20 and 30 wt%), were prepared by solvent evaporation technique. First, 0.6 g of PIL and 0.4 g of IL were dissolved in acetone (6% (w/v)) and stirred for 8 h. Separately, the respective amounts of MOF-5 were dispersed in acetone. All the prepared MOF solutions were sonicated in an ultrasound bath for 4 h and stirred another 4 h. Afterwards, the PIL/IL and MOF solutions were mixed and left stirring overnight. Free-standing PIL/IL and PIL/IL/MOF membranes were obtained by casting the prepared solutions into poly(tetrafluoroethylene) (PTFE) plates and left for slow solvent evaporation at room temperature. The composition of the membranes prepared in this work are described in Table 1.

Table 1. Composition of the prepared PIL/IL and PIL/IL/MOF membranes.

6

Membranes	PIL (60 wt%)	IL (40 wt%)	MOF-5 loading (wt%)
PIL Tf$_2$N / 40 IL BETI	Poly([Pyr$_{11}$][Tf$_2$N])	[C$_2$mim][BETI]	0
PIL Tf$_2$N / 40 IL BETI / 10 MOF-5			10
PIL Tf$_2$N / 40 IL BETI / 20 MOF-5			20
PIL Tf$_2$N / 40 IL BETI / 30 MOF-5			30

2.3. Fourier Transform Infrared Spectroscopy (FTIR) analysis. In order to evaluate possible interactions established between the different components in the MMMs, FTIR spectra of the prepared MMMs were acquired using a Perkin Elmer Spectrum spectrometer. All spectra were collected in the range of 400 to 4000 cm^{-1}, using 10 scans.

2.4. Scanning Electron Microscopy (SEM). Cross section images of the prepared MMMs were obtained using an analytical scanning electron microscope (FEG-SEM, JEOL7001F, USA Inc.), equipped with a field-emission electron source of 15 kV. Membrane samples of approximately 0.5x0.5 cm dimensions were coated with a Pd/Au thin layer to induce sample charge under the electron beam.

2.5. Thermal Analysis. Thermogravimetric analyses (TGA) were carried out on a TGA Q50 analyzer from TA instruments. The samples were heated at a constant rate of 10 K min^{-1}, from room temperature to 873 K, under nitrogen atmosphere. The Universal Analysis software was used to determine the onset (T_{onset}t) and decomposition (T_{dec}) temperatures.

2.6. Mechanical Analysis. The prepared MMMs were evaluated through puncture tests, carried out using a TA XT Plus texture analyzer (Stable Micro Systems, UK). Samples of each membrane, with 3x3 cm, were punctured through a hole, with a cylindrical probe of 2 mm diameter, at ambient temperature. Three replicates were performed, and the mean puncture strength is reported.

2.7. Gas Permeation Experiments. Single gas CO$_2$ and CH$_4$ permeation experiments were carried out using a gas permeation setup described in detail elsewhere,[49] and the membranes' permeability, as well as ideal CO$_2$/CH$_4$ selectivities were calculated. All the measurements were conducted at 303 K. Each experiment started by pressurizing the two-compartment stainless steel

cell with CH_4 or CO_2. Once the pressure was stabilized, a driving force of around 0.7 bar of relative pressure between the feed and permeate compartments was established. Two pressure transducers (Druck PCDR 910 models 99166 and 991675, UK) were used to control pressure variation in each compartment. The single gas permeability through the membrane was calculated according to the equation:

$$\frac{1}{\beta} \ln \frac{p_{feed_0} - p_{perm_0}}{p_{feed} - p_{perm}} = \frac{1}{\beta} \ln \frac{\Delta p_0}{\Delta p} = P \frac{t}{l}$$

Where p_{feed} and p_{perm} correspond, respectively, to the pressure in the feed and permeate compartments (bar), P is the membranes' permeability ($m^2.s^{-1}$, where 1 Barrer = 8.3×10^{-13} m^2/s), t is the time (s), l is the mean membrane thickness (m) and β symbolizes a geometric parameter (m^{-1}), given by:

$$\beta = A \left(\frac{1}{V_{feed}} + \frac{1}{V_{perm}} \right)$$

Where A is the membrane' area (m^2) and V_{feed} and V_{perm} correspond to the volume of the feed and permeate compartments (m^3), respectively.

