

Integrating MOFs and Ionic Liquid-Modified MOF Composites with Polymer to Achieve Enhanced Gas Separation in Mixed Matrix Membranes

by

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**Integrating MOFs and Ionic Liquid-Modified MOF Composites with Polymer to
Achieve Enhanced Gas Separation in Mixed Matrix Membranes**

Koç University

Graduate School of Sciences and Engineering

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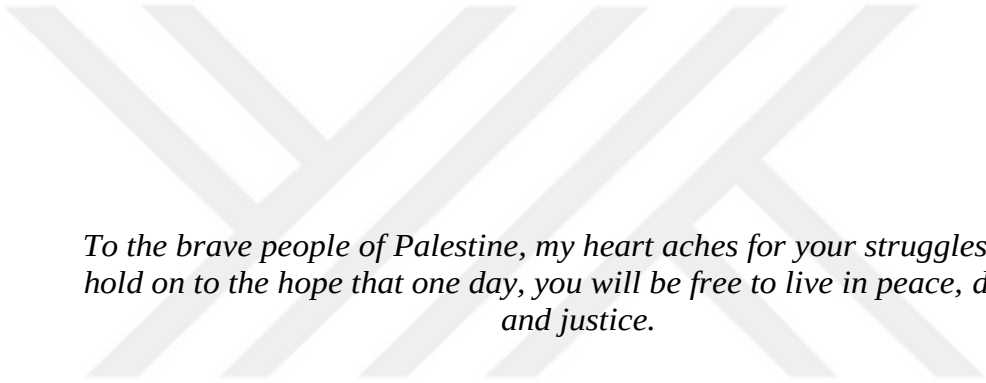
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To the brave people of Palestine, my heart aches for your struggles, and I hold on to the hope that one day, you will be free to live in peace, dignity, and justice.

ABSTRACT

Integrating MOFs and Ionic Liquid-Modified MOF Composites with Polymer to Achieve Enhanced Gas Separation in Mixed Matrix Membranes

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Mixed matrix membranes (MMMs) combining polymers and inorganic fillers have emerged as a promising approach to overcome the trade-off limitations defined by Robeson's upper bound for polymer membranes. This dissertation presents a comprehensive study of ionic liquid/metal organic framework (IL/MOF) composites incorporated into polymer matrices to synthesize IL/MOF/polymer MMMs for targeted gas separation applications, particularly for separating carbon dioxide (CO₂) and acetylene (C₂H₂) from other gases. Existing literature on IL/MOF composites and IL/MOF polymer MMMs has primarily focused on imidazolium-based ILs and well-known MOFs such as ZIF-8 and UiO-66, which, while effective, limits the exploration of broader IL and MOF families. To address this gap, this dissertation also investigates a diverse range of ILs and MOFs, synthesizing IL/MOF composites and assessing their impacts on gas separation applications when integrated into polymer matrices.

In the first part, a pyrrolidinium-based IL, [MPPyr][DCA], was incorporated into MIL-101(Cr) to synthesize the IL/MOF composite. The gas adsorption results showed that at low pressures, the composite demonstrates an infinite CO₂-selectivity over CH₄ and N₂. In the second part, the potential of this composite was further investigated by increasing the IL loading in the composite, and then the IL/MOF/polymer MMMs were synthesized and tested for CO₂/N₂ and CO₂/CH₄ separations. The MMM with 15 wt.% filler loading set a new benchmark value for CO₂/N₂ selectivity for all the IL/MOF/polymer MMMs reported in the literature. In the third part, we addressed the challenges in MMM synthesis, particularly in ensuring the structural integrity of the IL/MOF composites and their compatibility with the polymer matrix. MOF-177, with its exceptional porosity, stability, and CO₂ adsorption capacity, was combined with a pyrrolidinium-based IL, [BMPyr][TCM], to synthesize IL/MOF/polymer MMMs. A simultaneous improvement in both gas permeability and selectivity was achieved through optimized synthesis and filler dispersion. A key challenge in these MMMs was controlling the IL dispersion, particularly preventing IL leaching from the MOF pores. This was successfully tackled by synthesizing [EMIM][OAc]/CuBTC composite and [EMIM][OAc]/CuBTC/Pebax MMMs. Finally, the challenging C₂H₂/C₂H₄ separation was studied. MIL-100(Fe)-based MMMs were developed at various filler loadings for this separation. The MIL-100(Fe)/Pebax MMMs having filler loadings of 17 wt.% exhibited improved C₂H₂ permeability and C₂H₂/C₂H₄ selectivity, indicating a remarkable improvement in the gas separation performance as compared to the neat membrane. Furthermore, the long-term stability tests confirmed the robustness of these membranes under continuous operation, highlighting their potential for industrial applications. The findings established in this dissertation represent a significant advancement in the field of membrane technology, setting new benchmarks for selectivity and permeability and pushing the boundaries of IL/MOF/polymer MMMs, and, unlocking new opportunities for innovation and progress in the field.

ÖZET

Integrating MOFs and Ionic Liquid-Modified MOF Composites with Polymer to Achieve Enhanced Gas Separation in Mixed Matrix Membranes

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Kimya ve Biyoloji Mühendisliği, Doktora

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Polimerler ve inorganik dolguların birleştirildiği karışık matrisli membranlar (MMM'ler), polimer membranlar için tanımlanmış olan Robeson'un üst sınırını aşmak adına umut verici bir yaklaşım olarak ortaya çıkmıştır. Bu tez, özellikle karbondioksit (CO_2) ve asetilenin (C_2H_2) diğer gazlardan ayrılması için iyonik sıvı/metal organik çerçeve (IL/MOF) kompozitlerini polimer matrislerine dahil ederek IL/MOF/polimer MMM'lerinin sentezlenmesine yönelik kapsamlı bir çalışma sunmaktadır. IL/MOF kompozitleri ve IL/MOF polimer MMM'leri üzerine mevcut literatür, genellikle imidazolyum bazlı iyonik sıvılar, ve ZIF-8 ve UiO-66 gibi bilinen MOF'lara odaklanmıştır. Bu durum, daha geniş IL ve MOF ailelerinin keşfini sınırlamaktadır. Bu boşluğu gidermek için, bu tezde çeşitli IL ve MOF'lar araştırılmış, IL/MOF kompozitleri sentezlenmiş ve bu kompozitlerin polimer matrislerine entegre edildiklerinde gaz ayırma uygulamalarına olan etkileri değerlendirilmiştir.

Tezin ilk bölümünde, bir pirolidinyum bazlı IL olan [MPPyr][DCA], MIL-101(Cr) ile birleştirilerek IL/MOF kompoziti sentezlenmiştir. Gaz adsorpsiyon sonuçları, düşük basınçlarda bu kompozitin CH_4 ve N_2 'ye karşı sonsuz CO_2 seçiciliği gösterdiğini ortaya koymuştur. İkinci bölümde, bu kompozitin potansiyeli IL yüklemesi artırılarak ve ardından IL/MOF/polimer MMM'leri CO_2/N_2 ve CO_2/CH_4 ayırmaları için sentezlenip test edilerek incelenmiştir. 15% dolgu yüklemesine sahip MMM, literatürde bildirilen tüm IL/MOF/polimer MMM'leri arasında CO_2/N_2 seçiciliğinde yeni bir referans değeri belirlemiştir. Üçüncü bölümde, IL/MOF kompozitlerinin yapısal bütünlüğünün korunması ve polimer matrisiyle uyumluluğunun sağlanması gibi MMM sentezindeki zorluklar ele alınmıştır. Olağanüstü gözeneklilik, dayanıklılık ve CO_2 adsorpsiyon kapasitesine sahip MOF-177, bir pirolidinyum bazlı IL olan [BMPyr][TCM] ile birleştirilerek IL/MOF/polimer MMM'leri sentezlenmiştir. Optimize edilmiş sentez ve dolgu dağılımı sayesinde hem geçirgenlik de hem de seçicilik de eşzamanlı iyileştirme sağlanmıştır. Ayrıca, bu MMM'lerde IL'nin MOF gözeneklerinden sızmasını önlemek için IL dağılımını kontrol etmek önemli bir zorluktur. Bu zorluk, [EMIM][OAc]/CuBTC kompoziti ve [EMIM][OAc]/CuBTC/Pebax MMM'lerinin sentezi ile başarılı bir şekilde aşılmıştır. Son olarak, ayırması güç olan $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ gazları çalışılmıştır. MIL-100(Fe) bazlı MMM'ler, bu ayırma için çeşitli dolgu yüklemeleriyle geliştirilmiş ve alana önemli bir katkı sağlanmıştır. 17% dolgu yüklemesine sahip MIL-100(Fe)/Pebax MMM'ler, saf membrana kıyasla C_2H_2 geçirgenliğinde ve $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ seçiciliğinde iyileştirme göstermiştir. Ayrıca, uzun süreli dayanıklılık testleri, bu membranların sürekli çalışmada sağlamlığını doğrulamış ve endüstriyel uygulamalar için potansiyelini ortaya koymuştur. Bu tezde elde edilen bulgular, membran teknolojisi alanında önemli bir ilerlemeyi temsil etmekte, seçicilik ve geçirgenlik için yeni standartlar belirlemekte ve IL/MOF/polimer MMM'lerinin sınırlarını zorlamaktadır. $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ ayırmasındaki karmaşık sorunlara çözüm sunarak, bu tez membran teknolojisinin kapsamını genişletmekte ve alanında yenilik ve ilerleme için yeni fırsatların kapısını aralamaktadır.

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ABBREVIATIONS

IL: Ionic liquid
MOF: Metal organic framework
MMM: Mixed Matrix Membranes
BET: Brunauer–Emmett–Teller
SEM: Scanning electron microscope
TGA: Thermal gravimetric analysis
DFT: Density Functional Theory
S_{BET}: BET surface area
IR: Infrared spectroscopy
COSMO-RS: Conductor-like Screening Model for Realistic Solvents

ILs:

[BMIM][PF₆]: 1-butyl-3-methylimidazolium hexafluorophosphate
[BMIM][SCN]: 1-butyl-3-methylimidazolium thiocyanate
[BMIM][BF₄]: 1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM][CF₃CO₂]: 1-butyl-3-methylimidazolium trifluoroacetate
[BMIM][Cl]: 1-butyl-3-methylimidazolium chloride
[BMIM][DCA]: 1-butyl-3-methylimidazolium dicyanamide
[BMIM][Tf₂N]: 1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide
[BMIM][OcSO₄]: 1-butyl-3-methylimidazolium octyl sulfate
[BMIM][SbF₆]: 1-butyl-3-methylimidazolium hexafluoroantimonate
[BMIM][CH₃COO]: 1-butyl-3-methylimidazolium acetate
[BMIM][C(CN)₃]: 1-butyl-3-methylimidazolium tricyanomethanide
[MMIM][BF₄]: 1-methyl-3-methylimidazolium tetrafluoroborate
[HEMIM][DCA]: 1-hexyl-3-methylimidazolium dicyanamide
[P_{6,6,6,14}][DCA]: Trihexyl(tetradecyl)phosphonium dicyanamide
[EMIM][Tf₂N]: 1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide
[EMIM][OAc]: 1-ethyl-3-methylimidazolium acetate
[EMIM][Br]: 1-ethyl-3-methylimidazolium bromide
[MIM][Br]: 1-methylimidazolium bromide
[EMIM][Cd(BTC)]: 1-ethyl-3-methylimidazolium, 1,3,5-benzenetricarboxylate
[EMIM][DEP]: 1-ethyl-3-methylimidazolium diethylphosphate
[EMIM][EtSO₄]: 1-ethyl-3-methylimidazolium ethyl sulfate
[DnBM][Cl] : 1,3-di-n-butyl-2-methylimidazolium chloride
[APTMS][Ac]: 3-(trimethoxysilyl)propane-1-aminium acetate
[NH₂-PMIM][Tf₂N]: Amino-1-(2-methylimidazolium)
bis(trifluoromethanesulfonyl)imide.
[C₃NH₂BIM][Tf₂N] : 3-amino-1-butylimidazolium bis(trifluoromethanesulfonyl)imide
[TMGH][PhO] : tetramethylguanidinium phenol
[TMGH][IM] : tetramethylguanidinium imidazole
[PMIM][Tf₂N]: 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide
[BMPyr][TCM]: 1-butyl-1-methyl-pyrrolidinium tricyanomethanide
[BMPyr][DCA]: 1-butyl-1-methyl-pyrrolidinium dicyanamide
[MPPyr][DCA]: 1-methyl-1-propyl pyrrolidinium dicyanamide

[EMIM][Ala]: 1-ethyl-3-methylimidazolium alanine
[EMIM][Gly]: 1-ethyl-3-methylimidazolium glycine

MOFs:

HKUST: Hong Kong University of Science and Technology
Cu-TDPAT: Copper(II) 1,3,5-triazine-2,4,6-triamine.
CuBTC: Copper(II) Benzene-1,3,5-tricarboxylate
ZIF-8: Zeolitic Imidazolate Framework-8
UiO-66: University of Oslo-66

Polymers:

6FDA-durene:4,4'-(hexafluoroisopropylidene)diphthalic anhydride-2,3,5,6-tetramethyl-1,3-phenyldiamine
PSf: Polysulfone
Pebax: Poly-ether-block-amide
PIM: Polymer of intrinsic microporosity

Chapter 1

Introduction

Membrane technology has gained significant attention in gas separation applications thanks to their lower cost, enhanced mechanical and thermal stability, environmental benefits, and scalability compared to traditional separation technologies [1-4]. The performance of a membrane is generally assessed by two metrics: gas permeability, which defines the amount of gas that can pass through the membrane per unit time, and selectivity, which describes how effectively a material can differentiate between different gases, allowing some to pass while blocking others. Ideally, both high gas permeability and high selectivity are desired to enhance the separation efficiency in industrial processes. Gas separation membranes are generally categorized based on the type of membrane material: inorganic membranes, polymeric membranes, and MMMs. Inorganic membranes, such as carbon molecular sieves (CMSs), ceramics, metal oxides, zeolites, and MOFs, exhibit moderate permeability and excellent selectivity, making them efficient for gas separations [5, 6]. The key advantage is their high stability under extreme temperature and pressure conditions. However, the development and implementation of inorganic membranes have been limited by factors such as high production costs, brittleness, and difficulties in fabrication and processability, particularly in achieving defect-free membrane structures.

Conversely, polymeric membranes are more flexible, cost-effective, and more widely used in industrial applications thanks to their well-developed synthesis and easy implementation. However, polymeric membranes almost always suffer from the trade-off between selectivity and permeability, which restricts their separation performance. [7-9]. This trade-off is first illustrated by Robeson with the introduction of an upper bound that defines the maximum achievable balance between permeability and selectivity for polymeric membranes in 1991 [10], which was then updated in 2008 [11] and 2019 [12],

after the development of more rigid and highly structured polymers known as polymers of intrinsic microporosity (PIMs) that surpass the previous limits. Polymeric membranes are also known to be prone to plasticization, which typically occurs when condensable gases pass through the membrane, particularly in rubbery polymers, causing swelling and increased polymer chain mobility [13, 14], and physical aging that occurs in glassy polymers and affects the membrane's mechanical properties and gas separation performance over time [15]. All these drawbacks have limited the long-term use of polymeric membranes [16].

To address these limitations, MMMs and hybrid membranes have been developed, combining the desirable properties of both inorganic and polymeric membranes, such as the high selectivity of MOFs and zeolites and the ease of processability of the polymers. By incorporating MOFs into the polymer matrix, MOF/polymer MMMs have been synthesized and shown to offer enhanced gas separation performance, overcoming the permeability-selectivity trade-off of the pure polymer membranes [17, 18]. While MOF/polymer MMMs showed significant improvements in gas selectivity [19-21], several challenges remain concerning the compatibility and dispersion of MOF particles within the polymer matrix. Issues such as poor adhesion between the MOF particles and the polymer, inadequate wettability, and phase separation are also known to adversely affect the integrity and gas separation performance of MMMs [18]. These challenges can lead to non-uniform distribution of the MOFs, resulting in reduced separation efficiency and compromised mechanical properties of the MMMs [22]. Functionalization of MOFs with ILs helped to achieve a more homogeneous dispersion of MOFs within the polymer, mitigating phase separation and enhancing the stability and performance of MMMs [23]. ILs can also modify the surface properties of the MOFs, further optimizing their interactions with the polymer and improving the membrane's separation efficiency [24]. A wide variety of ILs and MOFs exist, with the majority of studies focusing on imidazolium-based ILs and well-known MOFs such as ZIF-8 and UiO-66.

This dissertation investigates different families of ILs and MOFs to synthesize IL/MOF composites and their gas adsorption performance. Subsequently, these IL/MOF composites were incorporated into the polymer, and detailed characterization and performance evaluation of the resulting IL/MOF/polymer MMMs were performed, focusing on their application for CO₂ and C₂H₂ separation. Chapter 2 presents an in-depth literature review of IL/MOF/polymer MMMs, while Chapter 3 details the experimental

and computational methodologies employed in this dissertation.

In Chapter 4, a pyrrolidinium-based IL, [MPPyr][DCA], was incorporated into MIL-101(Cr) to synthesize the IL/MOF composite, followed by extensive characterization to understand the interactions between the IL and MOF. The resulting [MPPyr][DCA]/MIL-101(Cr) composite was extensively characterized to elucidate the interactions between [MPPyr][DCA] molecules and MIL-101(Cr). The impact of these interactions on gas separation performance, specifically CO₂/N₂, CO₂/CH₄, and CH₄/N₂, was evaluated using volumetric gas adsorption studies, and the results were further supported by DFT calculations. Given this exceptional performance in Chapter 5, the potential of this composite was further investigated by increasing the IL loading in the composite, incorporating it into the Pebax polymer, and examining the impact of the composite on the gas separation properties of IL/MOF/polymer MMMs. The MMM with 15 wt.% composite loadings showed significantly higher CO₂/N₂ selectivity (1,348) and CO₂/CH₄ selectivity (121.5) compared to pure Pebax, setting a new benchmark value for the IL/MOF/polymer MMMs reported in the literature.

Chapter 6 addresses challenges in MMM synthesis, particularly in ensuring the structural integrity of the IL/MOF composites and their compatibility with the polymer matrix. Among a wide range of MOFs, MOF-177 stands out with its exceptional properties, such as ultrahigh porosity with remarkably high surface area, outstanding thermal and chemical stability, and superior CO₂ adsorption capacity. Leveraging these attributes, we synthesized a composite using MOF-177 and a pyrrolidinium-based IL, [BMPyr][TCM], and incorporated it as a filler into Pebax polymer at various loadings. The synthesis procedure was optimized to ensure the homogeneous dispersion of the composite within the polymer matrix. The resulting IL/MOF/polymer MMMs were thoroughly characterized and studied for CO₂ separation. Notably, MMMs with a filler loading of 10 wt.% demonstrated significant enhancements in both CO₂ permeability (137±1.80 Barrer) and CO₂/N₂ selectivity (622±105) compared to the neat Pebax membrane (98.0±2.0 Barrer and 64.5±5.8, respectively), surpassing the Robeson's upper bound. This simultaneous improvement in both permeability and selectivity effectively breaks the trade-off limitation typically observed in polymer membranes.

In Chapters 5 and 6, we faced a critical challenge in controlling the dispersion of ILs within the MMMs, as the ILs were not adequately contained and leached out of the MOF pores, and dispersed as free IL molecules in the membranes during the synthesis.

This issue was successfully tackled in Chapter 7, where we successfully synthesized an IL/MOF composite, [EMIM][OAc]/CuBTC, and incorporated it into Pebax to prepare IL/MOF/polymer MMMs. The membranes were fabricated by controlling the IL dispersion within the MOF cages and ensuring uniform filler distribution within the MMMs, which was confirmed through various characterization techniques.

The separation of acetylene (C_2H_2) and ethylene (C_2H_4) using membrane technology has yet to be explored, with the majority of research in the field focusing on CO_2 separation. Chapter 8 attempts to fill this gap by developing MMMs integrated with MIL-100(Fe), an iron-based metal-MOF, at various loadings. The MIL-100(Fe)/Pebax MMMs having filler loadings of 17 wt.% exhibited C_2H_2 permeability of 509.3 ± 7.3 Barrer, with corresponding C_2H_2/C_2H_4 selectivity of 35.6 ± 1.0 , indicating a remarkable improvement in the gas separation performance. Furthermore, long-term stability tests confirmed the robustness of these membranes under continuous operation, highlighting their potential for industrial applications. This research provides valuable insights into developing high-performance MMMs for a critical industrial separation challenge, contributing to the underexplored field of C_2H_2/C_2H_4 separation in membrane technology.

Chapter 9 concludes the dissertation by summarizing the essential findings and advancements in the development of IL/MOF/polymer MMMs for gas separation. It also provides an outlook on the future of this field, highlighting potential areas for improvement.

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Chapter 2

Literature Review*

2.1. IL/MOF Composites for Membrane-Based Gas Separation: As Fillers in MMMs

This chapter provides a comprehensive overview of advancements in membrane technology, focusing on the current state-of-the-art in IL/MOF/polymer MMMs. It discusses the latest strategies, significant challenges, and key achievements in enhancing the gas separation performance of the MMMs. Various approaches have been explored to incorporate the fillers consisting of various IL and MOF combinations into the MMMs, as illustrated in Figure 4. Three primary strategies involve (i) confining the IL within the pores of the MOF, (ii) positioning ILs at the interface between the MOF and the polymer. The first approach involves incorporating ILs directly within the MOF cages, and then mixing the composite with a polymer to form IL/MOF/polymer MMMs. This strategy leverages the MOF's porous structure to control the IL distribution and modulate its interactions with gas molecules to enhance selective separation. In the second approach, ILs are located on the surface of the MOF when they are incorporated into the polymer. Here, IL acts as a wetting layer, enhancing compatibility between the MOF and polymer and facilitating gas transport through the membrane.

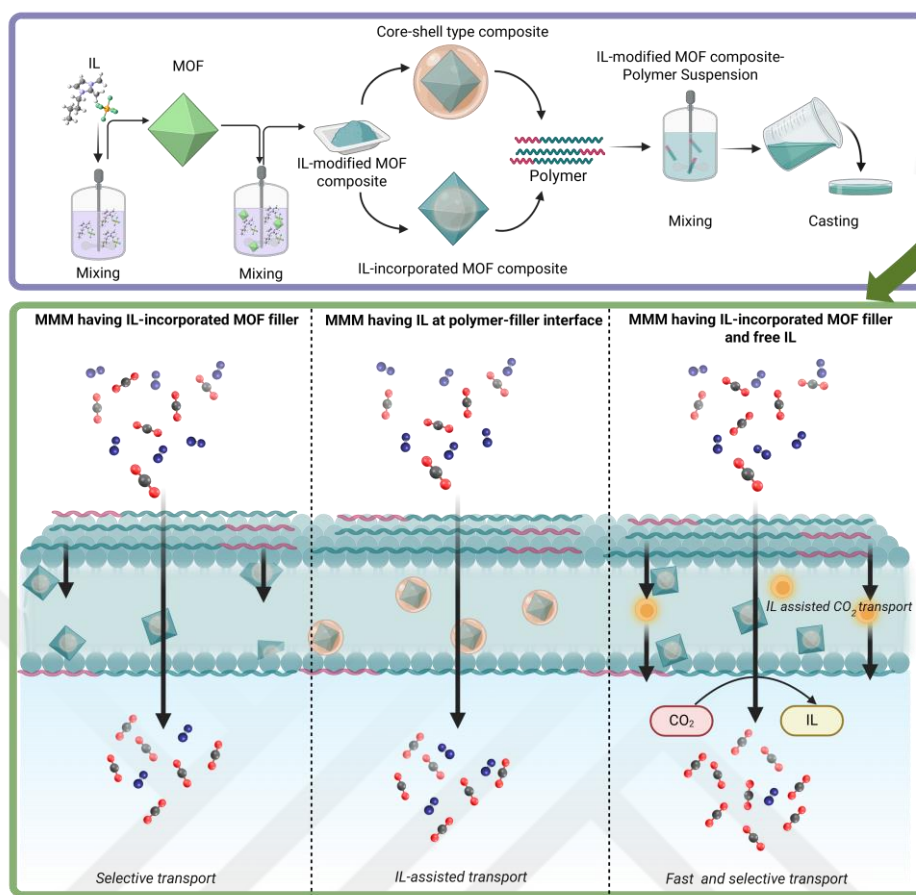


Figure 2.1. Schematic illustration of MMMs having IL-incorporated MOF filler, IL at the interface between the MOF and polymer, and IL presents both as a part of the IL/MOF composite and as free molecules within the polymer.

2.1.1. MMMs with the IL Confined in the Pores of the MOF

Several studies focused on introducing ILs into MMMs by confining them into the pores of MOFs to prepare an IL/MOF composite before the membrane fabrication. Pore engineering represents a promising strategy for creating IL/MOF composites, resulting in precise molecular sieving and enhanced gas diffusion. Ban et al. [1] were the pioneers in the field, introducing the concept of "cavity occupants" by incorporating [BMIM][Tf₂N] into ZIF-8 cages through *in-situ* ionothermal synthesis. This approach reduced the effective pore size of ZIF-8 from 1.12 nm to 0.59 nm and significantly improved its molecular sieving capabilities. [BMIM][Tf₂N]/ZIF-8/PSf MMMs demonstrated CO₂ permeability of 307 Barrer with CO₂/N₂ and CO₂/CH₄ selectivities of 53 and 26, respectively, at 30 °C and 6 bar, surpassing the 2008 upper bound.

A different strategy of two-step adsorption/infiltration technique was employed to synthesize [BMIM][PF₆]/ZIF-8 composite, which was then incorporated into Pebax to

synthesize the corresponding MMMs [2]. The larger [BMIM][PF₆] molecules were first adsorbed onto the outer surface of ZIF-8, afterward, through heat treatment at 105 °C, the apertures of ZIF-8 temporarily expand, allowing [BMIM][PF₆] molecules to enter ZIF-8 nanocages. This has enabled more precise separation of gas pairs with similar molecular sizes. MMMs having filler loadings of 30 wt.% exceeded the upper bound, achieving a CO₂ permeability of 120 Barrer and a CO₂/N₂ selectivity of 84.5 compared to pure Pebax membrane (CO₂: 59 Barrer, CO₂/N₂ selectivity: 55).