The gas permeability can be directly obtained from the slope when plotting $1/\beta\ ln(\Delta P_0/\Delta P)$ as a function of t/l. The ideal gas selectivity of each membrane was calculated by dividing the permeabilities of the two different gases, according to:

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}}$$

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis. The chemical structure of the prepared PIL/IL/MOF-5 membranes was confirmed by FTIR spectroscopy and the obtained spectra are depicted in Figure 2. The FTIR spectra of the MOF-5, [C_2mim][BETI] IL and PIL NTf$_2$/40 IL BETI membrane are also illustrated for comparison purposes.
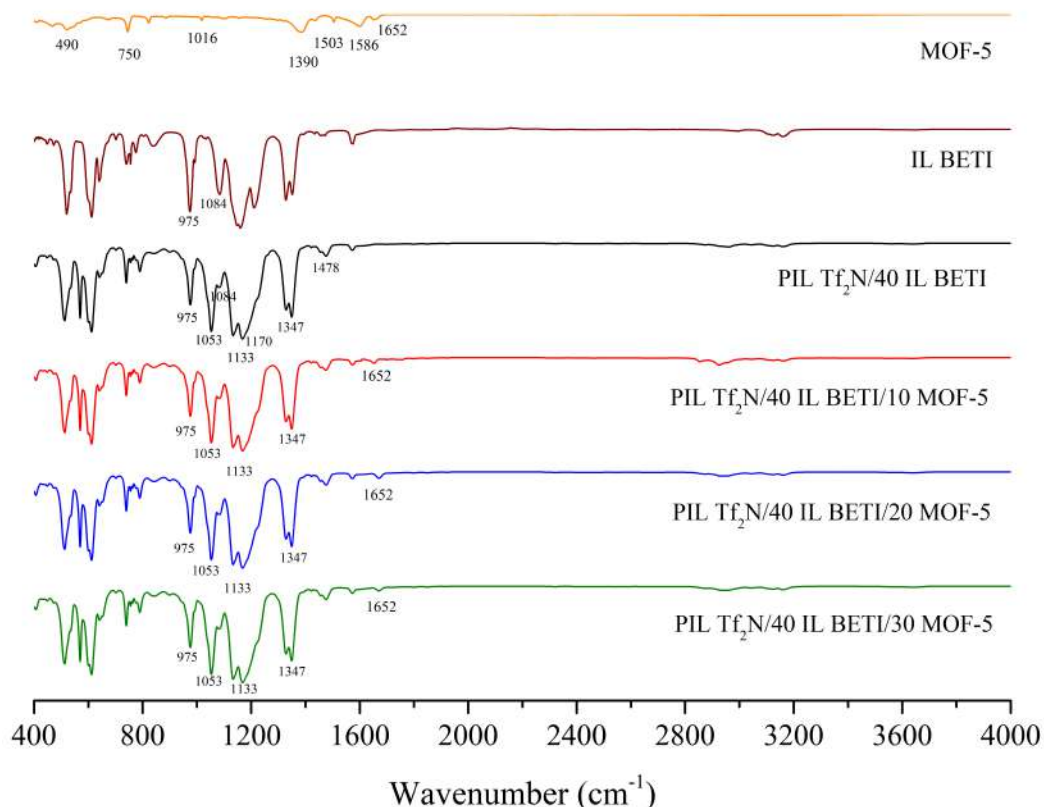
Figure 2. FTIR spectra of the MOF-5, [C₂mim][BETI] IL, PIL NTf₂/40 IL BETI membrane and MMMs with 10, 20 and 30 wt% MOF-5 loading.

The infra-red patterns obtained for MOF-5 are similar to those previously published in the literature.[50] The absorption bands located between 1652 and 1503 cm⁻¹ and at around 1390 cm⁻¹ are associated to the carboxylic (COO) symmetric and asymmetric stretching, respectively. The vibration bands between 750 and 1016 cm⁻¹ are characteristic of terephthalate compounds, which are present in the chemical structure of the MOF ligand. Moreover, the absorption peaks at around 522 cm⁻¹ and 466 cm⁻¹ are assigned to the Zn-O vibrations of the Zn₄O cluster. Regarding the PIL Tf₂N/40 IL BETI membrane, the small bands detected between 3150 and 2880 cm⁻¹ are associated to CH₂ stretching vibrations, while the peak observed at 1478 cm⁻¹ is assigned to the CH₃ bending vibrations originated from the pendant methyl groups of the pyrrolidinium polycation. The absorption bands attributed to the [Tf₂N] counter-anion of the PIL can also be seen at 1347, 1170, 1133 and 1053 cm⁻¹.[51] The incorporation of the [C₂mim][BETI] IL in the