MMMs are susceptible to plasticization and physical aging, which can significantly compromise their long-term performance, as discussed above [3, 4]. [BMIM][Tf₂N]/MOF-801 composite was incorporated into PIM-1 to investigate the effects of IL/MOF composite on the physical aging and separation performance of the MMMs [5]. The MMM with 5 wt.% filler loading exhibited improved CO₂ permeability of 9,420 Barrer and CO₂/N₂ selectivity of 29 compared to pure PIM-1 membrane having CO₂ permeability and CO₂/N₂ selectivity of 4,110 Barrer and 20, respectively, at 4 bar and 35 °C. With an increase in feed pressure, the pure PIM-1 membrane exhibited significant plasticization, leading to a 46% increase in CO₂ permeability and a 43% decrease in CO₂/N₂ selectivity at 4 MPa. Conversely, the [BMIM][Tf₂N]/MOF-801/PIM-1 MMM showed superior anti-plasticization properties, with only a 6% increase in CO₂ permeability and a slight reduction in selectivity. This was attributed to its stable structure and chemical properties. IL/MOF/polymer MMM demonstrated enhanced anti-aging properties, with a slight decrease in CO₂ permeability over a 100-day period, compared to the pure PIM-1 membrane, while the CO₂/N₂ selectivity showed an increase due to the reduced free volume within the membrane.

Controlling the IL loading in IL/MOF/polymer MMMs is another crucial aspect for optimizing their performance. For instance, the [PMIM][Tf₂N]/ZIF-67/PEO MMMs were synthesized and tested for propylene/propane separation [6]. [PMIM][Tf₂N]/ZIF-67 composite was synthesized using a mechanochemical method, demonstrating rapid scalability compared to solution-based approaches. The optimized IL loading was found to be as low as 0.136 wt.%, and the MMM containing 40% of the IL/MOF composite achieved an enhanced C₃H₆/C₃H₈ selectivity and a C₃H₆ permeability of 45.7 and 218.4 Barrer, respectively. The significantly improved performance indicates the role of confined IL acting as a C₃H₆ transfer bridge in the MMMs.

Different anions significantly alter the solubility and diffusion properties of gases within the membrane. A systematic study focused on ILs featuring different anions, [DCA]⁻, [Tf₂N]⁻, [TCM]⁻ but the same imidazolium cation, [EMIM]⁺, and synthesized IL/ZIF-8/PSf MMMs to understand how interactions between the anions and the MOF affect the MMMs' separation performance [7]. IL/MOF/polymer with the [Tf₂N]⁻ provided the highest CO₂ affinity and permeability. At [EMIM][Tf₂N]/ZIF-8 loading of 10 wt.%, the MMM exhibited a CO₂ permeability of 7.4 Barrer with CO₂/N₂ and CO₂/CH₄ selectivities of 67 and 82, respectively. This enhanced performance was attributed to the favorable interactions between [Tf₂N]⁻ anion and ZIF-8, which facilitated the CO₂ diffusion while effectively blocking CH₄ and N₂. When the loading was increased to 30 wt.%, CO₂ permeability, CO₂/N₂, and CO₂/CH₄ selectivities improved to 24 Barrer, 127, and 215, respectively. These results highlight the influence of increased IL loading on enhancing both the permeability and selectivity of MMMs, suggesting that optimizing both IL content and selecting cations and anions are critical for enhanced gas transport properties in IL/MOF/polymer MMMs.

Initial research on IL/MOF/polymer MMMs mostly focused on imidazolium-based cations in ILs for CO₂/N₂ and CO₂/CH₄ separations, as summarized in **Table 2.1**. While these imidazolium-based IL demonstrated tunable physicochemical properties and a strong affinity for CO₂, functionalized ILs with chemical reaction sites for targeted gas molecules present more opportunities for enhancing MMM's gas transport properties. The advantages of functionalized ILs in improving gas separation performance have been elaborated in the gas adsorption section of this review. ILs functionalized with amino acids demonstrate exceptional CO₂ absorption solubility, making them particularly suitable for use in MMMs. For instance, an amino-based IL, [APTMS][Ac], with its acetate anion and amino cation featuring both amine and methoxy groups, combined with the uniformly distributed ZIF-67 particles to synthesize [APTMS][Ac]/ZIF-67/PSf MMMs which exhibited improved CO₂ permeability of 22 Barrer, CO₂/N₂ and CO₂/CH₄ selectivities of 74 and 75, respectively, compared to pristine PSf membrane (CO₂ permeability: 7 Barrer, CO₂/N₂ selectivity: 27, CO₂/CH₄ selectivity: 25) [8]. The presence of amine groups in the IL contributed to the membrane's basicity and enhanced interactions with acidic CO₂. The performance of [NH₂-PMIM][Tf₂N]/MOF-808/PIM-1 MMMs was evaluated on the basicity of the IL present in the membrane [9]. The MMMs with moderate basicity demonstrated optimal separation performance, exhibiting a

CO₂/N₂ selectivity of 43.6 at 4 bar compared to the neat membrane having a CO₂/N₂ selectivity of 37.7.

Table 2.1 Gas separation performance of IL/MOF/polymers MMMs reported in the literature.

IL/MOF/Polymer MMMs	Filler loading (wt.%)	CO ₂ Permeability (Barrer)	Selectivity		Conditions
			CO ₂ /N ₂	CO ₂ /CH ₄	
[BMIM][TF ₂ N]/ZIF-8/PSf [1]	6	468	116	40	30 °C, 6 bar
[NH ₂ -PMIM][TF ₂ N]/ZIF-67/PIM-1 [10]	5	9,536	31	-	25 °C, 2bar
[BMIM][TF ₂ N]/MOF-801/PIM-1 [5]	5	9,420	29	-	35 °C, 4 bar
[BMIM][TF ₂ N]/ZIF-8/Pebax 1657 [11]	15	105	84	39	25 °C, 1 bar
[EMIM][TF ₂ N]/HKUST-1/6FDA-durene [12]	10	1,100	27	29	25 °C, 2 bar
[EMIM][TF ₂ N]/ZIF-67/6FDA-durene [13]	20	1,426	25.3	25.5	25 °C, 2 bar
[TMGH][IM]/ZIF-67/PIM-1 [14]	10	12,848	14	10.5	23 °C, 1 bar
[BMIM][PF ₆]/ZIF-8/Pebax 1657 [2]	30	120	85	-	25 °C, 3 bar
[C ₃ NH ₂ BIM][NTF ₂]/NH ₂ MIL-101(Cr)/PIM-1 [15]	5	2,979	37	-	25 °C, 3 bar
[C ₅ MIN][BF ₄]/ZIF-67/Pebax [16]	70	408.2	98	-	30 °C, 2 bar
[PMIM][Tf ₂ N]/ZIF-67/PEO [6]	40	218.7(C ₃ H ₆)	45.7 (C ₃ H ₆ /C ₃ H ₈)		30 °C, 3 bar
[EMIM][Tf ₂ N]/ZIF-8/PSf [7]	30	24	127	215	30 °C, 4 bar
[EMIM][B(CN) ₄]/ZIF-8/[Poly[vbim]][TF ₂ N] [17]	25.8	1,062	24	12.3	35 °C, 3.5 bar
[DnBM][Cl]/ZIF-8/Pebax 1657 [18]	32	260	72	39	30 °C, 2 bar
[APTMS][Ac]/ZIF-67/PSf [8]	30	22	74	72	25 °C, 10 bar
[BMIM][TF ₂ N]/NH ₂ -MIL101(Cr)/Matrimid [19]	7	19	-	113	35 °C, 10 bar
[PMIM][Br]/MIL101(Cr)/Matrimid [20]	20	10	27	-	30 °C, 0.7 bar
[TMGA][N ₃]/MOF-5/Matrimid [21]	2	37	36	-	35 °C, 0.7 bar
[BMIM][TF ₂ N]/UiO-66/PEI [22]	15	25	-	60	35 °C, 1 bar
[BMIM][Tf ₂ N]/NH ₂ -UiO-66/PIM-1 [23]	10	8,283.4	22.5	12.3	20 °C, 1 bar

[APTMS][Ac]/NH ₂ -UiO-66/Pebax [24]	30	135	34	78	25 °C, 10 bar
[EMIM][OAc]/ZIF-8/Chitosan [25]	10	5,431	12	-	25 °C
[NH ₂ -PMIM][Tf ₂ N]/MOF-808/PIM-1 [9]	10	43.6	37.7	-	30 °C, 4 bar
[Tf ₂ N]-based IL/ZIF-8/Pebax PEG-MEA [26]	5	800	24		25 °C, 2 bar
[MIM][Br]/MOF-808/Pebax [27]	5	426	69.6		25 °C, 2 bar

In addition to amino-functionalized ILs, amino-functionalized MOFs have also been explored by fabricating [BMIM][Tf₂N]/NH₂-UiO-66/PIM-1 MMMs, which exhibited improved CO₂ permeability of 8,283.4 Barrer and improved CO₂/N₂ and CO₂/CH₄ selectivity of 22.5 and 12.3, respectively, compared to pure PIM-1 membrane (CO₂ permeability: 7,061 Barrer, CO₂/N₂ selectivity: 10.3, CO₂/CH₄ selectivity: 6.3) [23]. This improvement was attributed to amino-functionalized UiO-66, with its abundant micropores that offer additional CO₂ permeation pathways and form hydrogen bonds with PIM-1, improving interfacial interactions and reducing non-selective defects in the membrane. These studies have demonstrated the potential of [APTMS][Ac] and NH₂-UiO-66 in improving gas separation performance. To leverage the properties of both materials, [APTMS][Ac]/NH₂-UiO-66/Pebax MMMs were synthesized [24]. At 30 wt.% composite loading, the MMM achieved improved CO₂ permeability (135 Barrer) and improved CO₂/N₂ selectivity (34) and CO₂/CH₄ selectivity (78), compared to the neat membrane. This improvement can be ascribed to the strong CO₂ affinity of amino-functionalized UiO-66 and IL which enables rapid and efficient CO₂ penetration, enhancing the overall gas separation performance of IL/MOF/polymer MMM.

While amino-functionalization improves CO₂ separation by increasing affinity through basic groups, task-specific ILs (TSILs) offer selective adsorption and facilitated transport of CO₂, which is also critical for effective gas separation, emphasizing the need for IL/MOF composites to efficiently facilitate CO₂ transport while restricting other gas molecules. These types of ILs can form strong, reversible bonds with CO₂, enhancing selectivity while maintaining high permeability. A TSIL, [C₃NH₂bim][Tf₂N], was incorporated in NH₂-MIL-101(Cr) to synthesize [C₃NH₂bim][Tf₂N]/NH₂-MIL-101(Cr)/PIM-1 MMMs [15]. At 5 wt.% filler loading, the MMM achieved CO₂ permeability and CO₂/N₂ selectivity of 2,979 Barrer and 37, respectively, showing 18.4%

and 119% increase compared to the neat PIM-1 membrane, and 116% increase in the selectivity compared to the NH₂-MIL-101(Cr)/PIM-1 membrane. The TSIL acted as a CO₂ transport carrier, facilitating fast CO₂ transfer while slowing down N₂ transport. This mechanism led to significant improvements in CO₂/N₂ separation performance that exceeded the Robeson upper bound. These studies collectively highlight the advantages of using functionalized ILs and MOFs to enhance gas separation capabilities in MMMs [10, 26, 28]. Through precise functionalization, IL/MOF/polymer MMMs achieve both high selectivity and permeability while maintaining robust structural integrity and strong gas affinity, thus representing a promising advancement in the field of membrane technology.

2.1.2. MMMs with the IL Present at the Filler-Polymer Interface

By externally coating the MOF particles, ILs can create a uniform filler distribution within the polymer matrix and help minimize the interfacial defects, a common issue in traditional MMMs. In this type of MMMs, the IL is present at the surface of the MOF, enhancing the interfacial adhesion between the fillers and the polymer matrix and facilitating better gas transport within the MMMs. In 2016, Lin et al. [12] coated the surface of a well-known MOF, HKUST-1, with an IL, [EMIM][Tf₂N] and embedded the particles into polyimide polymer (PI) to fabricate IL/MOF/polymer MMMs for CO₂/N₂ and CO₂/CH₄ separation. The synthesized composite was washed several times with chloroform to remove the excess IL layer and prevent it from dispersing in the polymer. After washing, the crystals were centrifuged and dried under a vacuum at 80 °C. Each wash gradually reduced the IL content and the weight percentage of IL in the composite, resulting in a final product with an IL content of 13.8 wt.%. The CO₂ permeability of [EMIM][Tf₂N]/HKUST/PI MMM (1,101 Barrer) was significantly higher than that of the pure polymer membrane (774.3 Barrer), and that was attributed to the enhanced free volume in the MMM because of the [EMIM][Tf₂N]/HKUST filler particles. CO₂/N₂ and CO₂/CH₄ selectivities of the MMM were reported as 27 and 29, respectively, only slightly higher than that of the PI membrane. That study highlighted an efficient approach to enhance the filler/polymer compatibility, which is crucial for the gas separation performance of the membranes.

Following this work, numerous studies have synthesized MMMs using this strategy. Due to their small pore sizes, ZIFs often form IL/MOF composites, where the larger IL molecules cannot penetrate the pores and instead coat the framework's exterior. These

qualities, along with their hydrophobicity and compatibility with various polymers, make ZIFs highly suitable as fillers MMMs, where they enhance membrane stability and separation performance. ZIF-67 was coated with three different ILs, namely [EMIM][Tf₂N], [BMIM][Tf₂N], and [BMIM][BF₄], and incorporated into 6FDA-durene to synthesize MMMs [13]. The [EMIM][Tf₂N]/ZIF-67/6FDA-durene MMM having 20 wt.% filler loading showed the best performance among these MMMs, exhibiting CO₂ permeability of 1,426 Barrer, CO₂/N₂, and CO₂/CH₄ selectivities of 25.3 and 25.5, respectively. The ILs acted as a "gas carrier agent," increasing the CO₂ affinity of the MMMs. Functionalized TSILs such as [TMGH][IM] and [TMGH][PhO] were coated onto ZIF-67 and incorporated into PIM-1 to make MMMs [14]. Results showed improved CO₂ permeability of 7,145 and 12,848 Barrer for [TMGH][PhO]/ZIF-67/PIM-1 and [TMGH][IM]/ZIF-67/PIM-1 MMMs, respectively, compared to the pure PIM-1 membrane (5,181 Barrer). Incorporating TSILs effectively minimized the physical aging of MMMs and enhanced the stability of the membranes. However, CO₂/N₂ and CO₂/CH₄ selectivities of MMMs were reduced (CO₂/N₂: 13.7, CO₂/CH₄: 10.5) compared to their pristine counterparts (CO₂/N₂: 18.0, CO₂/CH₄: 13.9) due to the interfacial voids in the MMM and poor compatibility at the polymer/filler interface.

Recently, the gas transport mechanism in these types of MMMs was explained using the term "cellveyor conveyor" [26]. In this study, a Tf₂N-based IL was coated on the surface of ZIF-8 through an in-situ synthesis method and then incorporated into a polymer blend of Pebax and PEG-MEA to form IL/MOF/polymers MMMs. The authors proposed that two transport pathways were created: a "cellveyor" system within the ordered pores of ZIF-8, responsible for multidirectional CO₂ transport, and a "conveyor" pathway facilitated by the IL layer, aiding CO₂ transfer between ZIF-8 cages. The gas separation performance for CO₂/CH₄ (20: 80, v/v) mixtures was performed at 25 °C and 2 bar. The IL/MOF/polymer MMM having 5 wt.% IL/MOF composite loading showed a 97.1% increase in CO₂ permeability (800 Barrer) and a 56.6% improvement in CO₂/CH₄ selectivity (24) compared to the neat membrane (400 Barrer, CO₂/CH₄ selectivity: 15). These improvements were attributed to the synergistic effect of ZIF-8's porous structure and the IL's role in optimizing CO₂ adsorption and transport.

While the findings from these studies underscored the importance of ILs in enhancing the membrane performance by improving the interfacial adhesion between the polymer and the MOF, acting as a wetting agent, the effectiveness of this method depends

heavily on the quality and uniformity of the IL coating. An uneven or insufficient coating can limit the interactions between the MOF and polymer, while an overly thick IL layer may block the MOF's pores, reducing its adsorption capabilities and resulting in selectivity-permeability trade-off limitation. To address these challenges, the IL layer on the MOF surface can sometimes be controlled by washing with a solvent to remove excess IL, successfully reducing the IL layer thickness, while in others, control over the IL coating remains challenging. An effective strategy to mitigate these issues is the employment of metal-site anchoring, whereby IL molecules are chemically grafted onto the MOF framework through coordination bonds [27]. This strategy facilitates a homogeneous IL distribution, mitigates aggregation and leaching issues that have been reported in several studies, and enhances both the structural integrity and gas separation efficiency of the composite materials. [MIM][Br]/MOF-808 was synthesized by metal-site anchoring and mixed with Pebax solution, the solution was then casted on PSf substrate to synthesize MMMs. To verify the stability of the IL grafting, [MIM][Br]/MOF-808 was washed to assess any IL leakage from the MOF. The elemental composition of the samples remained consistent, further confirming that the IL was chemically grafted onto the framework rather than being merely adsorbed within the MOF channels. The [MIM][Br]/MOF-808/Pebax MMM having 5 wt.% filler loading, exhibited improved CO_2 of 426.1 Barrer and the CO_2/N_2 selectivity rose to 69.6, at 2 bar and 25 °C, compared to the neat membrane (CO_2 permeability: 203 Barrer, CO_2/N_2 selectivity: 45). The study demonstrated an effective strategy to prepare stable and high-performance MMMs, exhibiting enhanced performance while managing IL distribution more effectively in MMMs.

In conclusion, integrating IL/MOF composites into MMMs offers significant benefits such as fine-tuning molecular interactions, enhancing interfacial compatibility, improving gas selectivity and permeability, and overcoming the trade-off limits of traditional polymer membranes. This approach opens new possibilities for developing advanced membranes with high stability, superior gas separation performance, and applicability in industrial gas separation processes.

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Chapter 3

Methodology*

This chapter provides a comprehensive overview of the computational and experimental methodologies utilized in this thesis. It includes a detailed explanation of the sample preparation techniques employed to synthesize IL/MOF composites and IL/MOF/polymer MMMs, the characterization methods used to investigate their structural, morphological, and functional properties, and the procedures followed for gas adsorption and permeation measurements. These methods collectively form the foundation for the analysis and interpretation of the research findings presented in subsequent chapters.

3.1. Experimental methods

3.1.1. Materials

In this dissertation, various materials and chemicals were utilized, sourced from reputable suppliers. Regarding the MOFs, MIL-101(Cr) was procured from Nanoshel, MOF-177 from Sigma-Aldrich, CuBTC from ACSYNAM, and MIL-100 (Fe) from Framergy. All ILs employed across the studies were purchased from IoLiTec. Acetone and ethanol were obtained from Sigma-Aldrich for sample preparation. High-purity gases, including carbon dioxide (CO₂, 99.9 vol.%), methane (CH₄, 99.999 vol.%), nitrogen (N₂, 99.998 vol.%), acetylene (C₂H₂, 99.999 vol.%), and ethylene (C₂H₄, 99.9 vol.%), were supplied by Air Liquide. Pebax® 1657 polymer, comprising 60 wt.% polyethylene oxide (PEO) and 40 wt.% polyamide (PA), was generously provided by Arkema for the fabrication of MMMs.

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3.1.2. Sample preparation

3.2.2.1 Synthesis of IL/MOF composite

Pristine MOFs were activated at 125 °C under vacuum before the IL incorporation. IL/MOF composites were prepared using the wet impregnation method [1, 2]. First, the calculated amount of IL with a target loading in the IL/MOF composite was dissolved in 20 ml of acetone and left to stir for 1 h. Then, activated MOF was added to the IL solution and kept under stirring at 35 °C in an open atmosphere until the solvent was completely evaporated. The resulting sample was further dried overnight in an oven at 80°C to obtain the IL/MOF composite.

3.2.2.1 Synthesis of MMMs

Pure polymer membranes, MOF/polymer MMMs, and IL/MOF/polymer MMMs were synthesized using the conventional solution-casting method. Before membrane fabrication, the polymer pellets, MOF particles, and IL/MOF composites were dried overnight at 80 °C to remove any residual moisture. For the pure polymer membrane, a 4 wt.% solution was prepared by dissolving the polymer in a water/ethanol mixture (30/70 wt.%) with continuous stirring for 4 h at 80 °C. The resulting solution was cast onto a Teflon petri dish, covered with an inverted funnel to allow slow solvent evaporation at room temperature for 24 h, and subsequently dried overnight at 100 °C to ensure complete solvent removal.

MOF/polymer MMMs were fabricated by incorporating vacuum-dried MOF particles into a water/ethanol solvent mixture at varying loadings (e.g., 10, 15, and 20 wt.%). The mixture was stirred for 4 h and sonicated for 30 minutes to achieve uniform dispersion of the MOF particles. The MOF suspensions were then added to the prepared polymer solution, followed by additional sonication (30 minutes) and stirring (4 h). The final mixtures were cast onto Teflon substrates, and solvent evaporation was carried out under controlled conditions with an inverted funnel.

IL/MOF/polymer MMMs were prepared using a similar approach, with varying IL/MOF loadings (e.g., 10, 15, and 20 wt.%). The IL/MOF fillers were dispersed in a water/ethanol solvent mixture, stirred for 4 h, and sonicated for 30 minutes. The dispersed IL/MOF mixture was then combined with the polymer solution, further sonicated and stirred, and cast onto Teflon substrates. To confirm the stability of the IL within the composite, the IL/MOF suspension was dried, and its IR spectrum was analyzed to rule

out potential leaching during processing. To evaluate the performance of the best-performing IL/MOF/polymer MMM, additional control membranes, including IL/polymer MMMs and free-IL/free-MOF/polymer MMMs, were also fabricated. In the free-IL/free-MOF MMMs, a pre-mixed suspension of IL and MOF was combined with the polymer solution using the same procedure as for MOF/polymer MMMs. All membranes, including the controls, were oven-dried overnight at 100 °C and stored in a desiccator. The thickness of all fabricated membranes was measured using a digital slide caliper.

3.2. Characterization techniques

3.2.1. Brunauer-Emmett-Teller (BET) analysis

BET measurements were performed to determine the surface area and pore volume of the pristine MOF and IL/MOF composite using a Micromeritics ASAP 2020 adsorption analyzer. MOF and IL/MOF composite particles were activated at 150 °C under vacuum for 12 h prior to the measurements. Afterwards, N₂ adsorption isotherms were obtained at 78 K from 10⁻⁶ to 1 bar. The BET equation and the t-plot method were used to calculate the surface area and pore volume in a relative pressure range of 0.05-0.65 (P/P₀), respectively.

3.2.2. Scanning electron microscopy (SEM)

SEM images of the MOF, IL/MOF composite, and all the MMMs were obtained using a Zeiss Evo LS 15 electron microscope operating under an ultra-high vacuum with an accelerating voltage of 20 kV. To obtain the cross-sectional images of MMMs, the samples were prepared by freeze cutting under liquid N₂, followed by gold coating.

3.2.3. X-ray diffraction (XRD)

XRD data of the pristine of the samples were recorded using a Bruker D2 Phaser instrument. A Cu-K α radiation with wavelength of 1.54060 Å was used to collect data in the 2 θ range between 5 and 50° with a step size of 0.0204°.

3.2.4. Thermal gravimetric analysis (TGA)

TGA measurements were conducted using a TA Instruments Q500 analyzer. For the MMMs, the experiments were performed at a heating rate of 10 °C min⁻¹, starting from room temperature up to 800 °C. All the measurements were conducted under N₂ flow as balance and purge gas at 40 and 60 mL/min, respectively. To analyze the thermal stability of the samples, the onset (T_{onset}) and derivative onset (T'_{onset}) temperatures were

determined from the thermogravimetric (TG) and derivative TG (DTG) curves, respectively. In this study, the T'_{onset} values were considered as the initial thermal decomposition temperature because the T_{onset} values generally overestimate the decomposition temperatures [3].

3.2.5. Infrared spectroscopy (IR)

IR spectra of the samples were collected using a Bruker Vertex 80v spectrometer in the range of 400 to 4000 cm^{-1} in transmittance mode at a spectral resolution of 2 cm^{-1} . IR bands deconvolution was performed using Fityk software by employing the Voigt function [4].

3.2.6. Washing samples with solvents

The IL loading in the synthesized IL/MOF composite was determined by thoroughly washing the IL/MOF composite with acetone, a solvent capable of penetrating the MOF's pore structure to remove any incorporated IL molecules. The washing process involved collecting the filtrate and drying the IL/MOF composite overnight at 80 °C. Infrared spectra of the dried composite, the filtrate, and the bulk IL is analyzed. The IL loading in the composite was quantified by weighing the dried sample and was then back-calculated. These deviations are likely due to minor IL loss during the synthesis process, such as adherence to the container walls.

3.2.7. Gas adsorption measurements

Volumetric gas adsorption measurements were conducted on pristine MOF samples and IL-incorporated MOF composites for target gas molecules using a volumetric gas adsorption analyzer. Adsorption isotherms were obtained at 15, 25, and 35 °C over a pressure range of 0.001–1 bar. Approximately 0.4 g of each sample was degassed under a high vacuum at 125 °C for 12 h prior to the measurements to ensure optimal surface activation.

To evaluate and compare the gas separation performance of pristine and IL-incorporated MOF samples, the adsorption isotherms were analyzed using various models, including the Langmuir-Freundlich, dual-site Langmuir (DSL), and dual-site Langmuir-Freundlich (DSL-F) models. These models were fitted using Ideal Adsorbed Solution Theory (IAST)⁺⁺ software [5] and the corresponding fitting parameters are presented in the appendices of the respective chapters. Detailed equations are also provided below:

$$q(P) = q \times \frac{(k \times P)^n}{1 + (k \times P)^n}$$

$$q(P) = q_1 \times \frac{k_1 \times P}{1 + k_1 \times P} + q_2 \times \frac{k_2 \times P}{1 + k_2 \times P}$$

$$q(P) = q_1 \times \frac{(k_1 \times P)^{n_1}}{1 + (k_1 \times P)^{n_1}} + q_2 \times \frac{(k_2 \times P)^{n_2}}{1 + (k_2 \times P)^{n_2}}$$

Here, P is the pressure of bulk gas at equilibrium with the adsorbed phase and q represents the saturation capacity. k denotes the affinity constants while n represents adsorption sites.