PIL/IL membrane can be confirmed by the presence of absorptions peaks at 1084 cm^{-1} and 975 cm^{-1}, associated to C-N stretching and C=C bending, respectively. The presence of MOF-5 in the PIL/IL matrix can be confirmed by the occurrence of a small absorption peak at around 1652 cm^{-1}, associated to the MOF-5 structure.

3.2. Morphology. The SEM cross section images of the PIL/IL membrane and respective MMMs comprising 10, 20 and 30 wt% of MOF-5 are shown in Figure 3.
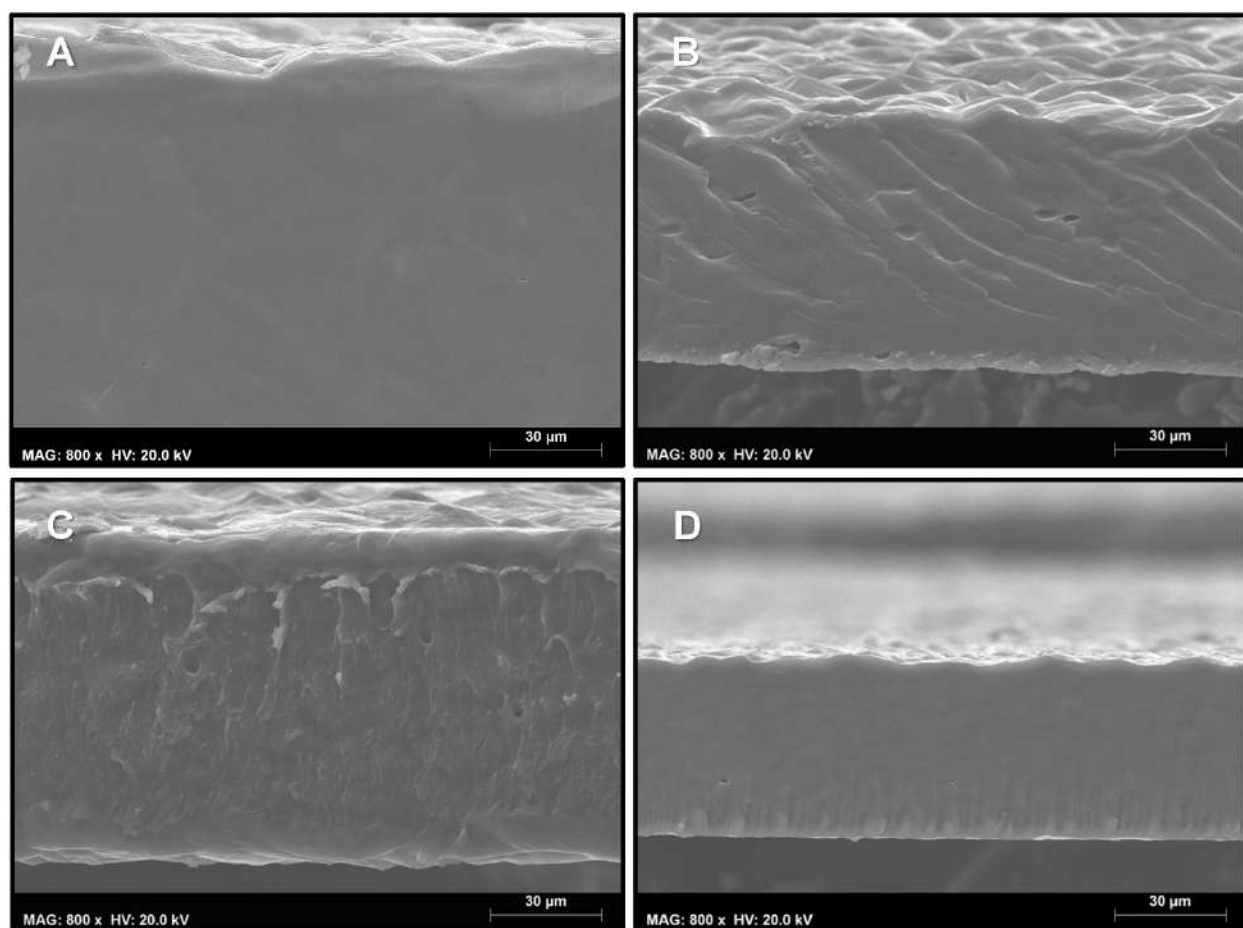