3.2.8. Gas permeation experiments using constant pressure setup

Single-component permeability measurements were conducted at 1 bar and 35 °C, using a custom-built setup as shown in **Figure 3.1**. Helium (He) was used as a sweep gas in the setup for all measurements. Each MMM was tested three times, and the average permeabilities and selectivities were reported along with the standard deviation. The MMMs were supported on porous stainless-steel module having an effective surface area of 7 cm² and were tightly sealed by rubber O-rings. Electronic mass flow controllers (MFCs, Alicat) and a back pressure regulator (BPR, Equilibar) were employed to adjust the flow rate and the upstream pressure of each gas, respectively. BPR maintained the upstream pressure at 1 bar (gauge pressure) and the downstream pressure was under atmospheric conditions. During the experiments, the permeation unit continuously flowed with He as a sweep gas, and after the experiments, He was used to purge the gases from the system. The permeate composition was determined by a mass spectrometer (Hiden) monitoring the permeate/sweep stream. The quantification of the concentration was done by using the Quantitative Gas Analyzer (QGA) software. The specific m/z signals were used to quantify the concentrations of respective gases. The background of each individual gas was taken and calculated automatically by the system and then added in the setup, which was deducted by the software from the measured values during the analysis. Mass spectrometric instrument was periodically calibrated by mixing each gas of interest with He in the same concentration range expected during the permeability measurements. The software calculated the un-calibrated volume concentration of each gas and determined the relative sensitivity (RS) values of the gases based on actual concentrations. After this, no special approximations or procedures were needed during the experiment to calculate the permeate gas composition. After the experiment was completed, the system was purged with He to clean the lines until the MS signal became

stable at the baseline. Between each measurement, the baseline was reached for starting the measurement for the next gas.

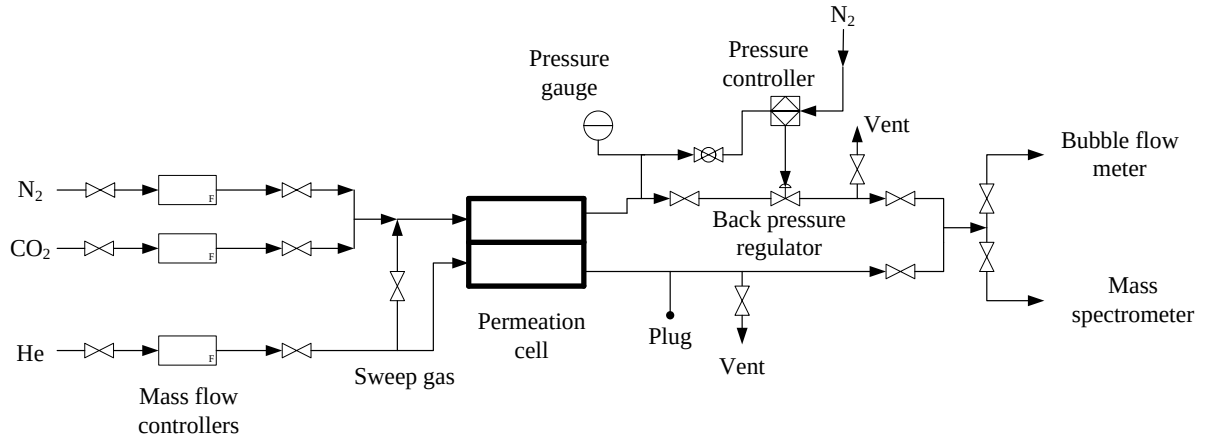


Figure 3.1. Schematic diagram of the constant-pressure gas permeation setup.

Based on the mass spectrometric analysis of the permeate and sweep gas stream, gas fluxes were calculated from the sweep gas flow rate. The permeability (Barrer) of the gas 'a', P_a was calculated by using the equation (1), where J_a is the flux ($\text{cm}^3(\text{STP})/(\text{s} \cdot \text{cm}^2)$). J_a is defined as the flowrate ($\text{cm}^3(\text{STP})/\text{s}$) of the gas, Q_a , divided by the unit area (cm^2), A , of the membrane. ΔP (cm Hg) is the pressure difference across the membranes, and l (cm) is the membrane thickness:

$$P_a = (J_a / \Delta P) \times l \quad (1)$$

The ideal selectivity of the membrane ($S_{a/b}$) was calculated by dividing the permeability values measured for different gases using equation (2), where a and b are two different gases:

$$S_{a/b} = P_a / P_b \quad (2)$$

3.2.9. Gas permeation experiments constant-volume variable-pressure setup

As part of my PhD research, I custom-built a variable-pressure constant-volume setup for measuring gas permeation properties of membranes as shown in **Figure 3.2**. The setup is equipped with the vacuum pump. After placing the membrane in the membrane module, the whole system is first subjected to a vacuum treatment to remove any residual gases or contaminants. To achieve this, both the upstream and downstream chambers are evacuated, and once this is complete, the valves connecting the permeation cell to the vacuum pump are closed. At this point, a slight increase in pressure in the downstream chamber is observed. After verifying the leak rate, a feed gas is introduced into the permeation cell, directed toward the upstream side of the membrane. The pressure

transducer in the downstream chamber measures the increase in pressure over time as gas permeates through the membrane.

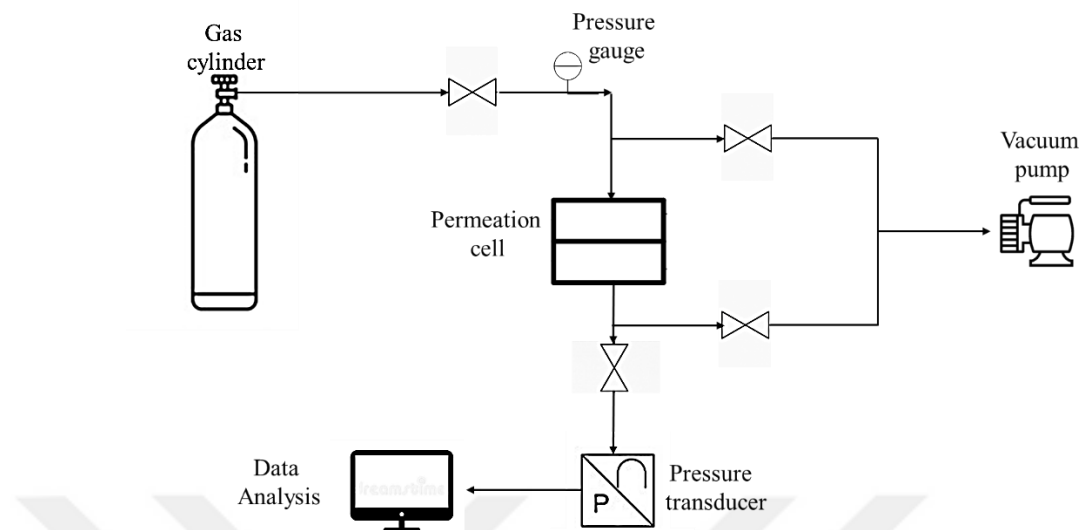


Figure 3.2. Schematic diagram of the constant-volume variable-pressure gas permeation setup.

The plot of ΔP versus time is generated and data is collected until the curve becomes linear. Once the curve reaches a linear region, the slope of the straight line is determined. This slope, representing the rate of pressure change with respect to time (dp/dt), is then used to calculate the gas permeability for the gas. The permeability is calculated using a formula given as follows:

$$P = \frac{273.15 \times 10^{10} \times V \times l}{760 \times AT \times \frac{(P_0 \times 76)}{14.7}} \times \frac{dp}{dt}$$

where P denotes the gas permeability across the membrane in Barrer. V represents the dead volume of the downstream chamber (cm^3) which was measure as 27 cm^3 , and l is the membrane thickness (cm). T refers to the experimental temperature in Kelvin, and A represents the effective membrane area (cm^2), which was 4.9 cm^2 . P_0 is the upstream feed gas pressure (psia), and $\frac{dp}{dt}$ is the steady-state rate of pressure change (mmHg/s) measured on the downstream side.

3.3. Computational methods

Solubilities of the guest gases in bulk IL were estimated by Conductor-like Screening Model for Realistic Solvents (COSMO-RS) calculations by the COSMOTermX software (version: C30_160) using respective triple-z valence polarized

basis set (TZVP-FINE) parameterizations. More details about these calculations and applications can be found in the literature [6, 7, 8]. DFT calculations were performed at a level of Becke-three-parameter-Lee-Yang-Parr (B3LYP), [9, 10] including Grimme's D2 correction [11], and using 6-311+G* basis set on Gaussian09 to evaluate the interactions between CO₂, CH₄, and N₂ and [MPPyr][DCA]. The electrostatic interactions were further evaluated by Natural Bond Orbital (NBO) analyses [12].



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Chapter 4

Composite of MIL-101(Cr) with a Pyrrolidinium-Based Ionic Liquid Providing High CO₂ Selectivity*

4.1 Abstract

Capturing CO₂ selectively from flue gas and natural gas addresses the criteria of a sustainable society. In this work, we incorporated an ionic liquid (IL) (1-methyl-1-propyl pyrrolidinium dicyanamide, [MPPyr][DCA]) into a metal organic framework (MOF), MIL-101(Cr), by wet impregnation method and characterized the resulting [MPPyr][DCA]/MIL-101(Cr) composite in deep detail to identify the interactions between [MPPyr][DCA] molecules and MIL-101(Cr). Consequences of these interactions on the CO₂/N₂, CO₂/CH₄, and CH₄/N₂ separation performance of the composite were examined by volumetric gas adsorption measurements complemented by the density functional theory (DFT) calculations. Results showed that the composite offers remarkably high CO₂/N₂ and CH₄/N₂ selectivities of 19180 and 1915 at 0.1 bar and 15 °C corresponding to 1144- and 510-times improvements, respectively, as compared to the corresponding selectivities of the pristine MIL-101(Cr). At low pressures, these selectivities reached practically infinity, making composites completely CO₂ selective over CH₄ and N₂. The CO₂/CH₄ selectivity was improved from 4.6 to 11.7 at 15 °C and 0.001 bar, yielding a 2.5-times improvement, attributed to the high affinity of [MPPyr][DCA] towards CO₂, validated by the DFT calculations. These results offer broad opportunities for the design of composites, where ILs are incorporated into the pores of MOFs, for high performance gas separation applications to address environmental challenges.

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4.2 Introduction

Carbon dioxide concentration in the atmosphere, reaching 420 ppm in June 2022 [1], is the root cause of climate change. CO₂ separation from the flue gas and natural gas is considered as a viable solution to mitigate CO₂ emissions [2, 3]. To selectively capture CO₂ and purify natural gas, various different applications, such as adsorption, absorption, and membrane-based separation, have been considered. Adsorption-based gas separation processes that utilize porous materials have been promising owing to their low energy demand and cost-effectiveness. Therefore, design and development of novel porous materials with an ability to selectively capture CO₂ from CH₄ and N₂ are critical. In this regard, several kinds of adsorbent exemplified by metal organic frameworks (MOFs) [4], zeolites [5], graphene-based materials [6], porous carbons [7], activated carbons [8], and carbon nanotubes (CNTs) [9], have been considered. Among these, MOFs have emerged as promising materials for capturing CO₂ from gas mixtures containing CH₄ and N₂ [10-12]. They are 3D crystalline materials having large surface areas, large porosity, and good mechanical, chemical, and thermal stability [13]. The physicochemical properties of MOFs can be easily tuned by changing the organic linker-metal node combination [14].

Recent studies demonstrated that post-synthesis modification of MOFs by incorporating ionic liquids (ILs), molten salts having high thermal stability and non-volatility with high affinity for CO₂ [15, 16], into their pores leads to IL/MOF composites offering higher gas separation performance compared to pristine MOFs [23-27]. The IL/MOF composites with imidazolium-based cations in the IL have been extensively studied for CO₂/N₂, CO₂/CH₄, and CH₄/N₂ separations [17-21]. For example, in one of the earliest studies [23], 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], was incorporated into the cages of CuBTC to synthesize an IL/CuBTC composite. The resulting composite provided approximately 1.5-times higher ideal selectivities for CH₄/H₂ and CH₄/N₂ compared to the pristine CuBTC at 0.2 bar. A few studies incorporated amine-functionalized ILs and polymerized ILs (PILs) into the MOFs. For instance, NH₂-MIL-101(Cr) was impregnated with an amine-functionalized *n*-aminopropyl-3-butylimidazoliumbis(trifluoromethylsulfonyl)imide ([C₃NH₂bim][Tf₂N]) to obtain a novel IL/MOF composite. The gas adsorption measurements indicated that IL incorporation led to an almost doubling of the CO₂/N₂ selectivity. This improvement in selectivity was claimed to be associated with the strong Lewis acid-base and dipole-dipole interactions between CO₂ molecules and the amine functional group [24]. Similarly, 1-vinyl-3-ethylimidazolium bromide (poly[VEIM][Br]) was confined in MIL-101(Cr) via

in-situ polymerization and the resulting composite offered an improved CO₂ uptake of 62 cm³/g compared to the one (57 cm³/g) with the pristine MIL-101(Cr) [19].

We recently applied this concept to a rarely used family of ILs and demonstrated that the pyrrolidinium-based ILs could be very promising in boosting the CO₂ separation performance of UiO-66 [27]. 1-*n*-butyl-1-methylpyrrolidinium dicyanamide, [BMPyr][DCA]-incorporated UiO-66 exhibited improved CO₂/N₂ and CH₄/N₂ selectivities (>100 000) at low pressures compared to the pristine UiO-66. The high potential of this composite as an adsorbent was attributed to the exceptionally strong CO₂-phillic characteristic of the [DCA]⁻ anion and the superior gas separation properties and less toxicity of pyrrolidinium cation as compared to the imidazolium-based ILs.²⁷⁶ Motivated with these promising results, in this work, we used an IL having the same anion but with a different cation, 1-methyl-1-propyl pyrrolidinium dicyanamide, [MPPyr][DCA], and incorporated it into chromium(III) terephthalate MIL-101(Cr), a MOF that offers a significantly high surface area and has unsaturated Cr(III) sites through which CO₂ can have strong Lewis acid-base interactions [29,30]. [MPPyr][DCA] was selected because it was identified as an IL having high CO₂ separation performance based on the quantum chemical equilibrium thermodynamics calculations predicting the gas solubilities in ILs [27]. MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite were deeply characterized to identify the interactions between the IL and the MOF. The volumetric adsorption method was used to obtain single-component adsorption isotherms of CO₂, N₂, and CH₄ at 15, 25, and 35 °C, up to 1 bar to assess the consequences of these interactions on the gas separation performance of the composite. The ideal selectivities demonstrated that the new composite has remarkably high CO₂/N₂ and CO₂/CH₄ selectivities, especially at low pressures (between 0.001-0.1 bar).

4.3 Results and Discussion

4.3.1 Characterization of MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr)

Figure 4.1a provides the ball and stick representations of the [MPPyr][DCA] and MIL-101(Cr). Due to the lack of any distinguishable elements in the IL (containing only C, H, N, and O, which are also present in the MOF), we could not perform X-ray fluorescence (XRF) spectroscopy measurements to quantify the corresponding IL loading in [MPPyr][DCA]/MIL-101(Cr). Instead, we washed the composite in acetone, which is small enough to enter the pores, to extract any IL present in the pores of the MOF.

The IR spectra presented in **Figure 4A-1** demonstrate the lack of any IL-related IR features on the washed-and-dried-composite and confirm the complete removal of the IL. By comparing the mass of the composite before and after this washing process, the IL loading was estimated as 38 wt.%, consistent with the amount of IL used for the synthesis of the composite. Having a lower IL loading of 38 wt.% eliminates the leaching out of IL which leads to a completely different IL/MOF composite, where all the IL molecules are located inside the pores of the MOF, as confirmed by the characterization results demonstrated below.

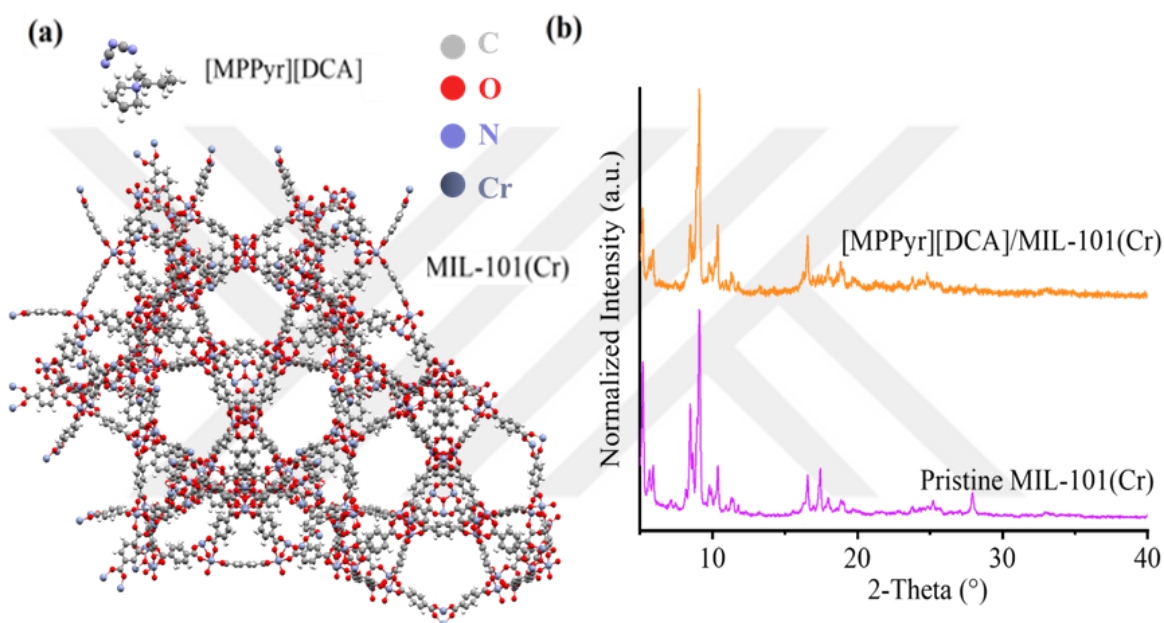


Figure 4.1. (a) Ball and stick representation of MIL-101(Cr) (snapshot taken from a* direction in Mercury software) and [MPPyr][DCA]. Grey, white, blue, red, and dark grey spheres represent the C, H, N, O, and Cr atoms, respectively. (b) XRD diffractogram of the [MPPyr][DCA]/MIL-101(Cr) composite having an IL loading of 38 wt.%.

The CO₂ uptakes of as-received and activated MIL-101(Cr) were compared with the literature-reported CO₂ uptakes (25 °C and 1 bar) on MIL-101(Cr) having different surface area and synthesis conditions, as shown in **Figure 4A-2**. The collected literature data were categorized based on the surface area and the solvent that was used for the synthesis of MIL-101(Cr). It was concluded that changes in surface area and solvents directly affect the gas uptake of MIL-101(Cr). Nonetheless, the comparison provided in **Figure 4A-2** shows that the CO₂ uptakes measured in this study are in the range of the literature values [31, 32]. Further comparison of experimental gas uptakes of MIL-101(Cr) with the literature were presented in **Table 4A-2**.

To determine the surface area and pore volume of the MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite, N₂ adsorption isotherms were measured. Results given in **Figure 4A-3** demonstrated that the BET surface area and the micropore volume of MIL-101(Cr) decreased from 1924 m²/g (having Type I isotherm based on IUPAC classification [33]) to 377 m²/g and from 1.001 cm³/g to 0.213 cm³/g, respectively, upon IL incorporation as tabulated in **Table 4A-3**. This decrease is expected, and it can be attributed to the blockage of the pores of MIL-101(Cr) by the IL molecules, confirming the successful incorporation of IL into the MOF pores [23]. The N₂ solubility in [MPPyr][DCA] was qualitatively estimated by the COSMO-RS calculations performed at the BET measurement conditions in the pressure range of 0.1 to 1 bar, at -196 °C, as shown in **Figure 4A-4**. Results showed that N₂ has almost negligible solubility in the IL at the BET measurement conditions. Hence, we infer that the IL molecules located at the pore openings of the MOFs might block the entrance of the N₂ molecules into the available pores, making the results of the BET measurements unreliable. These observations are also consistent with previous reports presenting different functionalized porous materials [34-37]. The CO₂ solubilities in [MPPyr][DCA] obtained from the COSMO-RS calculations, as presented in **Figure 4A-5**, were 0.0048 and 0.039 mol gas/mol IL at 0.06 bar and 0.92 bar, 25 °C, respectively, compared to the experimental CO₂ solubilities of the same IL as 0.00085 and 0.012 mol gas/mol IL, respectively, under the same conditions [38]. These results showed that the COSMO-RS results are comparable with the experimental measurements within an order of magnitude, consistent with the literature [39].

Next, we checked the morphology of the MOF and IL/MOF composite. XRD data of the pristine MIL-101(Cr) given in **Figure 4.1b** is consistent with the literature [40, 41]. **Figure 4A-6** represents the XRD data of the simulated and pristine MIL-101(Cr), which showed that MIL-101(Cr) has Fd3m symmetry with diffraction peaks located at 2-theta values of 8.4 for (606), 9.0 for (753) correspond to the main peaks of MIL-101(Cr) with a unit cell parameter of 88.3 Å, consistent with the literature [40]. The corresponding peaks of MIL-101(Cr) are also present in [MPPyr][DCA]/MIL-101(Cr) spectra depicting that the crystal structure of pristine MIL-101(Cr) remains intact upon the IL incorporation. The [MPPyr][DCA]/MIL-101(Cr) composite was characterized by slight shifts in peaks representing (606) and (753) to lower 2-theta values, while the unit cell parameter did not show any significant change. Moreover, the data showed a change in the peak intensities upon the incorporation of IL. These changes can be associated with

the possible changes in the electronic structure inside the pores upon the incorporation of IL molecules [22]. Besides, a comparison of SEM images of the as-received MIL-101(Cr) and its composite with [MPPyr][DCA] given in **Figure 4.2a-b** and **Figure 4.2c-d**, respectively, indicated that the octahedral structure of the MOF was maintained upon the incorporation of [MPPyr][DCA], consistent with the XRD results.

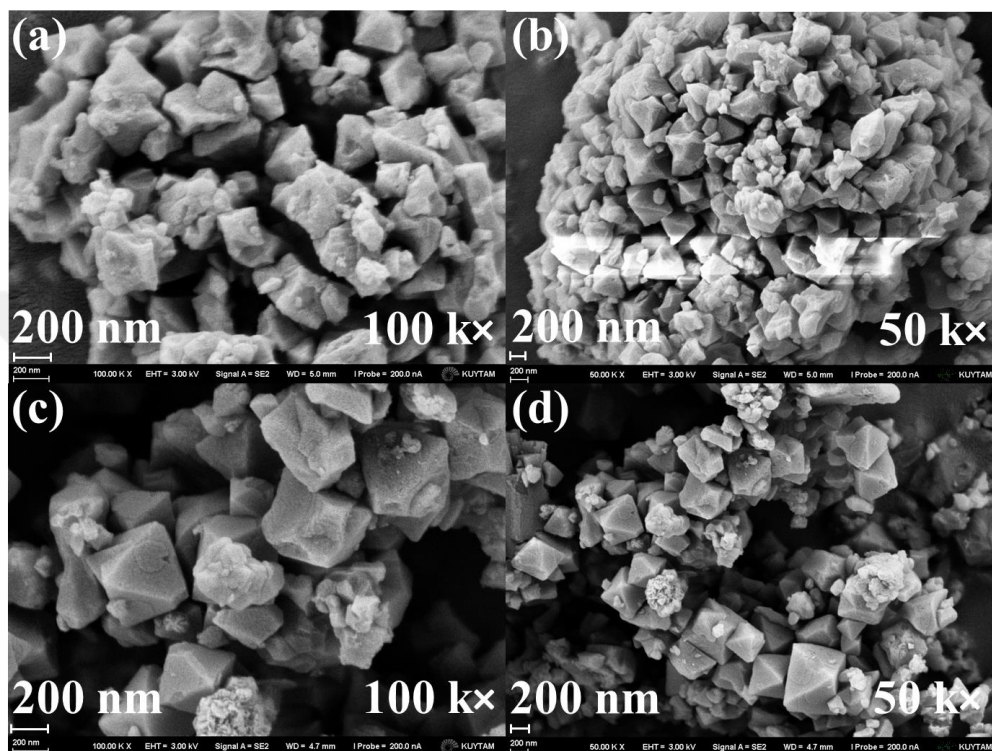


Figure 4.2. SEM images of (a, b) as-received MIL-101(Cr) and (c, d) [MPPyr][DCA]/MIL-101(Cr) composite with an IL loading of 38 wt.%. Images of the as-received MIL-101(Cr).

The TGA measurements were conducted for the as-received MOF and its composite with [MPPyr][DCA]. The corresponding results are shown in **Figure 4.3**. The initial weight loss in a temperature range of 100 to 200 °C in each thermogravimetric curve is associated with the evaporation of residual solvent or moisture. **Figure 4.3** indicates that MIL-101(Cr) has a T'_{onset} value of approximately 245 °C, which might be associated with the removal of the organic ligands. On the other hand, the T'_{onset} of the bulk IL was determined as approximately 230 °C, whereas that of the IL/MOF composite was at approximately 220 °C. These results indicate that the as-synthesized IL/MOF composite has a lower T'_{onset} compared to pristine MOF. This decrease in T'_{onset} was inferred to be associated with the presence of interactions between the IL molecules and the MOF cage [42].