Figure 3. SEM cross-section images of the membranes: (A) PIL Tf$_2$N/40 IL BETI, (B) PIL Tf$_2$N/40 IL BETI/10 MOF-5, (C) PIL Tf$_2$N/40 IL BETI/20 MOF-5 and (D) PIL Tf$_2$N/40 IL BETI/30 MOF-5.

The MOF-5 particles were successfully incorporated into the PIL/IL composite matrix for all the MOF-5 loadings tested. Besides, dense membrane morphologies and uniform dispersion of the MOF into the PIL/IL matrix were obtained, since agglomerates or noticeable deformations were not detected. Note that, for all the prepared membranes, it is possible to identify some randomly distributed holes, which are probably related with the solvent evaporation rate during

the membranes' preparation at room temperature, as high volume of acetone evaporation can outflow during polymer precipitation.

3.3. Thermal Stability. The degradation profiles of the pristine MOF-5, the PIL Tf$_2$N/40 IL BETI membrane and the respective MMMs, were assessed by thermogravimetric analysis and are represented in Figure 4, while the thermal decomposition values, determined in terms of onset (T_{onset}) and decomposition (T_{dec}) temperatures, are given in Table 2.
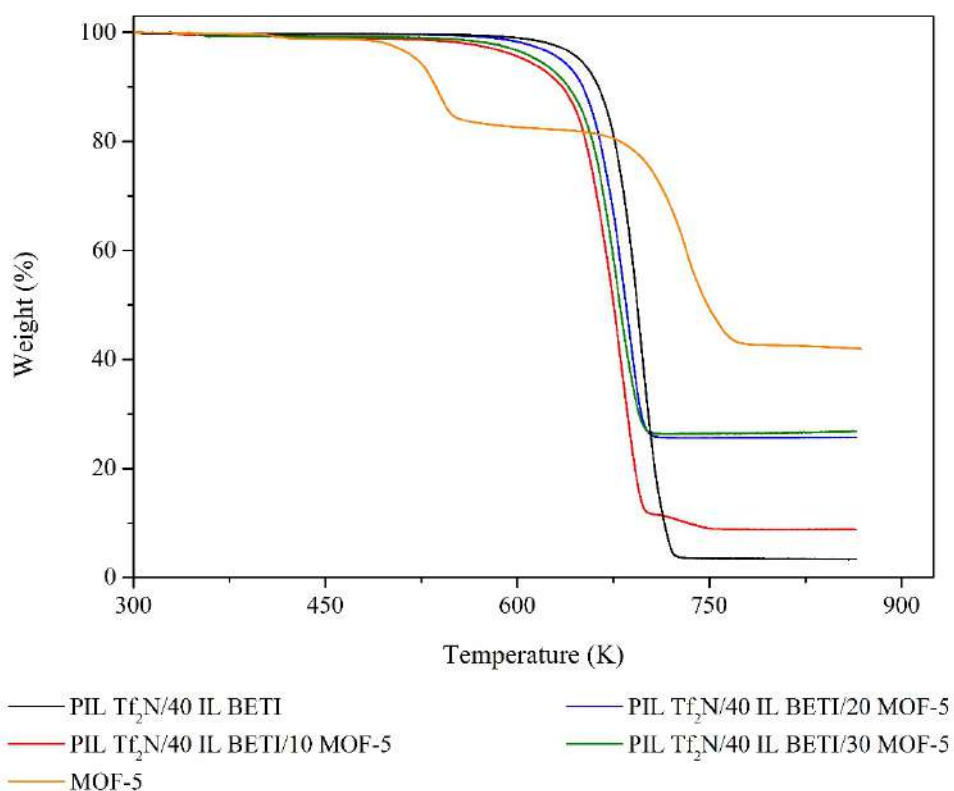

Figure 4. TGA thermograms of the MOF-5, PIL Tf$_2$N/40 IL BETI membrane and MMMs with 10, 20 and 30 wt% MOF-5 loading.