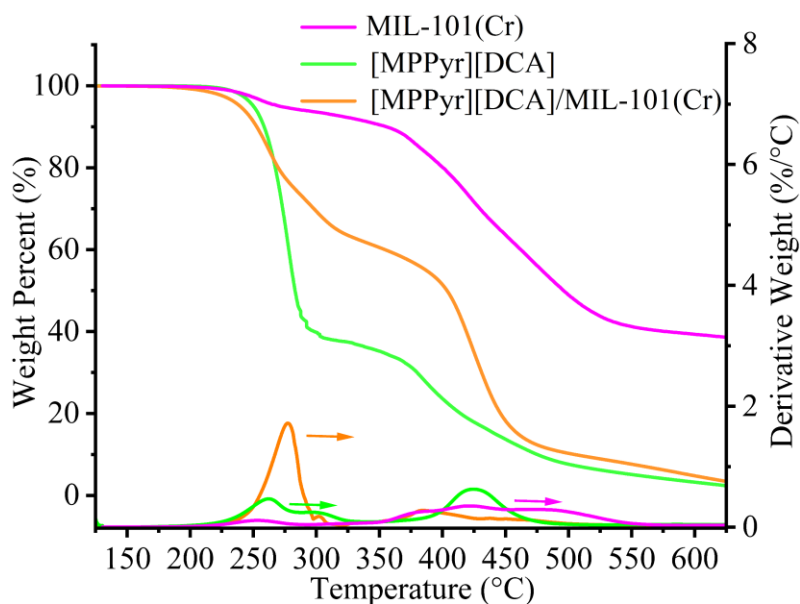


Figure 4.3. TGA and DTG curves of pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite with an IL loading of 38 wt.%.

To have a better understanding of these molecular IL-MOF interactions, we compared the IR spectrum of [MPPyr][DCA]/MIL-101(Cr) composite with those of MIL-101(Cr) and the bulk [MPPyr][DCA], as shown in **Figure 4.4(a, b)**. The IR features at 2881 and 2972 cm⁻¹ in the spectrum of the bulk [MPPyr][DCA] are assigned to the symmetric and asymmetric $\nu(\text{C-H})$ vibrations, and those at 1301, 2123, 2189, and 2223 cm⁻¹ are attributed to $\nu(\text{C}\equiv\text{N})$ on [DCA]⁻ [26, 43]. **Figure 4.4** demonstrates that the $\nu(\text{C}\equiv\text{N})$ bands located at 2123 and 2223 cm⁻¹ blue-shifted by 14 and 11 cm⁻¹, respectively, when the IL molecules were incorporated into the pores. These shifts were accompanied by a blue shift of 9 cm⁻¹ on the $\nu(\text{C-H})$ peak of the IL positioned at 2881 cm⁻¹.

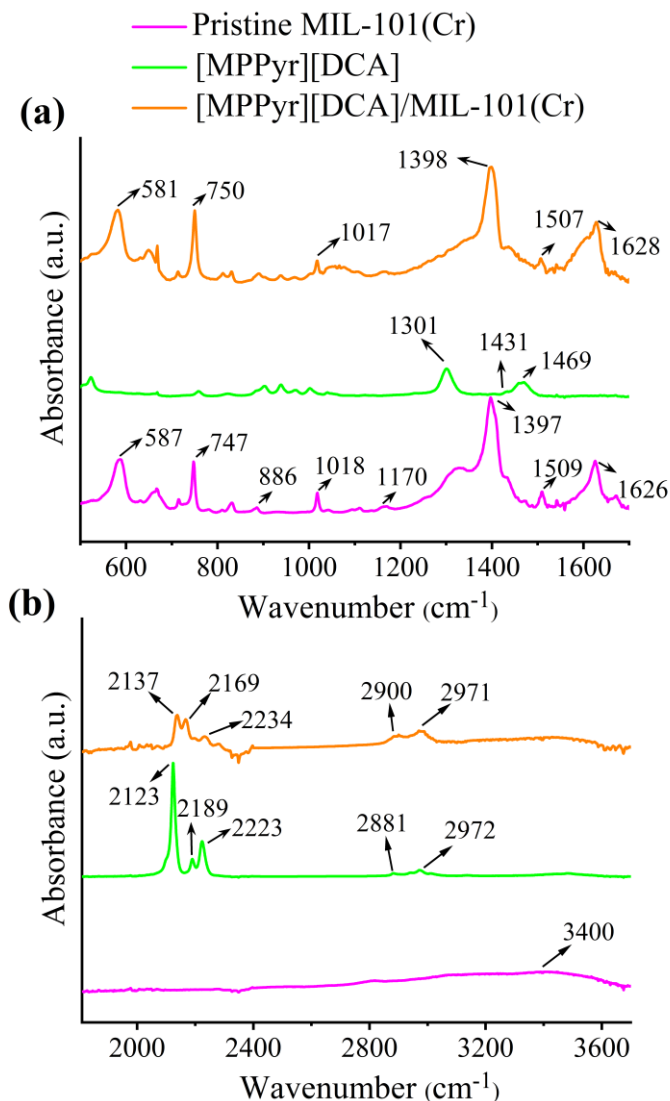


Figure 4.4. IR spectrum of the [MPPyr][DCA]/MIL-101(Cr) composite with an IL loading of 38 wt.% (a) 500-1800 cm⁻¹ and (b) 1800-3800 cm⁻¹.

The band at 587 cm⁻¹ presents in the lower frequency region of the pristine MIL-101(Cr) is attributed to the coordination of 1,4-benzene dicarboxylate (BDC) linker to the chromium nodes. Furthermore, the features present in a region from 587 and 1626 cm⁻¹ are associated with the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{H})$ of the benzene ring, positioned at 1509 cm⁻¹ and 747, 886, 1018, and 1170 cm⁻¹, respectively [44]. In addition to these features, MIL-101(Cr) was also characterized with peaks located at 1397 and 1626 cm⁻¹. These bands are assigned to the $\nu(\text{COO})_{\text{sym}}$ and $\nu(\text{C}-\text{O})_{\text{asym}}$ of the dicarboxylate groups of the linker, respectively [45]. The data showed that $\nu(\text{Cr}-\text{O})$ of the MOF present at 587 cm⁻¹ demonstrates a stronger red shift (6 cm⁻¹) than the one associated with the carboxylate group (remaining almost at the level of spectral resolution) when the IL is incorporated into the pores. These peak shifts further indicate that the interionic interactions in IL

weaken as the anion interacts more with the Cr nodes of the MOF and induces possible changes in the electronic structure, as also evident from the changes in the intensities of the characteristic features in the XRD data. Hence, we infer that the interactions between the IL and MOF are present mostly between the IL's anion and the metal nodes.

4.3.2 Gas adsorption and separation performance of [MPPyr][DCA]/MIL-101(Cr)

To investigate the consequences of IL impregnation on the CO₂/N₂, CO₂/CH₄, and CH₄/N₂ separation performance of the MOF, single-component adsorption isotherms of CO₂, CH₄, and N₂ in MIL-101(Cr) (having type I isotherm based on IUPAC classification [33]) and its composite with [MPPyr][DCA] were measured up to 1 bar at 15, 25, and 35 °C. Results presented in **Figure 4.5a-c** and **Table 4A-4** showed that CO₂, CH₄, and N₂ uptakes decreased upon the IL incorporation into MIL-101(Cr). These decreases in the uptake capacity of IL-incorporated MIL-101(Cr) are expected and attributed to the reduced available surface area and pore volume of the composite due to the presence of IL molecules in the pores. For instance, the composite exhibited no N₂ adsorption (undetectable, remains below the noise level) up to 0.3 bar at 15 °C and significantly poor CH₄ adsorption compared to the pristine MIL-101(Cr) at all temperatures, as shown in **Figures 4.5b, 4.5c, 4A-7**. However, the CO₂ uptakes of the composite showed a lower decrease compared to those on N₂ and CH₄ uptakes, which can be ascribed to the acidic nature of CO₂ molecules having a strong affinity for [DCA]⁻, which has a highly basic nature.

We also performed COSMO-RS calculations at 15, 25, and 35 °C from 0.1 to 1 bar to investigate the temperature effect on the gas solubilities in bulk [MPPyr][DCA]. The data presented in **Figure 4A-5** demonstrated that CO₂ has significantly higher solubility compared to CH₄ and N₂ at all temperatures and pressures in line with our adsorption measurements. At 1 bar and 25 °C, CO₂ solubility in bulk [MPPyr][DCA] is 25- and 50-times higher compared to CH₄ and N₂, respectively. In addition, CO₂ and CH₄ solubilities slightly decrease with increasing temperature. Nonetheless, data illustrated that the N₂ solubility in [MPPyr][DCA] was not significantly affected by temperature.

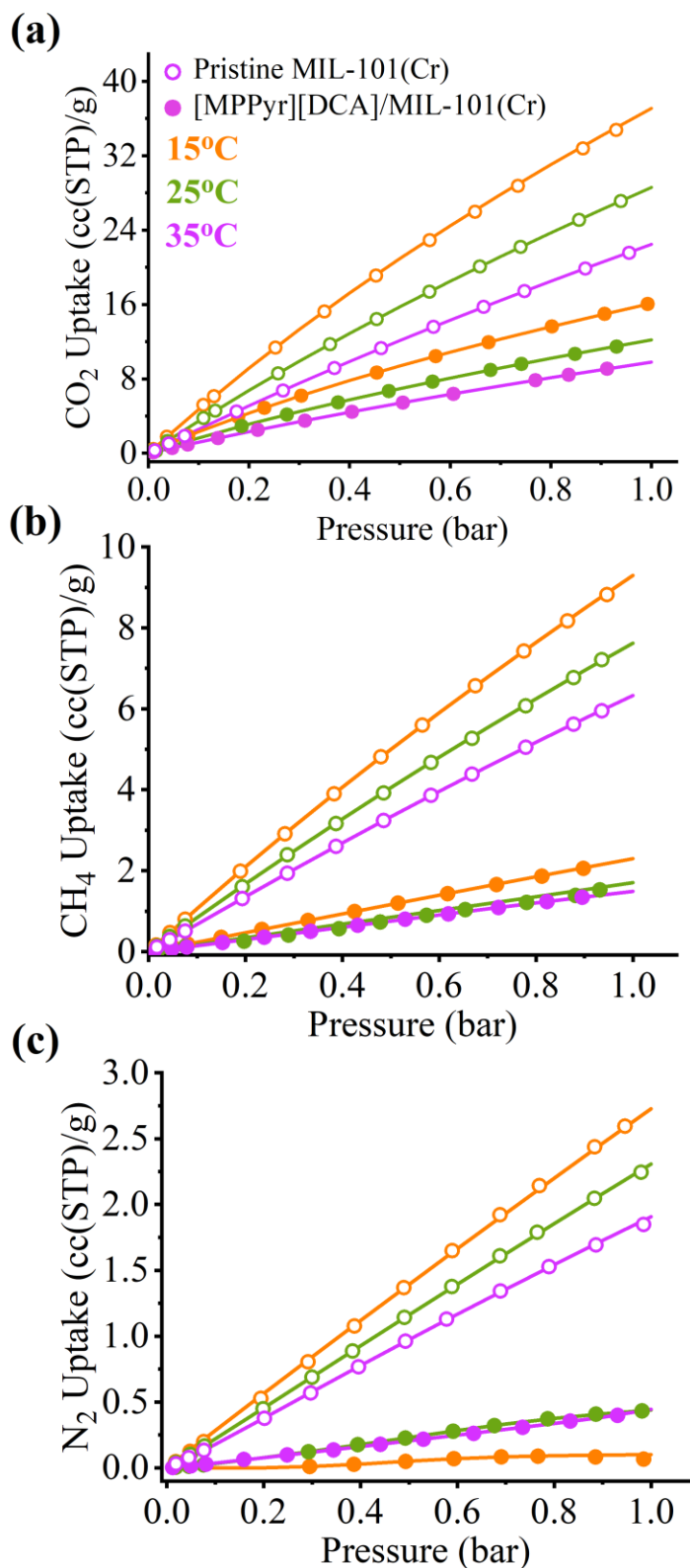


Figure 4.5. (a) CO₂, (b) CH₄, (c) N₂ adsorption uptakes of the MIL-101(Cr) and its composite with [MPPyr][DCA] (having an IL loading of 38 wt.%) at 15, 25, and 35 °C up to 1 bar. The empty symbols and filled symbols represent gas uptakes for pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite, respectively.

To complement the COSMO-RS results, we performed the DFT calculations. According to the results presented in **Figure 4A-8**, CO₂ contacts closely with both ions. One of its oxygen atoms forms hydrogen bonds with the pyrrolidinium ring. On the other hand, the positively charged C atom ($q_c = 1.027e$) interacts with the negatively charged N atom of the [DCA]⁻ ($q_c = -0.606e$), presenting a C–N distance of 2.82 Å. CH₄ forms hydrogen bonds with the N atoms of the [DCA]⁻, while the N₂ molecule is forming hydrogen bonds with the pyrrolidinium ring. The binding energy calculations demonstrate that CO₂ has the strongest interaction with the [MPPyr][DCA] with a binding energy of 23.4 kJ/mol compared to 9.0 and 6.8 kJ/mol for CH₄ and N₂, respectively. These differences in the binding energies of the gases are also consistent with their corresponding solubilities as estimated by the COSMO-RS calculations. Therefore, we infer that relatively lower CH₄ and N₂ adsorption capacities compared to that of CO₂ presented in **Figure 4.5** are associated with their weaker interactions with the IL, and hence their lower solubilities in the IL.

The CO₂ adsorption isotherm obtained at 15 °C presented in **Figure 4.5** was fitted to the Dual-Site Langmuir (DSL) model for pristine MIL-101(Cr), while all other isotherms were fitted to dual-site Langmuir-Freundlich (DSL-F) model. By using these fitting parameters, the corresponding ideal selectivities of the pristine MOF and its composite with [MPPyr][DCA] were calculated up to 1 bar at 15, 25, and 35 °C, as shown in **Figure 4.6a-c**. Results showed that, at low pressures, for instance, at 0.001 bar, the ideal CO₂/N₂, CO₂/CH₄, and CH₄/N₂ selectivities of MIL-101(Cr) were 20.2, 4.2, and 4.7 at 25 °C, respectively. As the pressure was increased to 1 bar, the ideal selectivities were observed to be slightly decreased to 12.4, 3.7, and 3.3 for CO₂/N₂, CO₂/CH₄, and CH₄/N₂, respectively.

In the case of IL-incorporated MIL-101 (Cr), the results demonstrated a remarkable increase in the ideal selectivities for all gas pairs, as represented in **Figure 4.6a-c**. The CO₂/N₂ and CH₄/N₂ selectivities of MIL-101(Cr) boosted from 14.6 to 33.5 and from 3.7 to 4.0 at 0.1 bar at 35 °C, respectively. Moreover, the CO₂/CH₄ selectivity of [MPPyr][DCA]/MIL-101(Cr) was 11.1 (8.3) at 0.001 (0.1) bar corresponding to 2.7-times (2.2-times) improvement compared to pristine MIL-101(Cr). The results demonstrated that these selectivities were increased with decreasing the temperature. At 25 °C, the CO₂/N₂, CO₂/CH₄, and CH₄/N₂ selectivities were computed as 3535, 231.9, and 15.24 at 0.1 bar. Moreover, the CO₂/N₂ and CH₄/N₂ selectivities of MIL-101(Cr) boosted from 16.7 to 19180 (13.6 to 160.5) and from 3.7 to 1914.9 (3.4 to 22.8) at 0.1 (1) bar at 15 °C,

respectively, upon the IL incorporation. We also considered 4.20×10^{-4} and 0.15 bar for the atmospheric and post-combustion CO₂ capture. The CO₂/N₂ and CH₄/N₂ selectivities of MIL-101(Cr) enhanced from 14.13 to 31.3 and from 3.7 to 3.85 at 0.15 bar at 35 °C, respectively. Moreover, the CO₂/CH₄ selectivity for the [MPPyr][DCA]/MIL-101(Cr) was 9.42 (8.12) at 4.20×10^{-4} bar (0.15) bar corresponding to 2.08-times (2.12-times) improvement compared to pristine MIL-101(Cr).

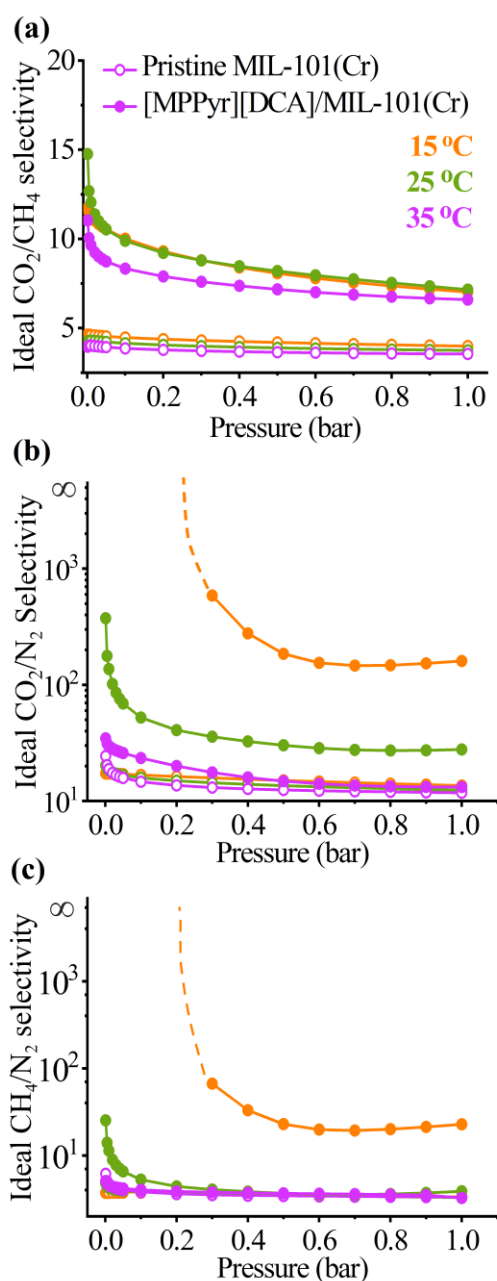


Figure 4.6. Ideal selectivities of MIL-101(Cr) and its composite with the [MPPyr][DCA] at an IL loading of 38 wt.% up to 1 bar and at 15, 25, and 35 °C for (a) CO₂/CH₄, (b) CO₂/N₂, and (c) CH₄/N₂. Ideal selectivities on the y-axis of (b) and (c) are given in a logarithmic scale, and the dotted lines represent practically infinite selectivity. The empty and filled symbols represent the selectivities for pristine MOF and its composite, respectively.

Moreover, CO₂/N₂ and CH₄/N₂ selectivities of pristine MIL-101(Cr) boosted to practically infinity below 0.3 bar and from 13.6 to 160.6 and 3.4 to 22.9 at 1 bar at 15 °C, respectively, upon the incorporation of IL. In addition, at 15 °C, the CO₂/CH₄ selectivity of pristine MIL-101(Cr) increased from 4.6 (4.5) to 11.7 (10.0) at 0.001 (0.1) bar and 4.76 (4.45) to 13.06 (9.6) at 4.20×10⁻⁴ bar (0.15) bar. These increases in selectivities with the decreasing pressure are associated with the change in what drives the adsorption. The gas adsorption in the low-pressure regions is governed by the interactions between the adsorbent and gas molecules, whereas, at high pressures, it significantly depends on the available pore volume [26,46]. Hence, such a remarkable boost in the selectivity of the composite in the low-pressure region can be ascribed to the change in the adsorption mechanism from pore availability to surface affinity.

Ideal selectivity is a general indication of the materials' separation properties. However, when a process is taken into consideration, gases exist in mixtures. Therefore, we calculated the IAST selectivities to investigate the mixture separation performance of the composite. The temperature was set to 25 °C to be able to get comparable results with the literature. **Figure 4A-9** shows the mixture (CO₂/CH₄:50/50, CO₂/N₂:15/85, and CH₄/N₂:50/50 representing the gas concentrations associated with methane purification, flue gas purification, and natural gas upgrading, respectively) selectivities of pristine MOF and its composite with the IL calculated using IAST. Normalized selectivities of IL/MOF composites were calculated by dividing the ideal selectivity of IL/MOF composites by that of the pristine MOF selectivities. At 0.01 bar, CO₂/CH₄:50/50 mixture selectivity of pristine MIL-101(Cr) improved from 4.4 to 12.2, indicating a normalized selectivity of 2.8, as shown in **Figure 4A-9a**. The normalized selectivity followed a decreasing trend as the pressure increased and became 1.8 at 1 bar. Similar trends were observed for CO₂/N₂ and CH₄/N₂ separations with normalized selectivities of 4.9 and 2.1 at 0.01 bar and 15.6 and 1.3 at 1 bar, as shown in **Figure 4A-9b-c**, respectively. Moreover, it is also important to examine the CO₂ separation performance of an adsorbent under post-combustion conditions corresponding to a pressure of 0.15 bar [47, 48]. Data indicate that the composite provides a CO₂/N₂ selectivity of approximately 44 at this pressure. Besides, we also note that these IAST results of the composite for CO₂/N₂ separation were found to be mostly comparable with those of various aminosilane-loaded UiO-67 materials under similar conditions [49]. Hence, considering the superior gas separation performance of the composite, it is reasonable to conclude that this material has a strong

potential to be used in flue gas separation and natural gas purification applications.

Table 4A-5 compares the selectivities of the [MPPyr][DCA]/MIL-101(Cr) composite presented in this work with other IL/MOF composites reported in the literature. The comparison shows that the ideal CO₂/N₂ and CH₄/N₂ selectivities of [MPPyr][DCA]/MIL-101(Cr) composite presented in this study are significantly higher than those of other IL/MOF composites at especially low pressures. Such high gas separation performance can be attributed to the superior solubility of pyrrolidinium-based ILs for CO₂.⁸⁶ Moreover, strong interactions present between the IL and the CO₂ molecules, which the COSMO-RS and the DFT results also validate, facilitate the diffusion of CO₂ molecules into the IL-incorporated MOF, while rejecting the N₂ molecules, making it completely selective for CO₂.

4.4 Conclusions

In this chapter, a new IL/MOF composite, [MPPyr][DCA]/MIL-101(Cr), with an IL loading of 38 wt.%, was prepared by the wet impregnation method. The composite was characterized in detail to identify the interactions between the IL molecules and the MOF surface. IR analysis showed that the IL's anion strongly interacts with the Cr metal nodes of the MOF. Moreover, DFT calculations demonstrated that CO₂, CH₄, and N₂ molecules interact differently with [MPPyr][DCA]: CO₂ interacts with both ions of [MPPyr][DCA], whereas CH₄ and N₂ form hydrogen bonds with the anion and cation, respectively. Gas adsorption measurements showed that the [MPPyr][DCA]/MIL-101(Cr) composite offers exceptional CO₂ and CH₄ selectivity over N₂: CO₂/N₂ and CH₄/N₂ selectivities of pristine MOF were improved to practically infinity below 0.3 bar at 15 °C upon the incorporation of the IL. It is noteworthy that the significant affinity of IL for CO₂ and the poor solubilities of CH₄ and N₂ in bulk [MPPyr][DCA] results in negligible adsorption of N₂ molecules in the composite, making it almost completely selective for CO₂/N₂ and CH₄/N₂. Overall, the CO₂/N₂, CH₄/N₂, and CO₂/CH₄ selectivity of [MPPyr][DCA]/MIL-101(Cr) composite that we measured is greater than the selectivities of imidazolium-based IL/MOF composites reported to date, showing the excellent potential of the synthesized composite.

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APPENDIX 4A

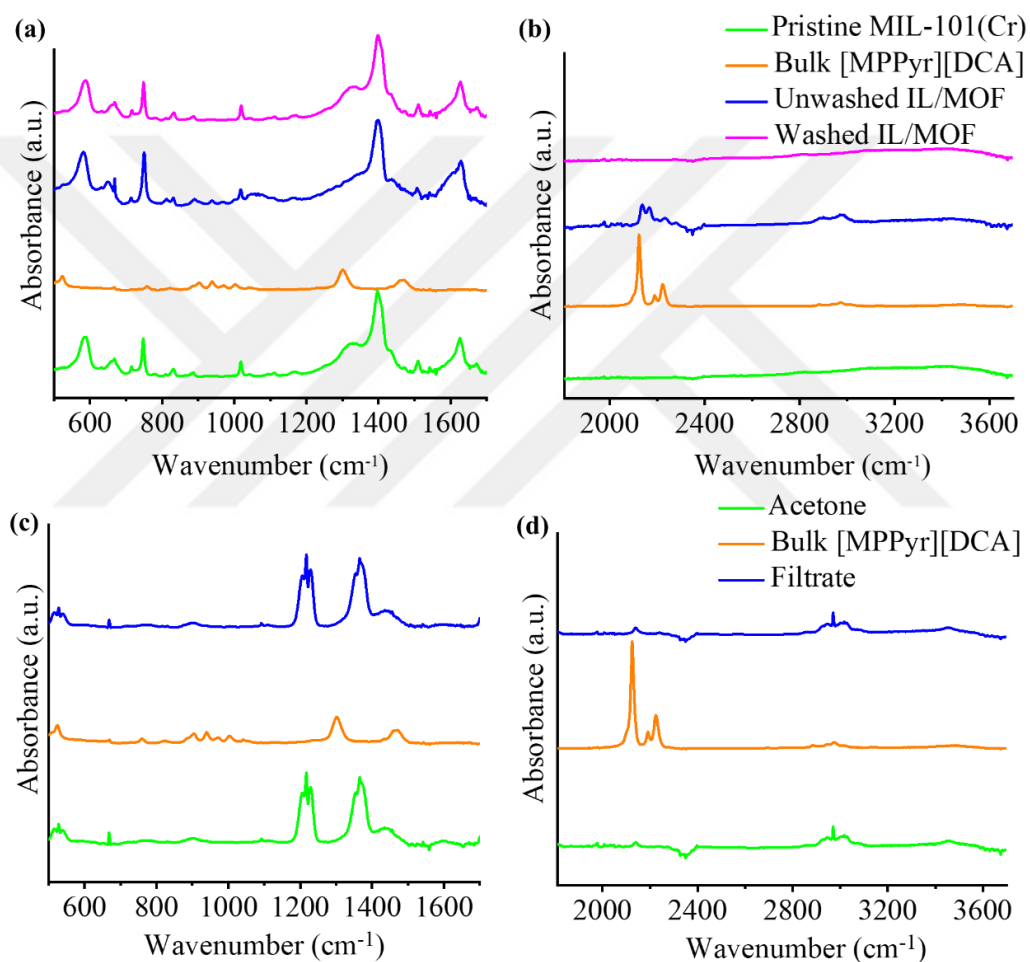


Figure 4A-1. IR spectra of MIL-101(Cr), bulk [MPPyr][DCA], and [MPPyr][DCA]/MIL-101(Cr) before and after washing with acetone in two different regions, 600-1700 cm^{-1} and 1800-3600 cm^{-1} ; Powder samples before and after washing with acetone in (a) and (b); the filtrate (liquid samples) in (c) and (d).