MOF-5 presents a first weight loss stage that occurs between 460 – 525 K, which can be attributed to the evaporation of DMF and adsorbed water molecules, trapped inside the structure during the crystallization period and washing process. The thermal decomposition pattern occurred in the range of 500 – 750 K is attributed to the decomposition of the material. These observations are in agreement to what has been published in the literature.[50] It is also possible to observe that all the prepared membranes presented a similar profile up to 500 K. Between 525 –

600 K all MMMs present a slight weight loss of around 2 to 4 wt%, that corresponds to the evaporation of trapped DMF and water molecules, as observed in the TGA thermogram of the pristine MOF-5.

Table 2. Puncture strength and thermal properties of the MOF-5 and PIL Tf_2N/40 IL BETI membrane, as well as their MMMs with 10, 20 and 30 wt% MOF-5 loading.

Sample	Puncture strength (MPa)	T_{onset} (K) [a]	T_{dec} (K) [b]
MOF-5	n.d.[c]	518	748
PIL Tf_2N / 40 IL BETI	0.41 ± 0.00	672	693
PIL Tf_2N / 40 IL BETI / 10 MOF-5	0.22 ± 0.13	646	675
PIL Tf_2N / 40 IL BETI / 20 MOF-5	0.21 ± 0.01	656	685
PIL Tf_2N / 40 IL BETI / 30 MOF-5	0.18 ± 0.00	651	680

[a] T_{onset} (onset temperature) defined as the temperature at which the baseline slope changes during the heating.
[b] T_{dec} (decomposition temperature) defined as the temperature at 50% weight loss.
[c] not determined.

Looking at Table 2, it can be seen that the T_{onset} slightly decreased from 672 K for the PIL Tf_2N/40 IL BETI membrane to 646 K upon the incorporation of MOF-5. Above these values of T_{onset}, all the membranes shown a pattern of continuous weight loss, resulting in complete degradation of the materials (Figure 4). The same behavior described for T_{onset} was also observed in the T_{dec} of the studied membranes, that decreased from 693 K (PIL/IL membrane) to 675 K once 10 wt% of MOF-5 was incorporated. Nevertheless, and despite the decreases obtained in both T_{onset} and T_{dec}, the thermal stability of the prepared MMMs are not significantly affected when increasing MOF-5 loading (from 10 to 30 wt%) (Table 2). Also worth mentioning is that PILs and ILs bearing fluorinated anions, namely [Tf_2N]⁻ and [BETI]⁻ anions, are well known for their high thermal stabilities.[52] Therefore, and even after the addition of a material having lower thermal stability, such as MOF-5, it can be concluded that the thermal properties of the prepared MMMs membranes were not significantly different from those of the PIL/IL membrane. Similar results have been previously observed for MOF-based MMMs,[53, 54] in particular for PIL/IL/MOF

membranes, when MIL-53 (Al), $Cu_3(BTC)_2$ and ZIF-8 were incorporated into the PIL $Tf_2N/40$ IL $[Pyr_{14}][Tf_2N]$.[42] Overall, and considering that the temperature of biogas streams ranges between 298 and 308 K,[13] it can be concluded that the prepared membranes fit in terms of thermal stability to be used for the biogas upgrading process.

3.4. Mechanical Properties. The results obtained from the mechanical properties study, in terms of the membranes' puncture strength, are summarized in Table 2. The PIL/IL/MOF membranes display lower values of puncture strength than that of the PIL $Tf_2N/40$ IL BETI. Actually, the puncture strength of the prepared membranes decreases as increasing MOF-5 concentration, ranging from 0.41 MPa for the former PIL/IL membrane to 0.18 MPa for the MMMs with the highest MOF loading (30 wt%). These results reveal that the addition of MOF-5 particles probably decreases polymer chain mobility and thus, the membrane' structure becomes more rigid and fragile. This behavior has also been observed by different authors for other MOF-based MMMs.[42, 46, 53, 55]

3.5. CO_2/CH_4 Separation Performance. The CO_2 single gas permeabilities of the prepared PIL/IL and PIL/IL/MOF membranes, as a function of the MOF-5 loading, are presented in Table 3. The obtained results showed that, as the MOF-5 concentration increases, CO_2 permeability also increases, from 146 Barrer for the PIL $Tf_2N/40$ IL BETI membrane to 340 Barrer for the PIL/IL/MOF membrane with the highest loading. It is likely that this improvement is due to a greater diffusion of the gas molecules across the membrane, as the incorporation of MOF particles provides an extra porous network for gas transport.[43] This result may also indicate a good interaction between the MOF particles and the polymeric matrix.

Table 3. Evolution of CO_2 of PIL/IL membranes' permeability as a function MOF-5 loading.

MOF-5 loading (%)	P CO_2(Barrer)	α (CO_2/CH_4)
0	146.1 ± 7.3	14.5 ± 1.0
10	261.4 ± 13.1	7.9 ± 0.6
20	281.9 ± 14.1	14.8 ± 1.0

| 30 | 339.8 ± 16.9 | 1.8 ± 0.1 |

Figure 5 displays the well-known CO_2/CH_4 Robeson upper bound limit,[56] where the CO_2/CH_4 ideal selectivity is represented as a function of the CO_2 pure gas permeability. This representation allows to evaluate the overall performance of the prepared membranes in comparison to what has been published in the literature. It can be observed that, even though all experimental points fall bellow the upper bound limit, there is an increase in the CO_2 permeability for the MMMs, comparatively to the PIL/IL membrane. On the other hand, except for the PIL Tf_2N/40 IL BETI/20 MOF-5 membrane, whose selectivity is similar to the PIL/IL membrane, the incorporation of MOF-5 resulted in a noticeable decrease in selectivity. This can be explained by the fact that the porosity of MOF-5 induces an increase in the gas diffusivity, which is slightly higher for CH_4 (1.8×10^9 $m^2 s^{-1}$) compared to that of CO_2 (1.2×10^9 $m^2 s^{-1}$).[57] Moreover, the cavity size of MOF-5 (around 6 Å) is significantly larger than the kinetic diameter of both tested gases (3.3 Å for CO_2 and 3.8 Å for CH_4), which also contributes to the observed decrease in selectivity. Nonetheless, and due to the fact that CO_2 solubility in MOF-5 is higher than that of CH_4,[43, 58] it can be concluded that CO_2 transport across the membrane is favoured over CH_4. Moreover, literature values reported for other MMMs are displayed in Figure 5. It is clear that depending on the selection and loading degree of the different components present in the MMM (PIL, IL and