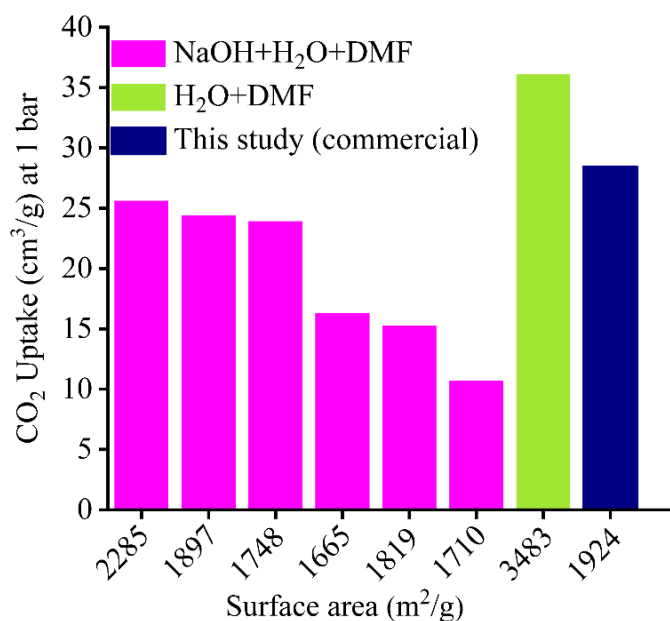


Figure 4A-2. Comparison of CO₂ uptakes and surface areas of the different MIL-101(Cr) samples from the literature. The entries were color-coded based on the types of solvents used for the synthesis.

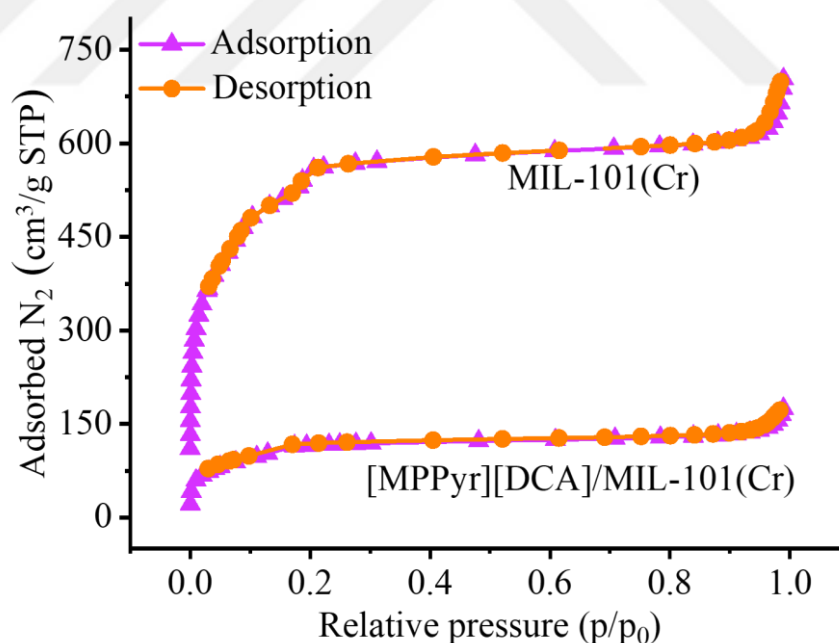


Figure 4A-3. N₂ physical adsorption-desorption isotherm of [MPPyr][DCA]/MIL-101(Cr) composite having an IL loading of 38 wt.%.

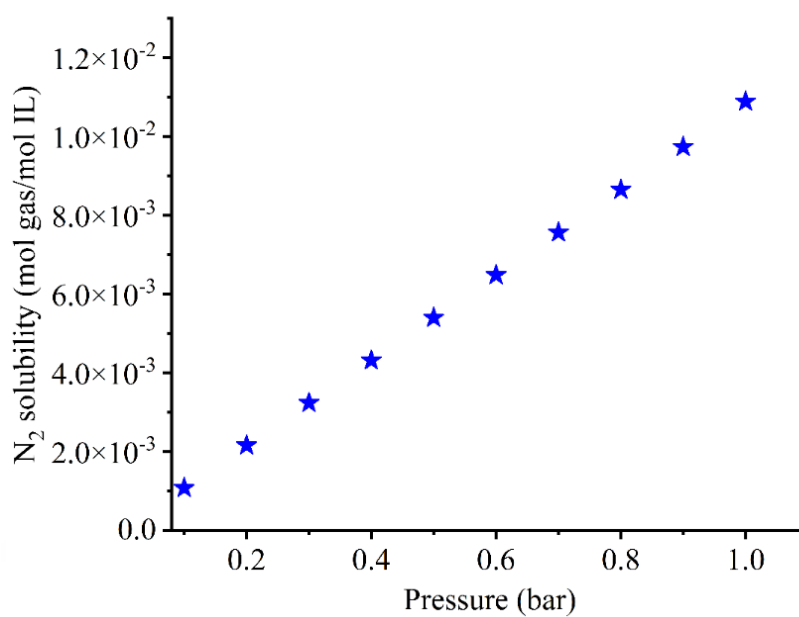


Figure 4A-4. The solubility of N₂ in bulk [MPPyr][DCA] calculated by COSMO-RS calculations at -196 °C between 0.1-1 bar.

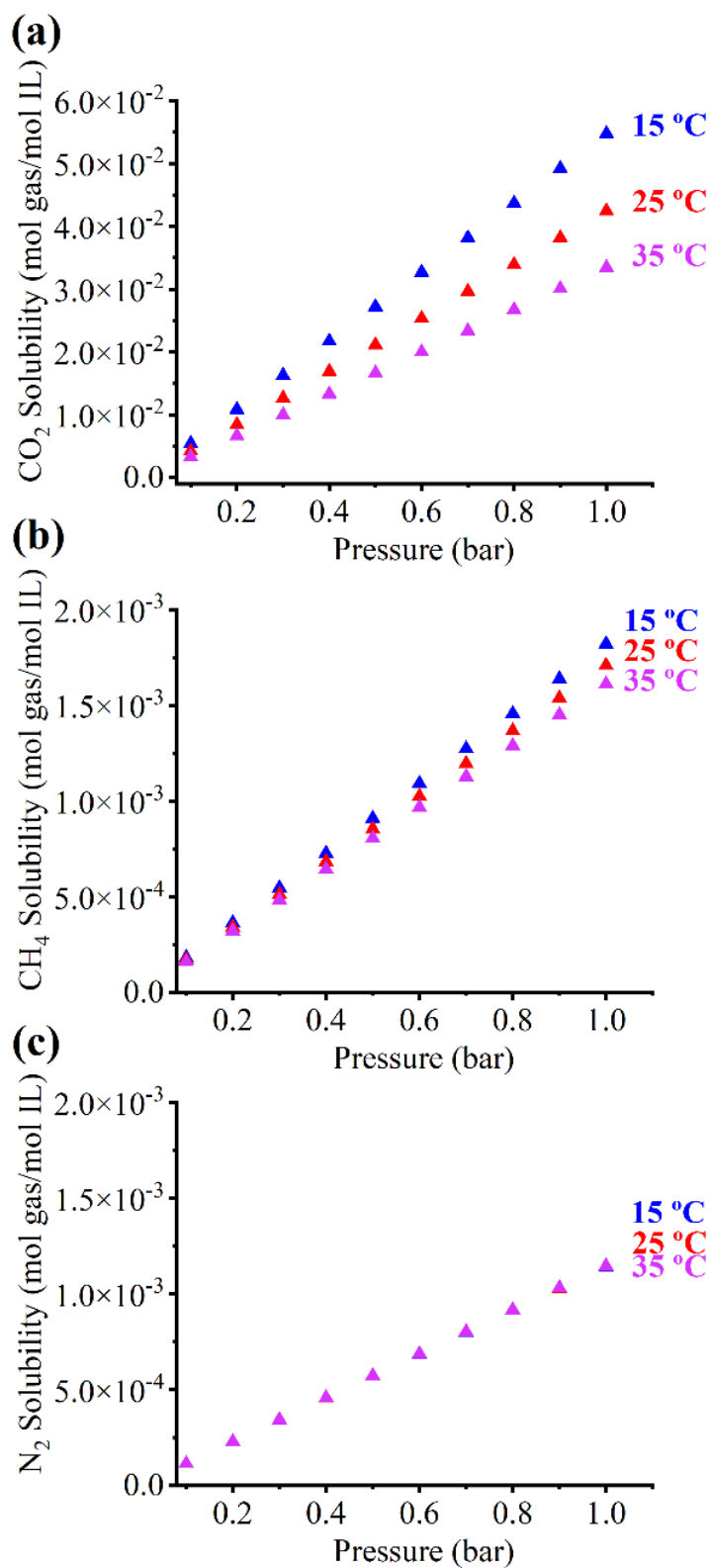


Figure 4A-5. The solubility of (a) CO₂, (b) CH₄, and (c) N₂ in bulk [MPPyr][DCA] calculated by COSMO-RS calculations at 15, 25, and 35 °C between 0.1-1 bar.

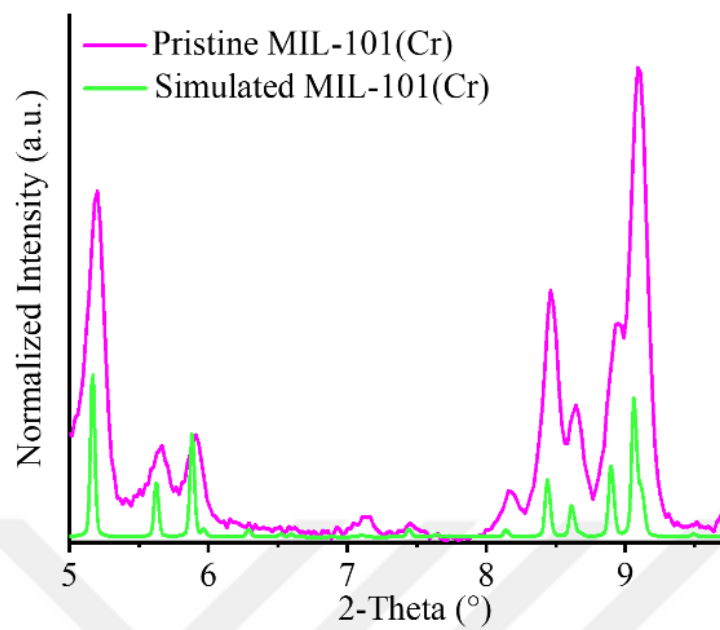


Figure 4A-6. X-ray diffraction pattern of simulated, pristine MIL-101(Cr) in 2θ range of 5-9.5°.

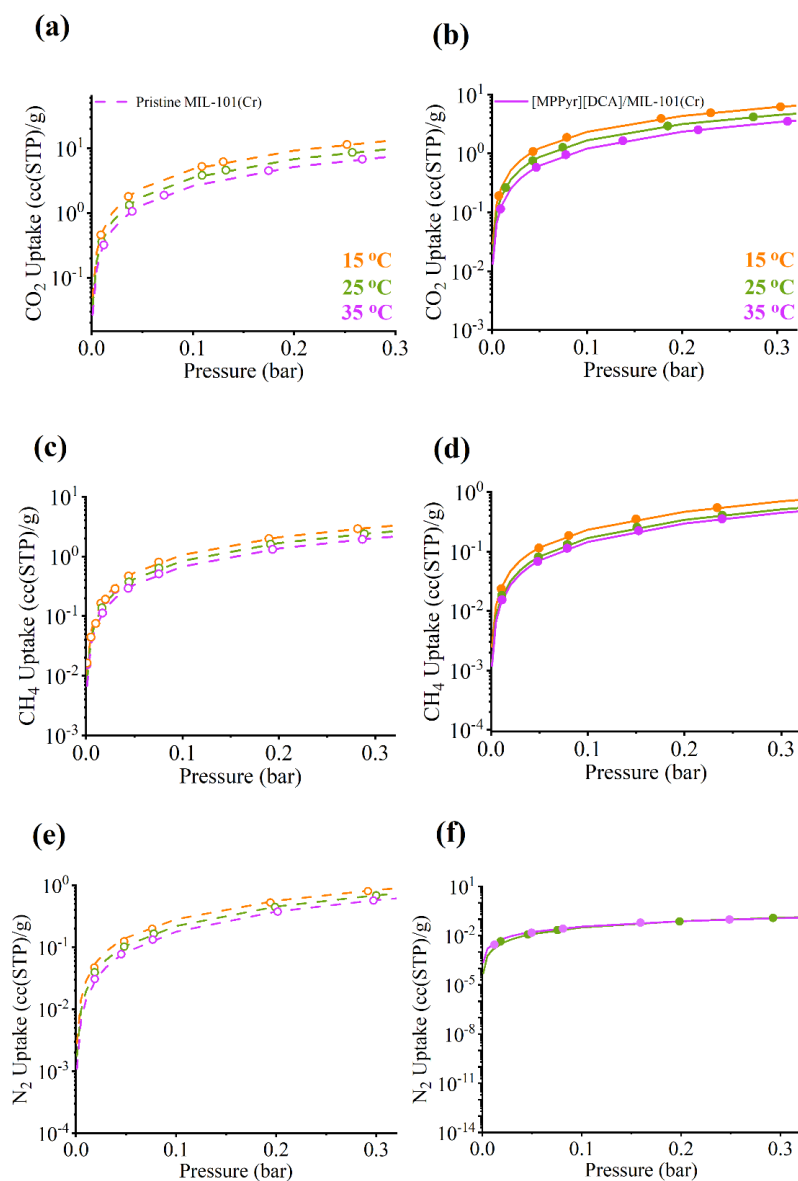


Figure 4A-7. (a) CO₂, (a) CH₄, (b) N₂ adsorption uptakes of pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite at 15, 25, and 35 °C up to 0.3 bar. The circles represent the experimental data points, and the lines represent the fit parameters.

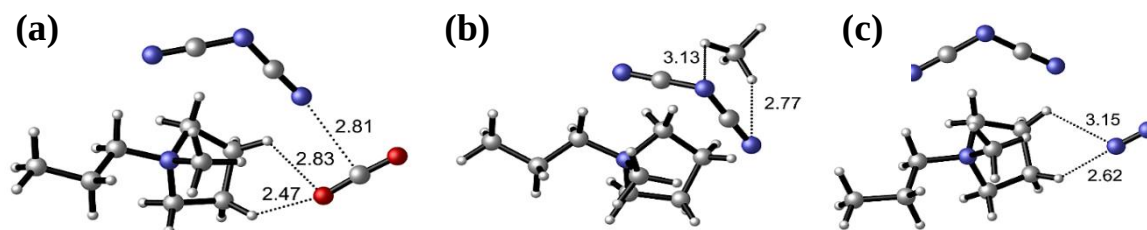


Figure 4A-8. The equilibrium geometries representing the interactions of [MPPyr][DCA] with (a) CO_2 , (b) CH_4 , (c) N_2 molecules calculated at the B3LYP-D2/6-311+G* level of theory. Bond distances are given in Å. Red, grey, white, and blue spheres represent O, C, H, and N atoms, respectively.

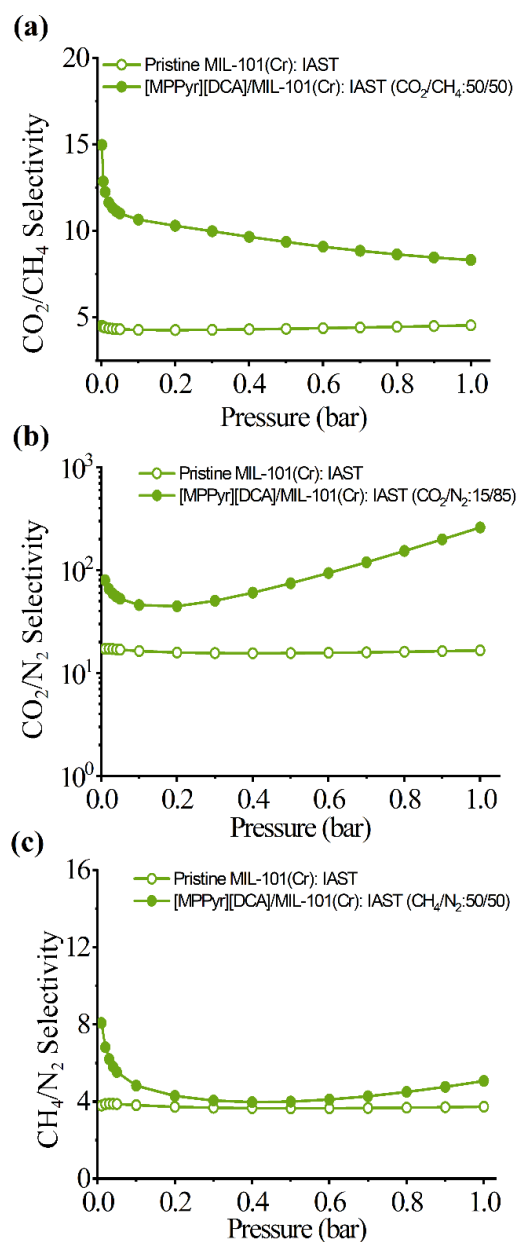


Figure 4A-9. (a) CO_2/CH_4 , (b) CO_2/N_2 , (c) CH_4/N_2 IAST selectivities of MIL-101(Cr), and [MPPyr][DCA]/MIL-101(Cr) composite up to 1 bar and at 25 °C. The empty symbols and filled symbols represent selectivities for pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite, respectively.

Table 4A-1. Dual-site Langmuir-Freundlich fit parameter for pristine in MIL-101(Cr) and [MPPyr][DCA]/MIL 101(Cr) composite with an IL loading of 38 wt.%.

	Dual-Site Langmuir Model							
MIL-101(Cr) 15 °C	Gas	q ₁ (cc/g)	k ₁ (1/mbar)	q ₂ (cc/g)	k ₂ (1/mbar)	R ²		
	CO ₂	244.82	0.13	14.43	1.21	1		
	N ₂	30.68	0.01	118.71	0.01	0.99		
	Dual-site Langmuir-Freundlich Model							
	Gas	q ₁ (cc/g)	k ₁ (1/mbar)	n ₁ [*]	q ₂ (cc/g)	k ₂ (1/mbar)	n ₂ [*]	R ²
	CH ₄	43.54	0.16	1.46	18.22	0.53	0.98	0.99
MIL-101(Cr) 25 °C	CO ₂	7.6×10 ⁻¹⁵	1.7×10 ⁻¹⁷	4.1×10 ⁻⁷	157.6	0.21	0.99	0.99
	N ₂	2.55	0.17	0.82	9.30	0.31	1.23	0.99
	CH ₄	33.77	0.16	1.31	16.51	0.40	0.97	0.99
MIL-101(Cr) 35 °C	CO ₂	70.65	0.25	1.50	35.42	0.66	0.97	0.99
	N ₂	12.70	0.20	1.09	0.002	0.006	1.48×10 ⁻¹¹	0.99
	CH ₄	30.22	0.19	1.23	8.52	0.46	0.94	0.99
[MPPyr] [DCA]/MIL-101(Cr) 15 °C	CO ₂	80.25	0.19	1.03	5.17	2.05	0.93	0.99
	N ₂	0.005	0.009	51.26	0.10	1.95	4.15	0.99
	CH ₄	55.17	0.33	5.51	14.1	0.19	1.04	0.99
[MPPyr] [DCA]/MIL-101(Cr) 25 °C	CO ₂	73.10	0.13	1.20	12.65	0.96	0.94	0.99
	N ₂	0.16	1.43	3.75	0.47	1.52	1.40	0.99
	CH ₄	4.21	0.48	1.05	12.17	0.21	2.28	0.99
[MPPyr] [DCA]/MIL-101(Cr) 35 °C	CO ₂	11.04	1.09	0.99	22.01	0.40	1.64	0.99
	N ₂	4.01	0.79	23.03	14.31	0.04	1.08	0.99
	CH ₄	1.73	0.58	2.02	2.97	0.55	1.04	0.99

Table 4A-2. Comparison of experimental CO₂, CH₄, and N₂ uptakes for pristine MIL-101(Cr) reported in the literature.

Reference	Pressure (bar)	Temperature (°C)	Experimental Uptakes (cm ³ /g)		
			CO ₂	CH ₄	N ₂
This study	0.001	15	0.049	0.0106	0.0028
		25	0.036	0.0085	0.0018
		35	0.027	0.0068	0.0011
	0.01	15	0.491	0.106	0.028
		25	0.359	0.083	0.020
		35	0.267	0.067	0.014
	0.1	15	4.754	1.062	0.283
		25	3.492	0.841	0.220
		35	2.614	0.676	0.178
	1	15	37.103	9.298	2.727
		25	28.601	7.623	2.307
		35	22.483	6.331	1.908
[1]	0.01	25	0.397		
		35	0.246		
	1	25	20.243		
		35	23.744		
[2]	0.01	25	0.448		
	1	25	36.064		
[3]	0.1	15	16.912	0.941	0.163
		30	5.488	0.587	0.105
		40	4.704	0.381	0.093
	1	15	53.760	8.960	4.928
		30	35.840	5.712	2.815
		40	35.280	5.152	2.778

Table 4A-3. BET and Langmuir surface areas and pore volumes of pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) having an IL loading of 38 wt.%.

Sample	S _{BET} (m ² /g)	S _{Langmuir} (m ² /g)	V _{Micropore} (cm ³ /g) ^a	V _{Micropore} (cm ³ /g) ^b	V _{total} (cm ³ /g)
MIL-101(Cr)	1924	2969	1.001	0.488	1.1574
[MPPyr][DCA]/MIL-101(Cr)	377	591	0.213	0.167	0.2702

^aBased on the Dubinin-Astakhov equation^bBased on the t-plot

Table 4A-4. CO₂, CH₄, and N₂ uptakes data for pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite at 15, 25, and 35 °C.

[MPPyr][DCA]/MIL-101(Cr)					
15 °C					
N ₂		CO ₂		CH ₄	
Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)
0.018	-0.004	0.007	0.191	0.011	0.024
0.047	-0.007	0.043	1.080	0.050	0.115
0.077	-0.010	0.079	1.874	0.080	0.186
0.200	-0.002	0.178	3.915	0.150	0.352
0.295	0.010	0.230	4.902	0.234	0.547
0.386	0.026	0.303	6.211	0.329	0.768
0.493	0.049	0.454	8.683	0.425	0.991
0.593	0.069	0.571	10.451	0.515	1.200
0.691	0.083	0.676	11.955	0.617	1.432
0.766	0.088	0.802	13.656	0.718	1.656
0.885	0.082	0.907	15.007	0.812	1.864
0.984	0.066	0.993	16.075	0.898	2.057
25 °C					
N ₂		CO ₂		CH ₄	
Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)
0.018	0.005	0.015	0.264	0.019	0.018
0.046	0.012	0.043	0.755	0.045	0.081
0.076	0.022	0.075	1.269	0.076	0.131
0.198	0.075	0.185	2.931	0.197	0.257
0.293	0.122	0.275	4.170	0.289	0.408
0.394	0.176	0.377	5.486	0.393	0.567
0.492	0.226	0.478	6.711	0.478	0.732
0.591	0.277	0.565	7.717	0.574	0.897
0.676	0.321	0.680	8.977	0.654	1.040
0.786	0.372	0.741	9.627	0.780	1.215
0.886	0.407	0.848	10.699	0.881	1.390
0.981	0.432	0.931	11.490	0.932	1.524
35 °C					
N ₂		CO ₂		CH ₄	
Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)
0.012	0.003	0.009	0.114	0.011	0.015
0.050	0.015	0.047	0.579	0.048	0.068
0.081	0.027	0.078	0.951	0.079	0.114
0.159	0.064	0.138	1.648	0.152	0.224
0.249	0.098	0.217	2.527	0.239	0.355
0.344	0.135	0.311	3.518	0.334	0.501
0.441	0.179	0.404	4.472	0.432	0.652
0.530	0.217	0.506	5.458	0.530	0.801
0.633	0.261	0.606	6.403	0.619	0.933
0.735	0.308	0.769	7.865	0.722	1.089
0.833	0.355	0.835	8.453	0.822	1.236
0.931	0.398	0.912	9.102	0.895	1.344
Pristine MIL-101(Cr)					
15 °C					
N ₂		CO ₂		CH ₄	
Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)

0.018	0.047	0.009	0.459	0.015	0.164
0.048	0.125	0.036	1.795	0.044	0.469
0.076	0.199	0.130	6.159	0.075	0.802
0.194	0.528	0.109	5.221	0.189	1.988
0.292	0.805	0.252	11.380	0.282	2.912
0.387	1.077	0.349	15.257	0.383	3.899
0.489	1.369	0.452	19.122	0.479	4.814
0.589	1.650	0.559	22.932	0.565	5.598
0.688	1.922	0.649	25.989	0.674	6.571
0.769	2.143	0.734	28.775	0.775	7.429
0.883	2.439	0.864	32.801	0.865	8.174
0.946	2.595	0.930	34.785	0.946	8.822
25 °C					
N ₂		CO ₂		CH ₄	
Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)
0.019	0.040	0.010	0.359	0.016	0.138
0.048	0.102	0.037	1.323	0.044	0.374
0.078	0.166	0.133	4.585	0.075	0.634
0.199	0.448	0.109	3.806	0.191	1.601
0.300	0.689	0.257	8.597	0.288	2.393
0.383	0.887	0.361	11.744	0.385	3.165
0.490	1.143	0.453	14.448	0.482	3.920
0.589	1.377	0.559	17.393	0.582	4.674
0.688	1.610	0.659	20.100	0.662	5.269
0.765	1.789	0.740	22.209	0.774	6.073
0.883	2.047	0.856	25.117	0.875	6.770
0.979	2.245	0.939	27.137	0.942	7.216
35 °C					
N ₂		CO ₂		CH ₄	
Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)	Pressure (bar)	Uptake (cc/g)
0.019	0.031	0.012	0.320	0.017	0.113
0.045	0.077	0.040	1.058	0.044	0.293
0.077	0.133	0.071	1.880	0.075	0.509
0.201	0.376	0.175	4.500	0.193	1.311
0.297	0.569	0.267	6.766	0.286	1.936
0.396	0.767	0.369	9.181	0.387	2.601
0.493	0.962	0.462	11.312	0.485	3.240
0.578	1.130	0.566	13.613	0.583	3.862
0.689	1.344	0.666	15.759	0.668	4.385
0.789	1.528	0.748	17.449	0.779	5.051
0.886	1.693	0.869	19.881	0.877	5.621
0.984	1.848	0.956	21.576	0.936	5.950

Table 4A-5. Comparison of IL-incorporated MOFs composites reported in the literature for adsorption-based gas separation applications.