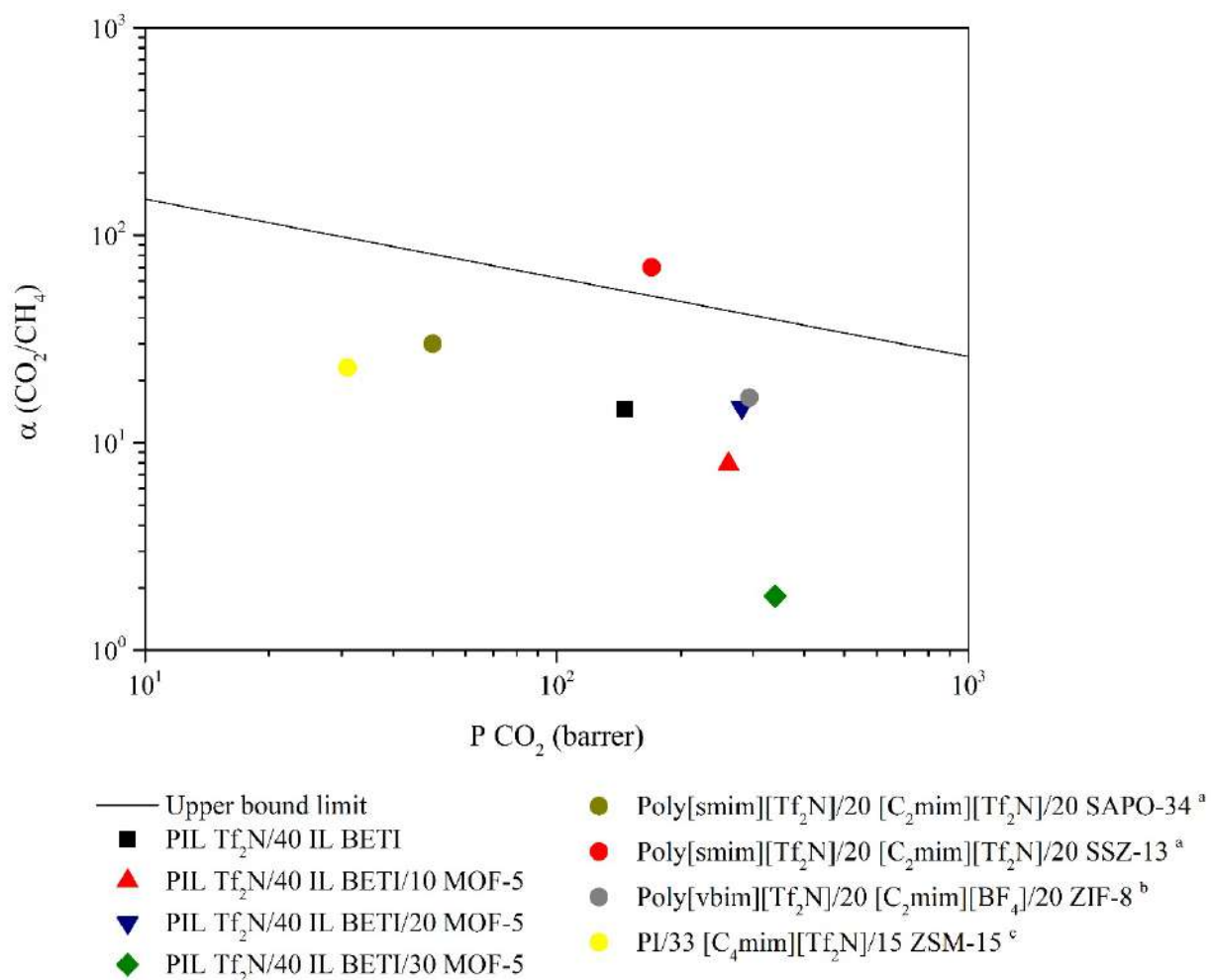MOF), different values of CO_2 permeability and CO_2/CH_4 ideal selectivity can be achieved.

Figure 5. CO_2/CH_4 MMMs ideal selectivity as a function of CO_2 permeability. Data are plotted on a log-log scale and the upper bound is adapted from Robeson.[56] Literature values reported for other MMMs are also illustrated by colored circles (a),[37](b),[41] and (c),[59] for comparison purposes.

4. CONCLUSIONS

In summary, three-component MMMs composed of poly([Pyr$_{11}$][Tf$_2$N]) PIL, [C$_2$mim][BETI] IL and MOF-5 were prepared by solvent evaporation technique. The influence of incorporating different MOF-5 loadings on membrane morphology, thermal and mechanical stability, as well as on the CO_2/CH_4 separation performance of the formed PIL/IL/MOF-5 membranes was evaluated.

The FTIR study confirmed the successful incorporation of [C$_2$mim][BETI] IL and MOF-5 within the PIL matrix, while the SEM images of the membrane cross sections revealed that dense, homogenous and defect-free membrane structures were obtained. Despite the lower thermal stability of MOF-5, the onset (< 656 K) and decomposition (< 685 K) temperatures of the PIL/IL/MOF membranes were not significantly different compared to those of PIL/IL membrane and thus, the prepared MMMs are suitable for biogas upgrading. On the other hand, the addition of MOF-5 particles originated more rigid and fragile membranes in comparison with the PIL/IL composite, but the hydrophilic character remained the same, which is quite important for CO$_2$-transport.

The pure gas permeation results showed that CO$_2$ permeability increased with the amount of MOF-5 incorporated. The MMM with 30 wt% of MOF-5 achieved the highest CO$_2$ permeability of 340 Barrer. The only observed drawback was that the incorporation of MOF-5 resulted in a noticeable decrease in CO$_2$/CH$_4$ selectivity, possibly explained by the cavity size of MOF-5. However, it should be possible to improve the CO$_2$/CH$_4$ separation performance of this MMM system by adjusting the amount of IL, or using different PILs, free ILs and MOF particles with higher CO$_2$/CH$_4$ selectivity. Although further research is needed to achieve PIL/IL/MOF with better performance properties, the results of this work opens up the relevance of understanding at a molecular level the role of each component, in order to better tune-design MMMs for biogas upgrading.

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Notes

ABBREVIATIONS

A	Membrane area
Barrer	1×10^{-10} cm^3(STP) cm cm^{-2} $cmHg^{-1}$ s^{-1}
BETI	Bis(pentafluoroethylsulfonyl) imide
BTC	Benzene-1,3,5-tricarboxylate
CH_4	Methane
CO_2	Carbon Dioxide
DMF	Dimethylformamide
FTIR	Fourier Transform Infrared Spectroscopy
H_2	Hydrogen
H_2S	Hydrogen sulfide
IL	Ionic liquid
l	Membrane thickness
N_2	Nitrogen
MIL	Materials of Institut Lavoisier
MMM	Mixed matrix membrane
MOF	Metal organic framework

P	Permeablity
p	Pressure
p_{feed}	Pressure in the feed compartment
PTFE	Poly(tetrafluoroethylene)
PIL	Poly(ionic liquid)
p_{perm}	Pressure in the permeate compartment
SAPO	Silicoaluminophosphate
SEM	Scanning Electron Microscopy
SILM	Supported Ionic Liquid Membrane
t	Time
T_{dec}	Decomposition temperature
TGA	Thermogravimetric analysis
T_{onset}	Onset temperature
V_{feed}	Volume of the feed compartment
V_{perm}	Volume of the permeate compartment
ZIF-8	Zeolitic imidazolate framework
α	Ideal selectivity
β	Geometric parameter

Cation

[C$_2$mim]	1-ethyl-3-methylimidazolium
[C$_4$mpyr]	1-butyl-3-methylpyrrolidinium

Polycations

[Pyr$_{11}$]	Poly(diallyldimethylammonium)
[smim]	Poly(1-styrenemethyl-3-methylimidazolium)
[vbim]	Poly(1-viny-3-butylimidazolium)

Anions

[B(CN)$_4$]	Tetracyanoborate
[BETI]	Bis(pentafluoroethylsulfonyl)imide
[BF$_4$]	Tetrafluoroborate
[Tf$_2$N]	Bis(trifluoromethylsulfonyl)imide

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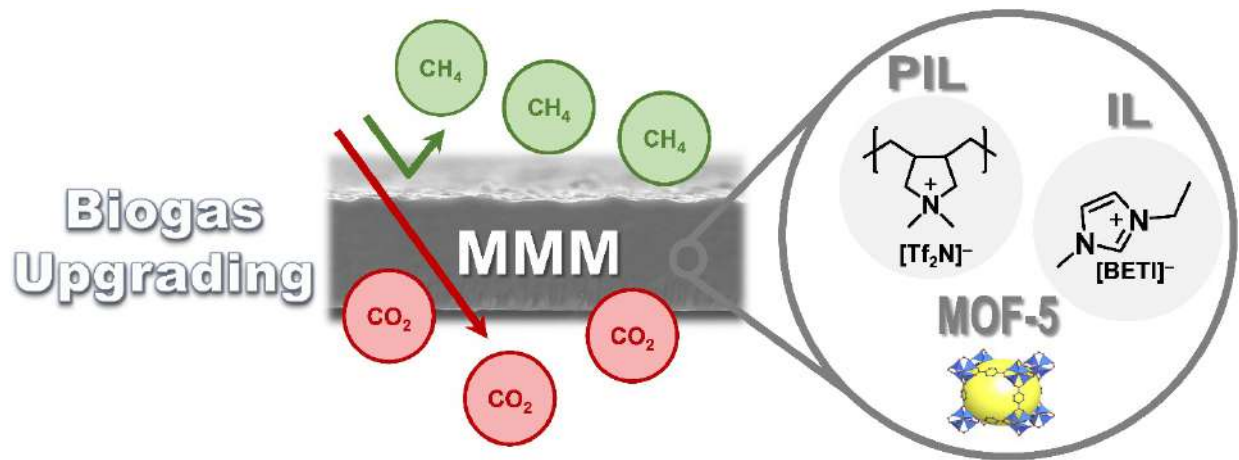
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