IL/MOF composites	Operating conditions	Ideal Selectivities			IAST Selectivities			Ref.
		CO ₂ /CH ₄	CO ₂ /N ₂	CH ₄ /N ₂	CO ₂ /CH ₄ (50/50)	CO ₂ /N ₂ (15/85)	CH ₄ /N ₂ (50/50)	
Pristine MIL-101(Cr)	0.001 bar, 25 °C	5.8	20.62	3.5	4.5	17.2	3.8	This study

	0.01 bar, 25 °C	5.8	19.4	3.3	4.5	17.2	3.8	
	1 bar, 25 °C	4.7	13.9	2.9	4.5	16.6	3.8	
[MPPyr][DCA]/MIL-101(Cr) with an IL loading of 38 wt. %	0.001 bar, 25 °C	14.8	374.5	25.4	14.9	163.7	14.3	This study
	0.01 bar, 25 °C	12.1	137.1	11.4	12.2	79.9	4.8	
	1 bar, 25 °C	7.2	27.8	3.9	8.3	260.0	5.0	
Pristine ZIF-8	0.01 bar, 25 °C	2.4	7.8	2.8	2.4	7.8	2.8	[4]
	0.1 bar, 25 °C	2.4	7.8	2.8	2.4	7.8	2.8	[4]
[BMIM][PF ₆]/ZIF-8	0.1 bar, 25 °C	8.9	24.2	2.8	8.9	28.0	2.7	[4]
[BMIM][BF ₄]/ZIF-8	0.1 bar, 25 °C	4.3	14.6	3.4				[5]
[BMIM][SCN]/ZIF-8	0.01 bar, 25 °C	6.5	21.2		6.5	20.9		[6]
[BMIM][MeSO ₃]/ZIF-8	0.01 bar, 25 °C	1.7	19.1	11.3				[7]
[BMIM][OcSO ₄]/ZIF-8	0.01 bar, 25 °C	4.7	2.6	0.53				[7]
[BMIM][OcSO ₄]/ZIF-8	1 bar, 25 °C	3.6	6.7	1.9				[7]
Pristine CuBTC	0.01 bar, 25 °C	4.6	17.6	3.7		19.0	3.5	[8]
[BMMIM][PF ₆]/ CuBTC	0.01 bar, 25 °C		23.1	4.4		21.6	4.6	[8]
[BMIM][PF ₆]/ CuBTC	0.01 bar, 25 °C		26.1	5.2		26.5	5.2	[8]
[EMIM][DEP]/CuBTC	0.01 bar, 25 °C	7.3	42.3		6.6	31.1		[9]
[BMIM][NTF ₂]/CuBTC	0.01 bar, 25 °C	3.2	13.1	3.8				[10]
[BMIM][CF ₃ SO ₃]/CuBTC	0.01 bar, 25 °C	4.1	19.4	4.5				[10]
[BMIM][BF ₄]/CuBTC	0.01 bar, 25 °C	4.6	21.1	4.7				[10]
[BMIM][MeSO ₄]/CuBTC	0.01 bar, 25 °C	4.4	21.8	4.9				[10]
[BMIM][SbF ₆]/CuBTC	0.01 bar, 25 °C	5.5	25.7	4.4				[10]
[BMIM][OcSO ₄]/CuBTC	0.01 bar, 25 °C	5.4	26.7	5.0				[10]
[BMIM][MeSO ₃]/CuBTC	0.01 bar, 25 °C	5.6	27.1	4.8				[10]
[BMIM][SCN]/CuBTC	0.01 bar, 25 °C	5.7	29.6	5.2				[10]

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Chapter 5

Incorporation of a pyrrolidinium-based ionic liquid/MIL-101(Cr) composite into Pebax sets a new benchmark for CO₂/N₂ selectivity*

5.1 Abstract

Mixed matrix membranes (MMMs) offer a broad potential for energy efficient removal of CO₂ from flue gas and natural gas. In this study, we synthesized a novel ionic liquid (IL)/metal organic framework (MOF) composite, [MPPyr][DCA]/MIL-101(Cr) and incorporated it as the filler into Pebax to make IL/MOF/polymer MMMs. The superior solubility of CO₂ in the [MPPyr][DCA] (1-methyl-1-propyl pyrrolidinium dicyanamide) and the strong interactions between IL and CO₂ molecules boost the CO₂ selectivity of the membrane over N₂ and CH₄. The results showed that CO₂ permeability of the MMM having 15 wt.% [MPPyr][DCA]/MIL-101(Cr) composite (148 Barrer) was similar to that of pure Pebax membrane (134 Barrer), while the ideal CO₂/N₂ selectivity (1347) and ideal CO₂/CH₄ selectivity (122) of the MMM were 45- and 10-times higher compared to selectivities of pure Pebax membrane, respectively. To the best of our knowledge, the remarkable enhancement in the CO₂/N₂ selectivity of the MMM sets a new benchmark value for previously reported IL/MOF/polymer MMMs in the literature. These results demonstrate the great potential of using [MPPyr][DCA]/MIL-101(Cr) composite as a filler for the fabrication of highly selective IL/MOF/polymer MMMs for CO₂/N₂ and CO₂/CH₄ separations.

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5.2 Introduction

Membrane-based CO₂ separation has been proven to be promising owing to its high efficiency, design simplicity, ease of fabrication, low energy requirement, and small carbon footprint [1, 2]. Although polymer membranes have been widely used for gas separation, their separation performance is limited by the trade-off between permeability and selectivity, as shown with the Robeson's upper bound [3]. To overcome this limitation, mixed matrix membranes (MMMs), which are fabricated by dispersing porous fillers (zeolites, graphene oxide, carbon nanotubes, metal oxides, and metal organic frameworks (MOFs)) into the polymer matrix, have been generated [4, 5]. MMMs combine the high selectivity of porous fillers with the ease of processability of the polymers to achieve an enhanced performance for various gas separations [6].

Among all kinds of fillers incorporated into the polymers to prepare MMMs, MOFs have been of great interest thanks to their high porosity, good mechanical, and thermal properties, along with their tunable pores and adsorption sites leading to superior gas separation performance [7]. Several MOF/polymer MMMs have shown promising results for different separations, such as CO₂/CH₄, CO₂/N₂, H₂/CO₂, compared to the corresponding pure polymer membranes [8-12]. Incorporation of MOFs into polymers generally improves the gas permeability and/or the selectivity of the polymer membrane [13]. For instance, MOF-801/PIM-1 MMMs (PIM-1: polymer of intrinsic microporosity) having different filler loadings were fabricated and the results showed that the MMM having 5 wt.% MOF-801 loading have a significantly higher CO₂ permeability (9686 Barrer) compared to pure polymer (4200 Barrer), whereas the CO₂/N₂ selectivities (27) and O₂/N₂ selectivities (4.8) showed negligible improvement compared to pure polymer membrane having selectivities of 20 and 4, respectively [14]. In some cases, addition of MOFs into the polymers leads to reduced gas permeabilities. For example, CO₂ and H₂ permeabilities were reported to decrease from 10 to 5 Barrer and from 30 to 20 Barrer, respectively, when ZIF-8 was incorporated into Matrimid. However, these decreases in permeabilities were accompanied with improvements in H₂/CO₂ and CO₂/CH₄ selectivities from 40 to 121 and 124 to 472, respectively [15]. Achieving simultaneous improvement of selectivity and permeability by generating MMMs is highly desired and might be possible by incorporation of novel filler materials into the polymers.

To obtain further improvement in the gas separation performance of MOFs, their

modification with other functional materials to generate MOF-based composites has been suggested [16, 17]. Ionic liquids (ILs) are molten salts made up of large organic cations with inorganic anions offering tunable physicochemical properties with almost unlimited structural variety [18]. Combining MOFs with ILs to enhance the gas separation performance of MOFs by modifying the MOFs' pore structure and facilitating CO₂ transport owing to the high solubility of CO₂ in most ILs has been reported [19]. Several studies demonstrated that the incorporation of ILs into MOFs to synthesize IL/MOF composites significantly improved the CO₂ selectivity of the parent MOF over N₂ and CH₄ [20-23]. Recently, IL/MOF composites have been incorporated as fillers into the polymers to fabricate IL/MOF/polymer MMMs, enhancing the CO₂ affinity and molecular sieving properties of the membranes, resulting in MMMs with improved permeability and selectivity [14, 24-28]. For instance, IL/ZIF-8 composite having 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM][Tf₂N], as the IL was synthesized and incorporated into Pebax [29]. The results showed that CO₂/CH₄ and CO₂/N₂ selectivities of the MMM having 15 wt.% IL/ZIF-8 composite were (34 and 84, respectively) higher than the selectivities of pure Pebax membrane (28 and 40, respectively). In another example, IL/ZIF-8 composite prepared by using a different IL, 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF₆], incorporated into Pebax at a loading of 25 wt.% [30]. The resulting MMM showed a higher CO₂ permeability (120 Barrers) and CO₂/N₂ selectivity (90) than the pure polymer membrane (59 Barrer and 55, respectively).

Recently, IL/MOF composites with amine-functionalized MOFs have been incorporated into different polymers. For instance, [NH₂-PMIM][Tf₂N]/ZIF-67 composite [NH₂-PMIM][Tf₂N] prepared and incorporated in the PIM-1 polymer [31]. The results showed that with 5 wt.% IL/MOF loading, CO₂ permeability of the MMM was almost double (7190 Barrer) of the polymer (4310 Barrer) with unchanged CO₂/N₂ selectivity (22). In another study, [BMIM][Tf₂N]/NH₂-MIL-101(Cr)/Matrimid MMM with a filler loading of 7 wt.% was synthesized [32]. Both the CO₂ permeability and CO₂/CH₄ selectivity were improved from 6 to 19 Barrer and from 35 to 113, respectively, compared to corresponding values of pure Matrimid. Similarly, [C₃NH₂bim][Br]/NH₂-MIL-101(Cr) ([C₃NH₂bim][Br]: 1-butylimidazole 2-bromopropylamine hydrobromide) composite was incorporated into PIM-1 [33] and the CO₂ permeability of IL/MOF/PIM-

1 MMM with 5 wt.% IL/MOF loading (3000 Barrer) was approximately 1.3-times higher than that of PIM-1 membrane (2400 Barrer). The CO₂/N₂ selectivity (27), on the other hand, was almost 1.6-times higher than the polymer (17).

All these studies demonstrate that the MMMs prepared by incorporation of IL/MOF composites into polymers offer significantly better separation performance than the pure polymer membrane. There exists a very large number and variety of ILs (in the order of 10¹⁸) [34] and MOFs (114,373) [35] yielding 10²³ IL/MOF composite possibilities, however, the number of reported MMMs having IL/MOF composite as a filler is very limited and most of the studies focused on ILs having imidazolium-based cations. Recently, we showed that incorporating a pyrrolidinium-based IL, namely 1-*n*-butyl-1-methylpyrrolidinium dicyanamide, [BMPyr][DCA], into UiO-66 to synthesize an IL/MOF composite resulted in exceptionally improved CO₂/N₂ and CH₄/N₂ adsorption selectivities [36]. However, we have no information about the potential impact of using a pyrrolidinium-based IL/MOF composite as the filler particle on the CO₂ separation performance of the resulting MMM.

In this chapter, we synthesized highly CO₂-selective IL/MOF/polymer MMMs for CO₂/N₂ and CO₂/CH₄ separations by specifically choosing a pyrrolidinium-based IL, 1-methyl-1-propyl pyrrolidinium dicyanamide ([MPPyr][DCA]), to prepare a novel IL/MOF composite. [MPPyr][DCA] was selected as an IL because of the high CO₂ solubility of [DCA]⁻ anion along with pyrrolidinium cation offering superior gas separation properties and less toxicity compared to the imidazolium-based ILs [37]. [MPPyr][DCA] has not been reported in the form of IL-incorporated MOF filler in previous MMM studies. Thus, to unlock the potential of this IL as a composite filler in MMM applications by extending the list of pyrrolidinium-based ILs, is highly desired to understand their potential for improved separation performance of the MMMs. MIL-101(Cr) was selected as the host MOF since it has a high surface area and unsaturated Cr(III) sites offering strong Lewis acid-base interactions with the oxygen of CO₂, leading to high CO₂ adsorption [38, 39]. [MPPyr][DCA]/MIL-101(Cr) composite having 45 wt.% IL was synthesized via wet impregnation method and incorporated into Pebax polymer as the filler to fabricate [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with filler loading of 10, 15, and 20 wt.%. This is the first attempt to study the effect of using pyrrolidinium-based IL/MOF composite as the filler on the separation performance of a polymer

membrane. Moreover, MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/Pebax MMMs were also synthesized for comparison. The structural characteristics and the molecular interactions between the individual components of the MMMs were characterized in detail and their influence on the CO₂/N₂, CO₂/CH₄ separation performances of the resulting MMMs were comprehensively investigated. Our results showed that [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs offer comparable CO₂ permeability with exceptionally high CO₂/N₂ ideal selectivity compared to the previously reported IL/MOF/polymer MMMs in the literature. These results will guide the design of new IL/MOF/polymer MMMs having extraordinarily good performances for CO₂ separations.

5.3 Results and Discussion

5.3.1 Characterization of the materials

5.3.1.1 Pristine MOF and IL/MOF composite

The IL loading in the as-synthesized [MPPyr][DCA]/MIL-101(Cr) composite was determined by washing the composite several times with acetone, which was chosen as the solvent because it can enter the pore window of MIL-101(Cr) (16 Å) [12] to remove any incorporated IL molecules. After washing, the filtrate was collected in a vial and the washed IL/MOF composite was dried overnight at 80 °C. The IR spectra of the dried composite, the filtrate, and the bulk IL are presented in **Figure 5A-2**. Data showed that the IL was completely removed from the composite upon the washing. By measuring the amount of the dried sample, the IL loading was determined as approximately 41 wt.%, which is slightly less than the stoichiometric IL loading of 45 wt.% targeted to prepare the [MPPyr][DCA]/MIL-101(Cr) composite. This difference can be attributed to the loss of some [MPPyr][DCA] on the walls of the container during the synthesis of the composite sample.

SEM images of the pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite (**Figure 5.1a-b** and **Figure 5.1c-d**, respectively) were obtained to examine the effect of IL incorporation on the morphology of the pristine MOF. SEM images of the composite given in **Figure 5.1c-d** showed the octahedral structure of MIL-101(Cr). Thus, the crystal morphology of the MIL-101(Cr) was well-preserved upon the incorporation of [MPPyr][DCA]. Moreover, it was also observed that the surface morphology of the MOF was not affected by the addition of IL, and no external layer formation was visible

in the SEM images, implying that the IL was successfully incorporated inside the MIL-101(Cr) cages.

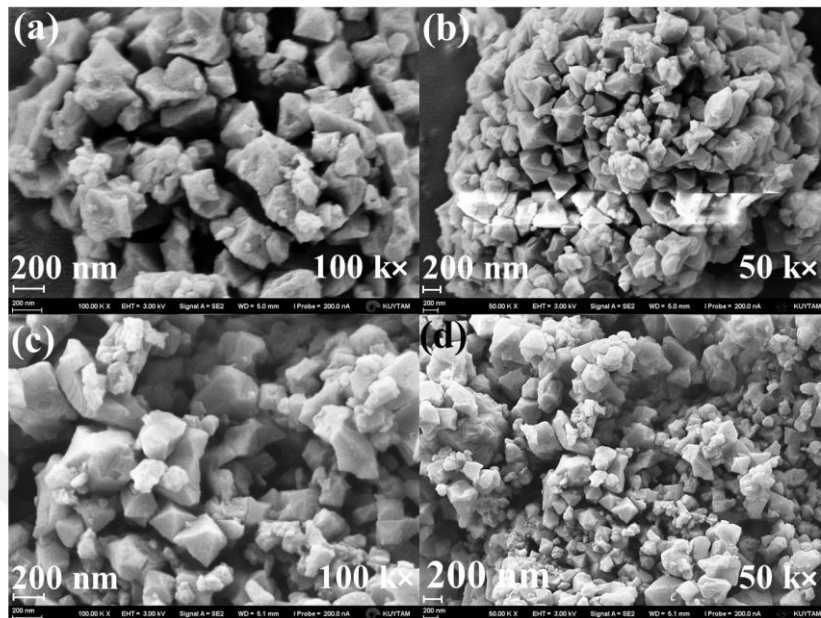


Figure 5.1. SEM images of (a, b) MIL-101(Cr) and (c, d) [MPPyr][DCA]/MIL-101(Cr) composite obtained at magnifications 100 × and 50 k×.

The N₂ adsorption isotherms obtained at the liquid nitrogen temperature on the pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite are presented in **Figure 5.2a**. Moreover, pore size distribution analysis was made for the pristine MIL-101(Cr) as given in **Figure 5A-3**. Data presented in **Figure 5.2a** showed that the surface area and pore volume of [MPPyr][DCA]/MIL-101(Cr) were significantly lower than those of pristine MIL-101(Cr). Upon the incorporation of [MPPyr][DCA], the surface area and pore volume of MIL-101(Cr) decreased from 1924 m²/g and 0.6 cm³/g to 109 m²/g and 0.08 cm³/g, respectively. This decrease can be attributed to the pore occupation of MIL-101(Cr) with the IL molecules, resulting in less N₂ uptakes, consistent with the literature [36]. Accordingly, N₂ solubility in bulk [MPPyr][DCA] was calculated by COSMO-RS calculations as presented in **Figure 5A-4**, which showed that IL has poor solubility for N₂ at the BET measurement conditions. Therefore, due to low N₂ solubility of [MPPyr][DCA], the pores of MIL-101(Cr) are mostly unavailable for N₂ especially if the IL molecules are present at their pore openings [39]. Hence, the BET results are not considered to be very reliable in providing precise surface area and pore volume of IL/MOF composites, however, they indicate the successful incorporation of the IL.

Consistently, the XRD patterns presented in **Figure 5.2b** showed that there are no significant changes in the diffraction peaks of MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite. Specifically, the sharp peaks located at $2\theta = 8.4, 9.0,$ and 16.5° , corresponding to the main diffraction peaks of MIL-101(Cr) [40], remained intact in IL-incorporated MOF composite, confirming that the crystal structure of the MIL-101(Cr) was preserved upon the incorporation of IL. However, some changes in the intensities of the peaks present in [MPPyr][DCA]/MIL-101(Cr) composite were observed compared to those on the pristine MIL-101(Cr). These differences can be attributed to a possible change in the electronic structure or the preferential orientation of the MOF crystals, because of the incorporation of IL molecules inside the MOF's pores, consistent with earlier reports [41].

The TGA analysis was conducted for pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) as shown in **Figure 5.2c**. The thermogravimetric analysis was started after the complete evaporation of moisture content and any residual solvent present in the samples at 130°C . The results showed that MIL-101(Cr) starts to decompose at a T'_{onset} value of approximately 330°C , which can be attributed to the decomposition of the organic ligand present in the MOF structure [42]. The T'_{onset} value of bulk [MPPyr][DCA] was found to be at 230°C , whereas for IL/MOF composite, T'_{onset} value was around 300°C . These results showed that the T'_{onset} of the as-synthesized IL/MOF composite is lower than that of the pure MOF, which can be associated with the presence of direct IL-MOF interactions in the composite. These interactions between the IL and the MOF changed the MOF composite's decomposition mechanism (from one to multiple steps) and decreased the thermal stability limits of the IL/MOF composite as compared to the pristine MOF [43].

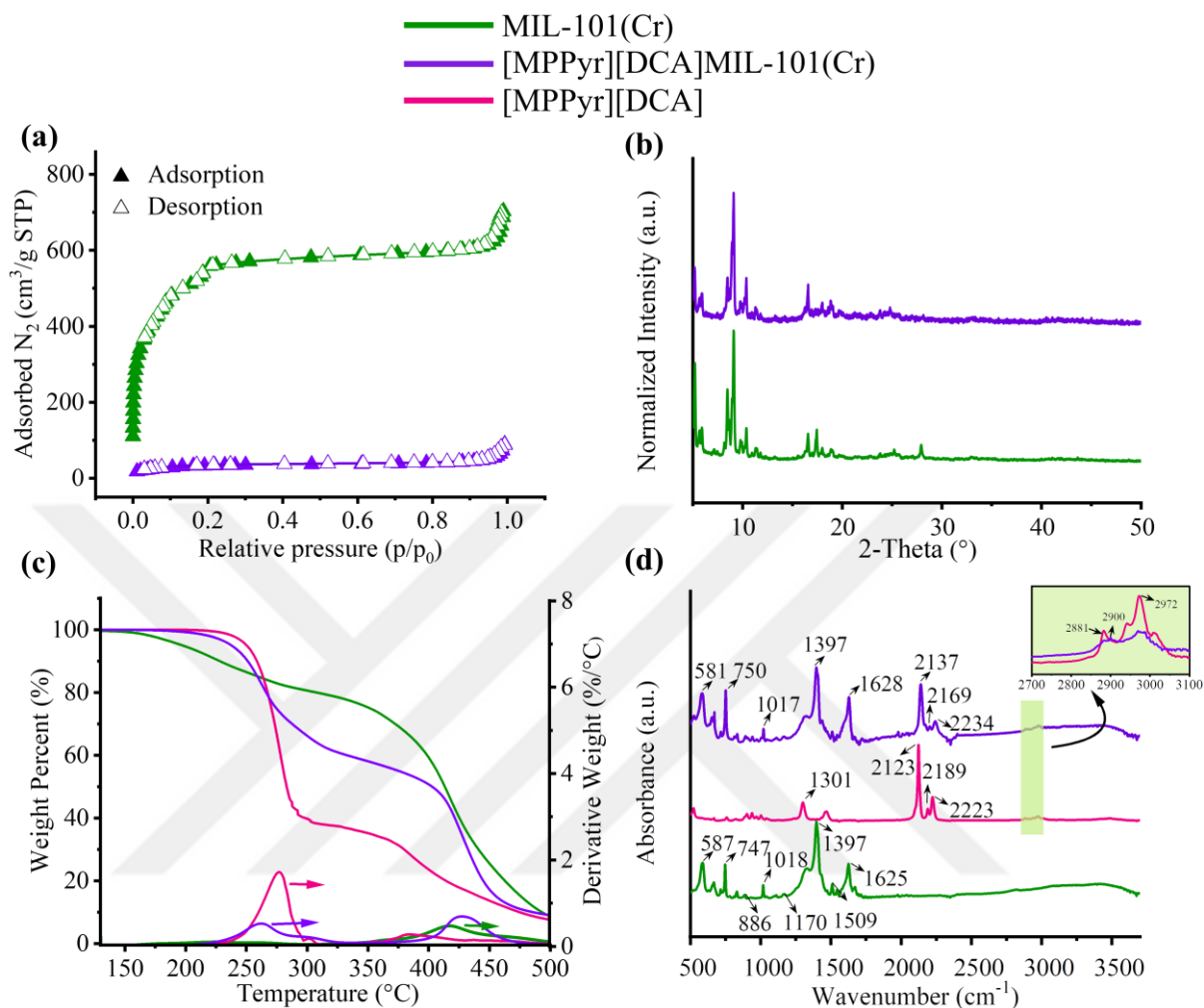


Figure 5.2. (a) N₂ adsorption-desorption isotherms, (b) XRD diffractogram, (c) TGA curves, (d) IR spectra of pristine MIL-101(Cr), bulk [MPPyr][DCA], and [MPPyr][DCA]/MIL-101(Cr) composite.

To have insights into the IL-MOF interactions, IR analysis was performed on the MIL-101(Cr), bulk [MPPyr][DCA], [MPPyr][DCA]/MIL-101(Cr) composite as shown in **Figure 5.2c**. In the IR spectrum of [MPPyr][DCA], the peaks located at 2881 and 2972 cm⁻¹ were assigned to the symmetric and asymmetric $\nu(\text{C-H})$ vibrations on the IL's cation, respectively, whereas the IR bands at 1301, 2123, 2189, and 2223 cm⁻¹ were attributed to $\nu(\text{C}\equiv\text{N})$ vibrations of the [DCA]⁻ anion [44]. It was observed that $\nu(\text{C}\equiv\text{N})$ characteristic vibrations of the [DCA]⁻ anion exhibited blue-shifts of 14 and 11 cm⁻¹, in the spectrum of the composite, respectively. Moreover, data further indicated that the characteristic $\nu(\text{C-H})$ peak located at 2881 cm⁻¹ blue-shifted to 2900 cm⁻¹ upon the incorporation of the IL into the MOF. A spectral shift towards lower energy and lower

frequency is called a red-shift which occurs because the H–C bond is weakened. A spectral shift towards higher energy and higher frequency is called a blue-shift which increases the positive charge on the H. This causes a blue-shifting of the H–C stretching frequency because the H–C bond is strengthened.

In the lower frequency region of the IR spectrum of the pristine MIL-101(Cr), the band at 587 cm⁻¹ was associated with the coordination of 1,4-benzene dicarboxylate (BDC) linker to the chromium sites. Besides this feature, the bands located between 600 and 1630 cm⁻¹ were attributed to the benzene ring, including the stretching $\nu(\text{C}=\text{C})$ vibrations at 1509 cm⁻¹ and $\nu(\text{C}-\text{H})$ vibrations at 747, 886, 1018, and 1170 cm⁻¹ [45]. Furthermore, the peaks located at 1397 and 1625 cm⁻¹ corresponded to the symmetric $\nu(\text{COO})$ and asymmetric $\nu(\text{C}-\text{O})$ vibrations of dicarboxylate groups in the BDC linker, respectively [46]. Upon the incorporation of IL into the MIL-101(Cr), characteristic $\nu(\text{Cr}-\text{O})$ peak of MIL-101(Cr) located at 587 cm⁻¹ presented a red-shift of 6 cm⁻¹, while the peaks at 747 and 1625 cm⁻¹ exhibited blue-shifts of 3 cm⁻¹. These shifts in the characteristic $\nu(\text{Cr}-\text{O})$ band of pristine MIL-101(Cr) indicate the Cr nodes of the MOF strongly interacts with the anion of IL. The changes in the characteristic peak positions of anion of the IL suggest that the interionic interaction between anion and cation of IL weakens as it interacts more with the metal nodes of MIL-101(Cr). Hence, the electronic environment of the MOF structure changes upon the IL incorporation because of the existence of direct interactions between IL (anion) and MOF.

5.4.1.2 MOF /polymer and IL/MOF/polymer MMMs

Cross-sectional SEM images of all MMMs were obtained to investigate the changes in the morphologies of MMMs upon the incorporation of the filler. The images of MIL-101(Cr)/Pebax MMMs represented in **Figure 5.3a-c** and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs presented in **Figure 5.3d-f** showed obvious differences in the morphology of two types of the membranes. As the loadings of MOF and IL/MOF fillers were increased, the MMMs showed less-smooth structure, especially the ones containing 20 wt.% filler. In the case of the MIL-101(Cr)/Pebax MMM with 20 wt.% MOF loading, agglomeration of particles was clearly observed which can be attributed to the poor compatibility between MOF and polymer especially at higher loadings. The comparison between IL/MOF/polymer and MOF/polymer MMMs, on the other hand, revealed that

IL addition improved the filler/polymer compatibility resulting in more uniform and homogenous distribution of the filler at all loadings. This improvement suggests that IL molecules might be partially leaching out from the MOF cages in the presence of the solvent (ethanol/water mixture) during the synthesis of MMMs. To confirm this possibility, we washed the IL/MOF composite in ethanol/water mixture and checked the IR spectra of both the washed sample and the filtrate. The data presented in **Figure 5A-1** demonstrated that some IL molecules leached out from the cages of MOF. Hence, we infer that IL molecules might be present both inside and outside of the MOF in the composite. The presence of IL on the external surface of the MOF improves the compatibility of the filler with the polymer matrix [47]. Details are presented in the discussion of IR results.

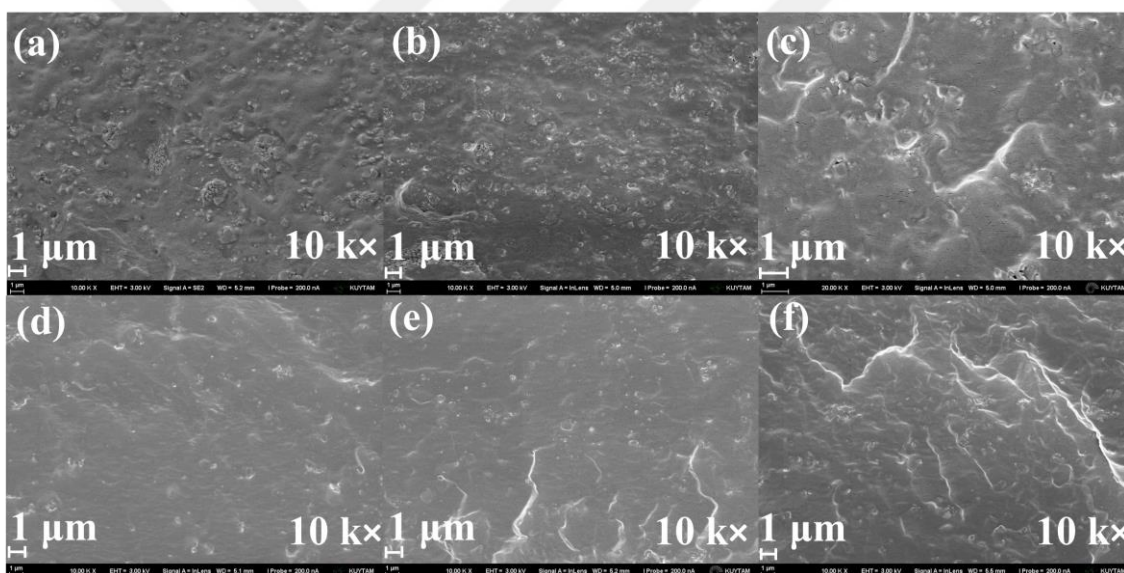


Figure 5.3. Cross-sectional SEM images of MIL-101(Cr)/Pebax MMMs with (a) 10 wt.%, (b) 15 wt.%, (c) 20 wt.% MIL-101(Cr) loadings and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with (d) 10 wt.%, (e) 15 wt.%, (f) 20 wt.% [MPPyr][DCA]/MIL-101(Cr) loadings.

The XRD analyses of the pure Pebax, MIL-101(Cr)/Pebax, and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with 10, 15, and 20 wt.% fillers were performed to study the structural properties of MMMs as shown in **Figure 5.4a-g**. For the pure Pebax membrane, a broad peak present at $2\theta = 13-23^\circ$ corresponded to the polyamide (PA) segment [48], which was also observed in the XRD spectra of all the prepared MMMs without any change in its peak position. In the XRD patterns of MMMs

some new peaks were observed at $2\theta = 8.6$, 9.0 , and 16.8° , which were attributed to the characteristic peaks of pristine MIL-101(Cr). In the case of MIL-101(Cr)/Pebax MMMs, **Figure 5.4b-d**, the intensities of characteristic MIL-101(Cr) peaks were observed to increase as the filler loading was increased from 10 to 20 wt.%, indicating the high crystallinity of the MMMs at higher MOF loadings. However, the relative intensity of characteristic diffraction peaks of MIL-101(Cr) was reduced in all the IL/MOF/polymer MMMs as shown in **Figure 5.4e-g**, which can be ascribed to the lower loading (wt.%) of MIL-101(Cr) in IL/MOF composite incorporated into the Pebax to form the MMMs. Moreover, the intersegmental distance, known as d -spacing, between the polymer chains was also calculated from Bragg's equation for all the MMMs synthesized in this work. The results are presented in **Table A5-1**. As, it can be seen from the **Figure 5.4** the characteristic peaks of the Pebax showed no significant change in the 2 -theta values, therefore the d -spacing of the polymer chains in the MMMs showed slight changes. Moreover, the [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs showed smaller d -spacings values which can be attributed to the interactions of the [MPPyr][DCA]/MIL-101(Cr) composite with the polymer while MIL-101(Cr)/Pebax MMMs were characterized with slightly higher d -spacings values resulting in slightly high gas permeabilities.

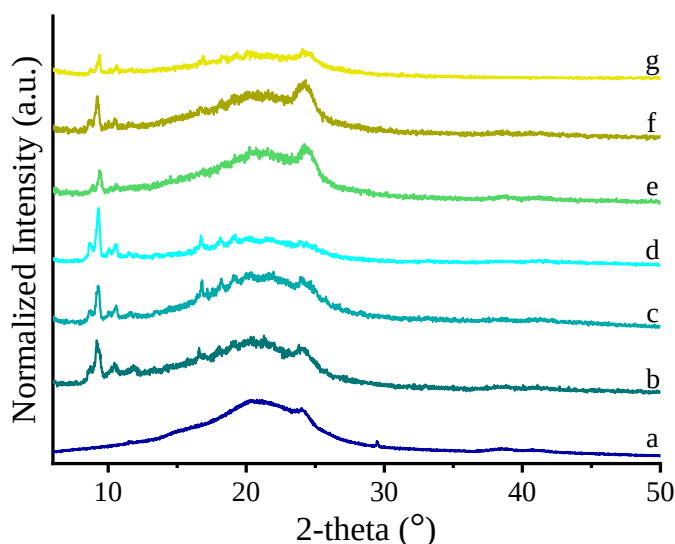


Figure 5.4. XRD spectra of membranes. Pure Pebax (a), MIL-101(Cr)/Pebax MMMs with 10 wt.% (b), 15 wt.% (c), 20 wt.% (d) MIL-101(Cr) loadings. [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with 10 wt.% (e), 15 wt.% (f), 20 wt.% (g) [MPPyr][DCA]/MIL-101(Cr) loadings.

The TGA curves of MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs at different filler loadings are shown in **Figure 5.5**. It was observed that decomposition temperature of MMMs did not have any noticeable difference and all displayed one-step decomposition mechanism. Accordingly, the weight loss observed at approximately 350 and 360 °C in the TGA curves of MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs, respectively, indicated the decomposition of the polymer backbone present in the MMMs. A slight increase (higher than the error range of the measurements, ± 5 °C) in the decomposition temperature of IL/MOF/polymer MMMs as compared to MIL-101(Cr)/Pebax MMMs indicated a slight improvement in the thermal stability of MMMs, most probably associated with the incorporation of IL/MOF composite filler into the polymer [49]. Generally, none of the MMMs synthesized in this work show significant weight loss up to 340 °C, indicating a high thermal stability of the MMMs.

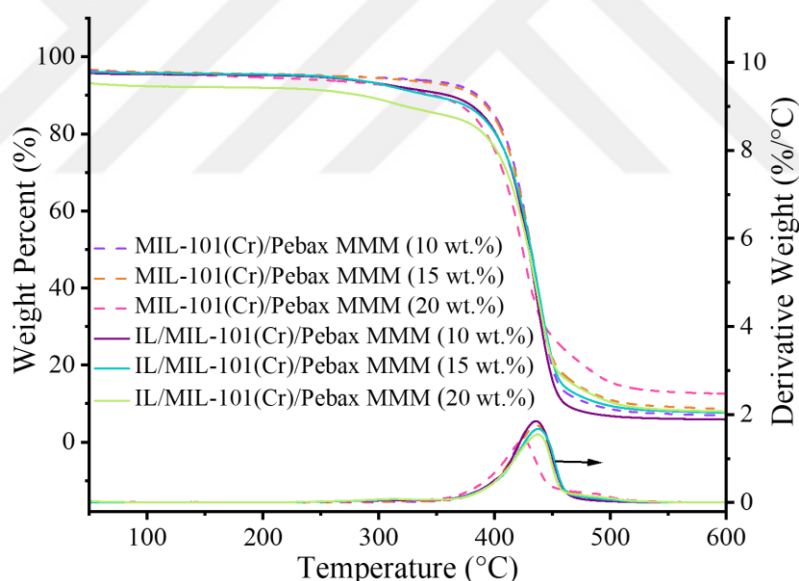


Figure 5.5. TGA and DTG curves of MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with 10 wt.%, 15 wt.% and, 20 wt.% MIL-101(Cr) loadings and [MPPyr][DCA]/MIL-101(Cr) composite loadings respectively.

FTIR spectra of pure Pebax, MIL-101(Cr)/Pebax MMMs, and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs are represented in **Figure 5.6a-g**. The IR spectrum represented as **Figure 5.6a**, corresponds to the pure Pebax membrane, showed the characteristic band of PEO segment at 1100 cm⁻¹ representing the $\nu(\text{C}-\text{O}-\text{C})$ group [50], whereas the peaks located at 1637, 1732, and 3297 cm⁻¹ belong to PA segment of

Pebax, attributed to the $\nu(\text{O}-\text{C}-\text{O})$ group, $\nu(\text{H}-\text{N}-\text{C}=\text{O})$ group [51], and $\nu(\text{N}-\text{H})$ group [52], respectively. The IR spectra of MMMs given in **Figure 5.6b-g** showed the similar characteristic IR peaks of Pebax. In the case of MIL-101(Cr)/Pebax MMMs having 10 wt.% MIL-101(Cr) loading, **Figure 5.6b**, the corresponding Pebax bands were located at 1080 cm^{-1} $\nu(\text{C}-\text{O}-\text{C})$, 1617 cm^{-1} $\nu(\text{O}-\text{C}-\text{O})$, 1726 cm^{-1} $\nu(\text{H}-\text{N}-\text{C}=\text{O})$, and 3295 cm^{-1} $\nu(\text{N}-\text{H})$. As the loading of MIL-101(Cr) was increased in the polymer matrix to 15 and 20 wt.% (**Figure 5.6c-d**), $\nu(\text{C}-\text{O}-\text{C})$ and $\nu(\text{O}-\text{C}-\text{O})$, exhibited red-shifts of 8 cm^{-1} in both peak positions and a red-shift of 7 cm^{-1} in $\nu(\text{H}-\text{N}-\text{C}=\text{O})$ band, representing the presence of MOF/polymer interaction. Moreover, new IR bands were observed at 575, 746, 1393 cm^{-1} are associated with the $\nu(\text{Cr}-\text{O})$, $\nu(\text{C}-\text{H})$, and $\nu(\text{COO})$ groups present in MIL-101(Cr) structure.

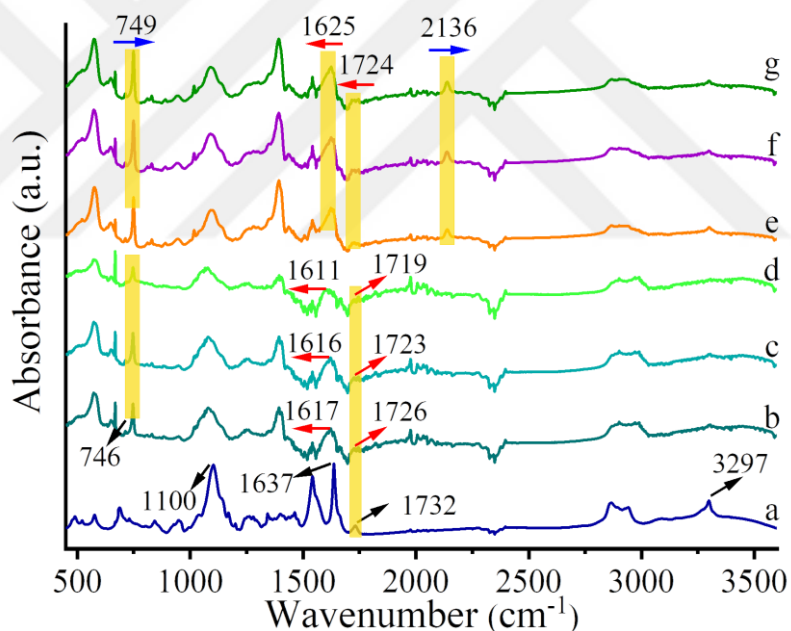


Figure 5.6. IR spectra of the membranes. Pure Pebax (a), MIL-101(Cr)/Pebax MMMs with 10 wt.% (b), 15 wt.% (c), 20 wt.% (d) MIL-101(Cr) loadings, and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with 10 wt.% (e), 15 wt.% (f), 20 wt.% (g) [MPPyr][DCA]/MIL-101(Cr) loadings.

The IR spectra of the IL/MOF/polymer MMMs are represented in **Figure 5.6e-g**, with characteristic Pebax peaks located at 1093 cm^{-1} $\nu(\text{C}-\text{O}-\text{C})$, 1625 cm^{-1} $\nu(\text{O}-\text{C}-\text{O})$, 1724 cm^{-1} $\nu(\text{H}-\text{N}-\text{C}=\text{O})$, and 3299 cm^{-1} $\nu(\text{N}-\text{H})$. Red-shifts of 7, 12, and 9 cm^{-1} were observed in $\nu(\text{C}-\text{O}-\text{C})$, $\nu(\text{O}-\text{C}-\text{O})$, and $\nu(\text{H}-\text{N}-\text{C}=\text{O})$ bands, respectively, whereas $\nu(\text{N}-\text{H})$ peak showed a slight blue-shift as compared to its position on the pure Pebax

membrane. However, with an increase in IL/MOF composite loadings, no significant changes in the IR bands of Pebax groups were observed (**Figure 5.6e-g**). The characteristic band corresponding to MIL-101(Cr) observed at 746 cm⁻¹ exhibited a slight blue-shift of 3 cm⁻¹ in the IR bands of IL-modified MMMs. The strong shifts in the peak positions of the polymer functional groups and the $\nu(\text{Cr-O})$ band present in [MPPyr][DCA]/MIL-101(Cr), are attributed to the strong interaction between the IL/MOF composite and Pebax polymer. Moreover, a new peak was also observed at 2136 cm⁻¹, corresponding to the $\nu(\text{C}\equiv\text{N})$ vibrations of [DCA]⁻ anion present in the IL. The corresponding peak showed a blue shift of 13 cm⁻¹ as compared to its position (2123 cm⁻¹) in [MPPyr][DCA]/MIL-101(Cr) composite spectra as shown in **Figure 5.2c**. The significant shift in the IL peak indicated the strong interactions present between the IL and the polymer matrix. To further validate these IL/polymer interactions, as discussed briefly above, we recorded the IR spectra of [MPPyr][DCA]/MIL-101(Cr) composite mixed in ethanol/water solution prior to membrane synthesis shown in **Figure 5A-1**. It was observed that the intensity of IL peaks in the sample after mixing in ethanol/water mixture solution were decreased. This can be attributed to the fact that the pore window of MIL-101(Cr) (~16 Å) is larger as compared to the size of solvent molecules, ethanol (4.5 Å) and water (2.3 Å) [53], which can enter the pores of MIL-101(Cr). Based on these results, it can be inferred that some of the IL molecules left the pores of MIL-101(Cr) and were freely dispersed in the polymer matrix during the membrane synthesis. Hence, the bulk [MPPyr][DCA] strongly interacted with the Pebax, which is consistent with the IR spectra of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs. Moreover, the presence of these IL molecules in the polymer matrix enhances the MIL-101(Cr)/polymer interfacial compatibility which can lead to improved gas separation performance of MMMs [47], discussed in the following section.

5.3.2 Separation Performances of the materials

5.3.2.1 Adsorption-based separation with MOF and IL/MOF composite

Volumetric gas uptakes of CO₂, N₂, and CH₄ in MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite were measured at 25 °C and 1 bar as shown in **Figure 5.7a**, to study the effect of IL incorporation on the gas separation performance of MIL-101(Cr). Adsorption isotherms were fitted to the dual-site Langmuir-Freundlich

(DSLFF) model to compare the separation performance of MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite and the corresponding fitting parameters were given in **Table 5A-1**. CO₂, N₂, and CH₄ uptakes of IL/MOF composite were less than the corresponding uptakes of pristine MIL-101(Cr). For instance, [MPPyr][DCA]/MIL-101(Cr) showed lower CH₄ and CO₂ uptakes of 0.02 and 0.91 cm³/g, respectively, as compared to pristine MIL-101(Cr), 0.28 and 1.59 cm³/g at 0.1 bar. These decreases in the gas adsorption uptakes were ascribed to the incorporation of IL in the pores of MIL-101(Cr) resulting in reduced surface area and pore volume of the [MPPyr][DCA]/MIL-101(Cr) composite. Moreover, the N₂ uptakes in the IL/MOF composite at a low-pressure of 0.1 bar were slightly higher than the detection limit of the equipment. The COSMO-RS calculations performed at 25 °C in a pressure range of 0.1 to 1 bar (**Figure 5A-5**) demonstrated that N₂ solubility in the [MPPyr][DCA] is almost negligible at low pressures as compared to the significantly high CO₂ solubility, therefore, at low pressures the N₂ uptakes of the [MPPyr][DCA]/MIL-101(Cr) composite are critically low.

Based on the gas adsorption isotherms, ideal CO₂/N₂, CO₂/CH₄, and CH₄/N₂ selectivities of pristine MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite were determined up to 1 bar, as shown in **Figure 5.7b** and **c**, respectively. Adsorption selectivity data illustrated that separation performance of [MPPyr][DCA]/MIL-101(Cr) composite was significantly higher than the pristine MIL-101(Cr), especially at low-pressure region. Upon the incorporation of IL, ideal CO₂/N₂ and CH₄/N₂ selectivity of MIL-101(Cr) increased from 17.9 to 64173.1 and from 3.1 to 1874.1, respectively, at 0.1 bar, 25 °C, which corresponds to approximately 3600- and 600-times selectivity improvement for the MOF upon the IL incorporation. In the case of CO₂/CH₄, on the other hand, IL/MOF composite showed six-times improvement with the corresponding selectivity of 34.2 at 0.1 bar. Moreover, the data further demonstrate that [MPPyr][DCA]/MIL-101(Cr) composite offers practically infinite selectivity for CO₂/N₂ and CH₄/N₂ at 0.001 bar as shown in **Figure 5.7c**. Comparison of these adsorption selectivity results with other IL/MOF composites reported in the literature is given in **Table 5A-2** which shows that [MPPyr][DCA]/MIL-101(Cr) composite has exceptionally high adsorption selectivities for CO₂/N₂, CO₂/CH₄, and CH₄/N₂, especially at low pressures, outperforming other reported IL/MOF composites.

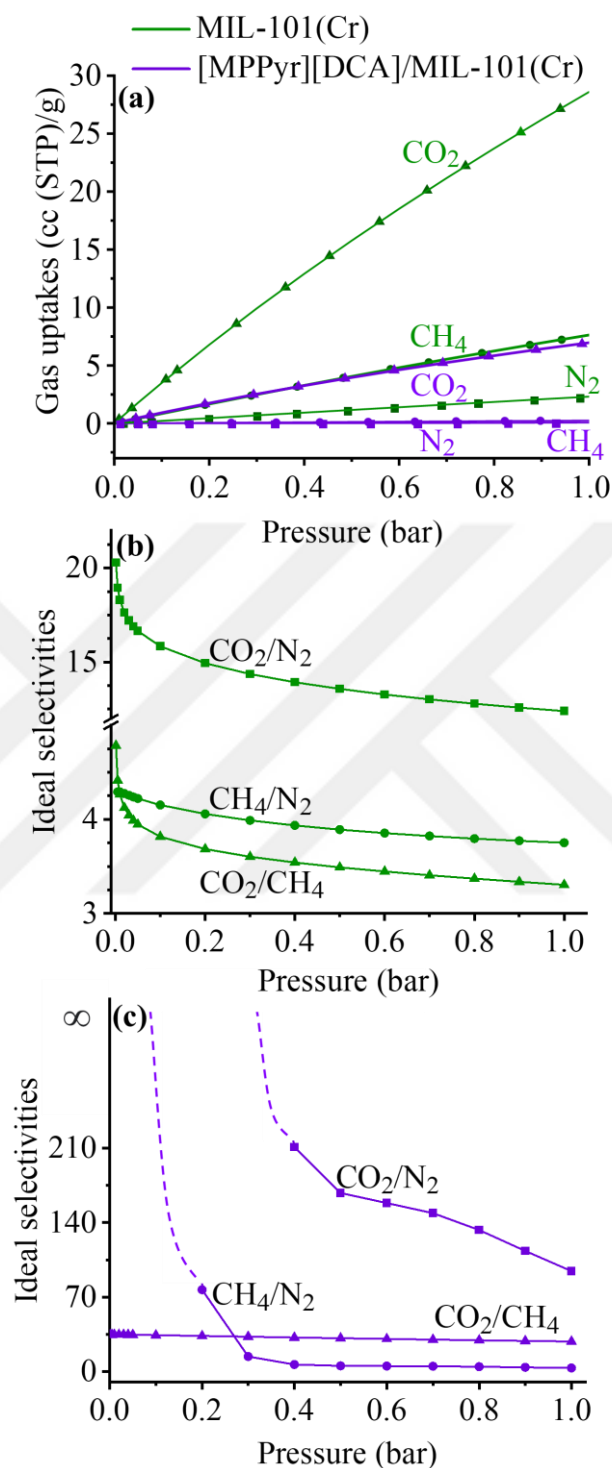


Figure 5.7. (a) Gas adsorption uptakes of MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite, (b) ideal adsorption selectivities of MIL-101(Cr), (c) ideal adsorption selectivities of [MPPyr][DCA]/MIL-101(Cr) composite. The dotted lines in (c) represent practically infinite selectivities as the N₂ uptakes becomes unmeasurable at these pressures.

Furthermore, decreases in CO₂/N₂, CO₂/CH₄, and CH₄/N₂ selectivities of [MPPyr][DCA]/MIL-101(Cr) were observed with an increase in pressure. For instance, at 1 bar, CO₂/N₂, CO₂/CH₄, and CH₄/N₂ selectivities of [MPPyr][DCA]/MIL-101(Cr) composite were measured as 9.4, 28.3, and 3.3, respectively. The decrease in gas uptakes with increasing pressure is attributed to the fact that, at high pressures, gas adsorption is dependent on the available pore volume of the material. However, in the case of low-pressure region, interactions between the adsorbent and the gas molecules become the dominant factor [54]. Therefore, as the adsorption mechanism is changed from surface affinity to pore availability at high pressure, CO₂/N₂, CO₂/CH₄, and CH₄/N₂ selectivities of [MPPyr][DCA]/MIL-101(Cr) composite decreases. Overall, [MPPyr][DCA]/MIL-101(Cr) composite is highly CO₂ selective in adsorption-based separations especially at low pressures (as demonstrated in **Table 5A-3**), thus it offers a broad potential as a filler to boost the separation performance of a polymer membrane.

5.4.2.2 Membrane-based separation with MOF/polymer and IL/MOF/polymer MMMs

Permeability measurements of CO₂, N₂, and CH₄ were carried out at 1 bar and 35 °C, and the corresponding CO₂/N₂ and CO₂/CH₄ ideal selectivities were determined for MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs. **Figure 5.8a, b, and c** showed CO₂ permeabilities, CO₂/N₂ and CO₂/CH₄ permeation selectivities, respectively, of the MMMs having different loadings of MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite. Moreover, the CO₂, N₂, and CH₄ permeability data, CO₂/N₂ and CO₂/CH₄ selectivity data are also given in **Table 5A-3**. Pure Pebax membrane has CO₂, N₂, and CH₄ permeabilities of 134.6±2.1, 4.2±0.5, and 10.9±1.3 Barrer, respectively, with CO₂/N₂ and CO₂/CH₄ selectivities of 31.8±1.7 and 12.3±1.4, respectively. For MIL-101(Cr)/Pebax MMM having 10 wt.% MIL-101(Cr) loading, CO₂, N₂, and CH₄ permeabilities were measured as 146.0±1.1, 0.9±0.8, and 6.6±1.3 Barrer, respectively. The corresponding CO₂/N₂ and CO₂/CH₄ selectivities were calculated as 162.2±20.7 and 22.1±4.6, respectively. As the loading of MIL-101(Cr) in MMM was increased to 15 wt.%, CO₂ and CH₄ permeabilities slightly increased to 153.0±8.4 and 9.6±0.1 Barrer, respectively, with a further decrease in N₂ permeability to 0.5±0.02 Barrer, leading to CO₂/N₂ and CO₂/CH₄ selectivities of 300.0±40.5 and 15.9±0.9, respectively. These results demonstrated that MIL-101(Cr) filler increased the CO₂

permeability of pure polymer, however, N₂ permeability was significantly decreased, resulting in enhanced CO₂/N₂ selectivity. Overall, MIL-101(Cr)/Pebax MMMs with 10 wt.% filler loading exhibited 5.4-times (1.7-times) improvement in CO₂/N₂ (CO₂/CH₄) selectivity, and the MOF/polymer MMM with 15 wt.% loading showed 10-times (1.2-times) improvement in CO₂/N₂ (CO₂/CH₄) selectivity as compared to pure Pebax. Such improvement in CO₂/N₂ and CO₂/CH₄ selectivities of the MIL-101(Cr)/Pebax MMM can be attributed to the presence of unsaturated Cr(III) sites in MIL-101(Cr) structure offering strong affinity towards CO₂ [38, 39].



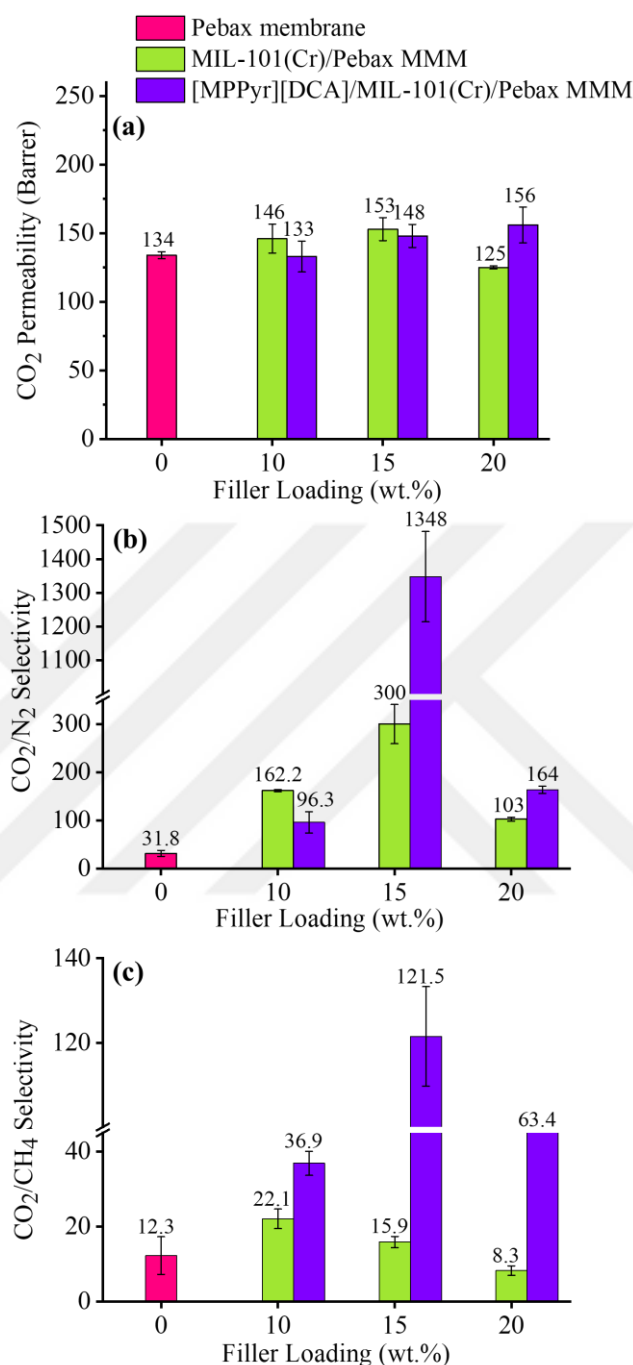


Figure 5.8. (a) CO₂ permeability, (b) CO₂/N₂ selectivity, (c) CO₂/CH₄ selectivity of MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with 10, 15, and 20 wt.% MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) loadings, measured at 1 bar and 35 °C.

The CO₂ permeabilities and CO₂/CH₄ selectivities of MIL-101(Cr)/Pebax MMMs obtained in this study are comparable to literature, however, CO₂/N₂ selectivities of MIL-101(Cr)/Pebax MMMs were found to be superior compared to the other MOF/Pebax

MMMs reported in the literature. For example, ZIF-8/Pebax MMM having 15 wt.% ZIF-8 loading was reported to have a CO₂ permeability of 100 Barrer at 23 °C and 1 bar [55]. MIL-101(Cr)/Pebax MMM that is presented in this work has an approximately 1.5-times higher permeability (153 Barrer) than ZIF-8/Pebax MMM. The CO₂/N₂ selectivity of MIL-101(Cr)/Pebax MMM was 8.5-times higher (71) than reported CO₂/N₂ selectivity (35) of ZIF-8/Pebax MMM with no significant difference in CO₂/CH₄ selectivities. CO₂ permeability and CO₂/CH₄ selectivity of MIL-101(Cr)/Pebax MMM having 15 wt.% MIL-101(Cr) loading was almost the same as BIT-72/Pebax MMM reported in literature at 25 °C and 10 bar [56], however, CO₂/N₂ selectivity was observed to be 5.3-times higher, compared to the highest reported CO₂/N₂ selectivity (56) of BIT-72/Pebax MMM. A more detailed comparison of the synthesized MIL-101(Cr)/Pebax MMMs with the previously reported literature is given in **Table 5A-4** which shows the superior CO₂/N₂ selectivity of MIL-101(Cr)/Pebax MMMs having 10 and 15 wt.% MIL-101(Cr) loadings.

In the case of IL/MOF/polymer MMMs, the separation performance of Pebax membrane was further enhanced with the incorporation of IL/MOF composite. At 10 wt.% [MPPyr][DCA]/MIL-101(Cr) loading, CO₂, N₂, and CH₄ permeabilities were measured as 133.0±11.2, 1.38±0.2, and 3.6±0.3 Barrer, respectively. Based on these results, the corresponding CO₂/N₂ and CO₂/CH₄ selectivities were calculated as 96.3±21.8 and 36.9±3.2, respectively. As the loading of [MPPyr][DCA]/MIL-101(Cr) composite in the MMM was increased to 15 wt.%, CO₂ permeability slightly increased to 148.2±8.4, with a further decrease in CH₄ and N₂ permeabilities to 1.2±0.08 and 0.1±0.02 Barrer, respectively, leading to CO₂/N₂ and CO₂/CH₄ selectivities of 1347±134 and 121.5±11.8, respectively. Incorporation of IL/MOF composite into the polymer slightly changed the CO₂ permeability, however, CH₄ and N₂ exhibited poor permeabilities, resulting in a significant boost in the CO₂/CH₄ and CO₂/N₂ selectivities. Overall, [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs with 10 wt.% [MPPyr][DCA]/MIL-101(Cr) composite loading exhibited 3.2-times (3-times) improvement in CO₂/N₂ (CO₂/CH₄) selectivity, and with 15 wt.%, the corresponding CO₂/N₂ (CO₂/CH₄) selectivity showed 42-times (9.8-times) improvement compared to the pure Pebax. Moreover, the [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs having 15 wt.% IL/MOF loading also showed 4.4-times (7.6-times) higher CO₂/N₂ (CO₂/CH₄) selectivity compared to the MIL-101(Cr)/Pebax MMM having 15 wt.% MIL-101(Cr) loading. The ideal CH₄/N₂ selectivities were also computed

for pure Pebax, MIL-101(Cr)/Pebax MMMs, and [MPPyr][DCA]/MIL-101(Cr)/Pebax MM as 2.42 ± 1 , 6.79 ± 1.1 , and 11.9 ± 2 .

To compare the separation performance of the best performing IL/MOF/polymer MMM, an IL/polymer MMM and an MMM with free-IL and free-MOF at an identical filler loading (15 wt.%) were synthesized and tested for CO₂/N₂ and CO₂/CH₄ separation (**Table 5A-3**). In the case of IL/polymer MMM, CO₂, N₂, and CH₄ permeabilities were measured as 146.1 ± 7.3 , 1.7 ± 0.4 , and 2.1 ± 0.4 Barrer, respectively, with the corresponding CO₂/N₂ and CO₂/CH₄ selectivities of 85.9 ± 23.4 and 69.5 ± 15.8 , respectively. On the other hand, for free-IL/free-MOF/polymer MMM, the CO₂, N₂, and CH₄ permeabilities were measured as 129.4 ± 8.1 , 0.4 ± 0.2 , and 2.08 ± 0.5 Barrer, respectively. The corresponding CO₂/N₂ and CO₂/CH₄ selectivities were calculated as 323.5 ± 69.7 and 62.2 ± 10.9 , respectively. The IL/MOF/polymer MMM having 15 wt.% IL/MOF composite as a filler showed 4.1- and 1.9-times higher CO₂/N₂ and CO₂/CH₄ selectivity, respectively, as compared to the MMM which have free-IL and free-MOF as filler.

The exceptionally high gas separation performance of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs that we present here can be attributed to the superior solubility of CO₂ in the [MPPyr][DCA], and interactions between IL and CO₂ molecules over N₂ and CH₄. Moreover, IL incorporation into MIL-101(Cr) resulted in reduced pore size of IL/MOF composite compared to pristine MOF, leading to improved molecular sieving effect [28]. The permeability is the physical property of the polymer therefore, the CO₂ permeability of all the MMMs is not observed to be increased. Moreover, it was also observed that by the addition of the filler to the polymer matrix, the d-spacing of the membranes does not change significantly, as a result the permeabilities of the gases were slightly improved [57, 58]. In contrast, the dramatic increases in CO₂/N₂ selectivities of MMMs compared to pure polymer were attributed to very poor solubility of N₂ in the bulk [MPPyr][DCA], which is supported by the Conductor-like Screening Model for Realistic Solvents (COSMO-RS) calculations. The gas adsorption experiments performed for MIL-101(Cr)/[MPPyr][DCA] composite presented in **Figure 5.7** also demonstrated significantly low N₂ uptakes. Therefore, low N₂ permeability of the MIL-101(Cr)/[MPPyr][DCA]/Pebax MMM resulted in high CO₂/N₂ selectivity. As discussed in the characterization section, the addition of [MPPyr][DCA] boosted the IL/polymer and IL/MOF interfacial interactions which resulted in improved gas separation

performance of MMMs. Moreover, a decrease in the separation performance of the MMMs was observed when the filler loading was increased beyond 15 wt.%, which was also observed in previous studies [59, 60]. This can be attributed to the reduced compatibility between the filler and the polymer at higher loadings and agglomeration of the filler particles [15, 61].

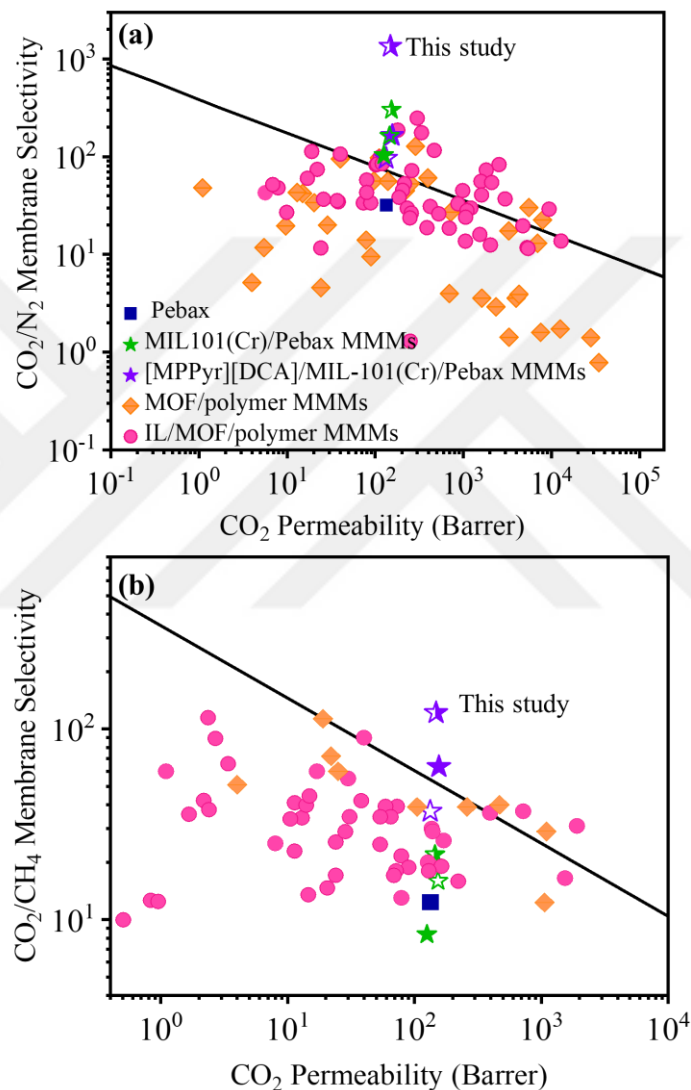


Figure 5.9. (a) Comparison of CO₂/N₂ selectivity, (b) CO₂/CH₄ selectivity and CO₂ permeability of MMMs synthesized in this study with the literature data. The line represents the Robeson's upper bound [3]. The open star represents 10 wt.% filler loading, half closed, and fully closed stars represent 15 wt.% and 20 wt.% filler loading, respectively. Details of the data shown in this figure are reported in Table 5A-4.

CO₂ permeabilities of the MMMs along with their CO₂/N₂ and CO₂/CH₄ selectivities were compared with the Robeson's upper bound as shown in **Figure 5.9a** and **b**, respectively. The gas separation performances of MIL-101(Cr)/Pebax MMMs and

[MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs were shown together with the literature data of MOF/polymer MMMs and IL/MOF/polymer MMMs collected under different conditions of temperature and pressure as given in **Table 5A-4**. MIL-101(Cr)/Pebax MMMs and [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs outperformed the Robeson's upper bound (2008) and previously reported membranes for CO₂/N₂ separation at all loadings. Similarly, in the case of CO₂/CH₄ upper bound (**Figure 5.9b**), [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs having 15 and 20 wt.% [MPPyr][DCA]/MIL-101(Cr) provide superior CO₂/CH₄ selectivity and acceptable CO₂ permeability leading them to surpass the upper bound limit.

Next, we compared the separation performance of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMM with IL/MOF/Pebax MMMs that have been reported in the literature and presented in **Figure 5.9**. For example, [BMIM][TF₂N]/ZIF-8/Pebax MMM having 15 wt.% ZIF-8 loading was reported to have CO₂ permeability of 105 Barrer and CO₂/N₂ selectivity of 84.5 at 1 bar and 25 °C [29]. The [MPPyr][DCA]/MIL-101(Cr)/Pebax having 15 wt.% [MPPyr][DCA]/MIL-101(Cr) that was synthesized in this work showed 1.4- and 16-times improved CO₂ permeability (148 Barrer) and CO₂/N₂ selectivity (1347), respectively, than [BMIM][Tf₂N]/ZIF/Pebax MMM with no significant difference in CO₂/CH₄ selectivities.

[MPPyr][DCA]/MIL-101(Cr)/Pebax MMM having 15 wt.% of filler loading was also compared with the [BMIM][PF₆]/ZIF-8/Pebax MMMs reported at 3 bar and 35 °C [62]. It was observed that the CO₂ permeability and CO₂/N₂ selectivity of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMM was 1.2- and 15.8-times higher compared to the best performing [BMIM][PF₆]/ZIF-8/Pebax having CO₂ permeability of 120 Barrer and CO₂/N₂ selectivity of 85. **Table 5A-4** showed that CO₂/N₂ selectivities of [MPPyr][DCA]/MIL101(Cr)/Pebax MMMs presented in this study, especially with 15 wt.% [MPPyr][DCA]/MIL101(Cr) loading, are superior to all the literature data reported up to date. In view of these comparisons, the selectivity data reported here set a new benchmark for CO₂/N₂ separation, demonstrating a broad potential of incorporating pyrrolidinium-based IL/MOF composites in polymers to fabricate IL/MOF/polymer MMMs. The results will significantly contribute to the literature of MMMs for accelerating the design and development of new IL/MOF/polymer MMMs in near future.

The reproducibility of the separation results was confirmed by synthesizing the

MMMs several times to obtain different batches of the same membrane, which were then tested under identical conditions, and the separation performances of each batch were compared with each other. Moreover, for the long-term stability test of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMM given in **Figure 5.10**, we synthesized the MMM from scratch, and it was observed that the results are in the error range of what we reported in the gas permeation results with a different batch of the MMM. The long-term gas separation performance of the [MPPyr][DCA]/MIL-101(Cr)/Pebax MMM with 15 wt.% [MPPyr][DCA]/MIL-101(Cr) loading was also investigated up to 75 h to evaluate the stability of the membrane under continuous operating conditions. Data presented in **Figure 5.10** showed that the data fluctuated within a narrow range having CO₂ permeability of 151 ± 5.9 Barrer with corresponding average CO₂/N₂ and CO₂/CH₄ selectivities of 1298 ± 208 and 116 ± 9.7 , respectively. The results showed a good long-term working stability of IL/MOF/polymer MMM synthesized in this work, making it a promising gas separation material.

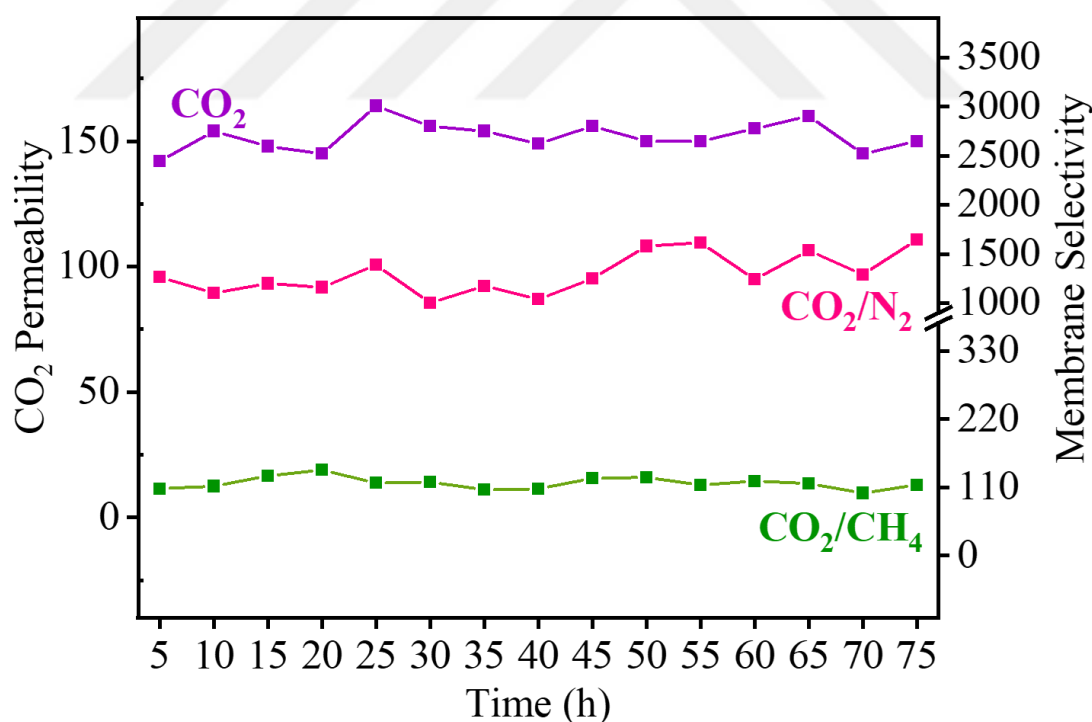


Figure 5.10. Long-term stability test of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMM with 15 wt.% [MPPyr][DCA]/MIL-101(Cr) loading.

5.4 Conclusions

In this chapter of thesis, we combined the highly CO₂-selective MIL-101(Cr) and a pyrrolidinium-based IL, 1-methyl-1-propyl pyrrolidinium dicyanamide ([MPPyr][DCA]), to prepare a novel IL/MOF composite which showed excellent CO₂/N₂, CO₂/CH₄ and CH₄/N₂ adsorption selectivities. The [MPPyr][DCA]/MIL-101(Cr) composite was incorporated into Pebax to generate [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs for attaining exceptional CO₂/N₂ and CO₂/CH₄ separation performances. At 15 wt.% [MPPyr][DCA]/MIL-101(Cr) loading, the MMM showed an improved CO₂ permeability of 148 Barrer with significantly higher CO₂/N₂ (1347) and CO₂/CH₄ (121.5) ideal selectivity as compared to the pure Pebax having a CO₂ permeability of 134 Barrer with CO₂/N₂ and CO₂/CH₄ selectivities of 31.8 and 12.3, respectively. The CO₂/N₂ and CO₂/CH₄ selectivities of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMM having 15 wt.% [MPPyr][DCA]/MIL-101(Cr) loading was observed to be 42- and 9.8-times higher than the pure Pebax membrane and significantly superior to all other IL/MOF/polymer MMMs reported in the literature. All the [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs that we synthesized in this work were found to be located above the Robeson's upper bound for CO₂/N₂ separation. Results showed the outstanding performance of [MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs, especially for CO₂/N₂ separation. Considering the existence of a large number and variety of ILs, MOFs, and polymers, our results will contribute significantly into the literature of new IL/MOF/polymer MMMs for various gas separations by setting a new benchmark for CO₂/N₂ selectivity.

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APPENDIX 5A

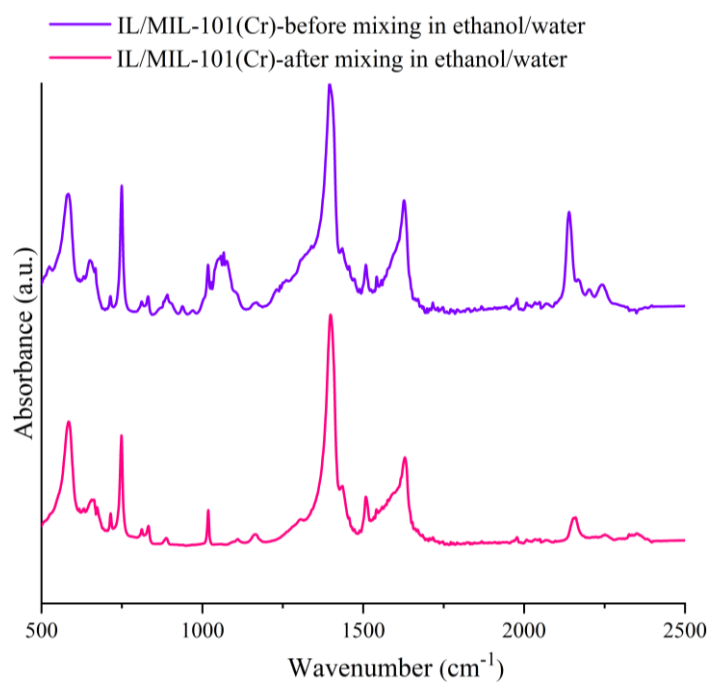


Figure 5A-1. The IR spectra of [MPPyr][DCA]/MIL-101(Cr) composite before and after mixing in ethanol/water mixture for MMM synthesis.

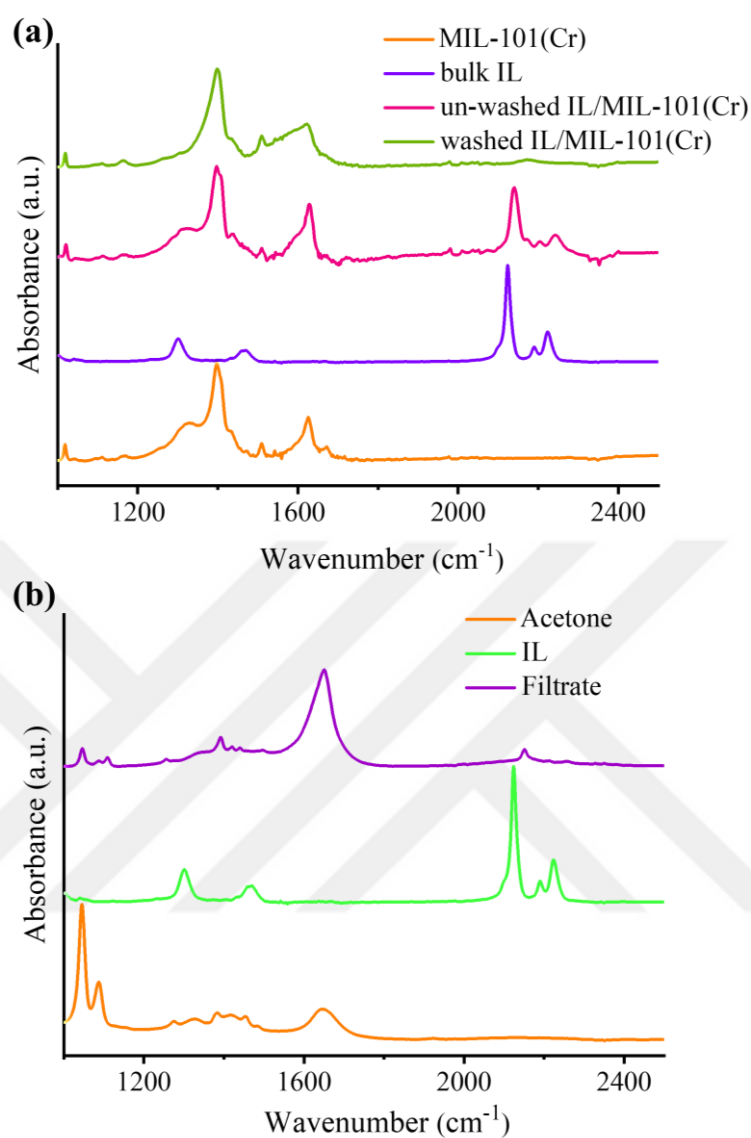


Figure 5A-2. IR spectra of pristine MIL-101(Cr), [MPPyr][DCA], and [MPPyr][DCA]/MIL-101(Cr) before and after washing with acetone. (a) [MPPyr][DCA]/MIL-101(Cr) samples before and after washing with acetone solvent, (b) filtrate obtained after the washing of [MPPyr][DCA]/MIL-101(Cr) with acetone.

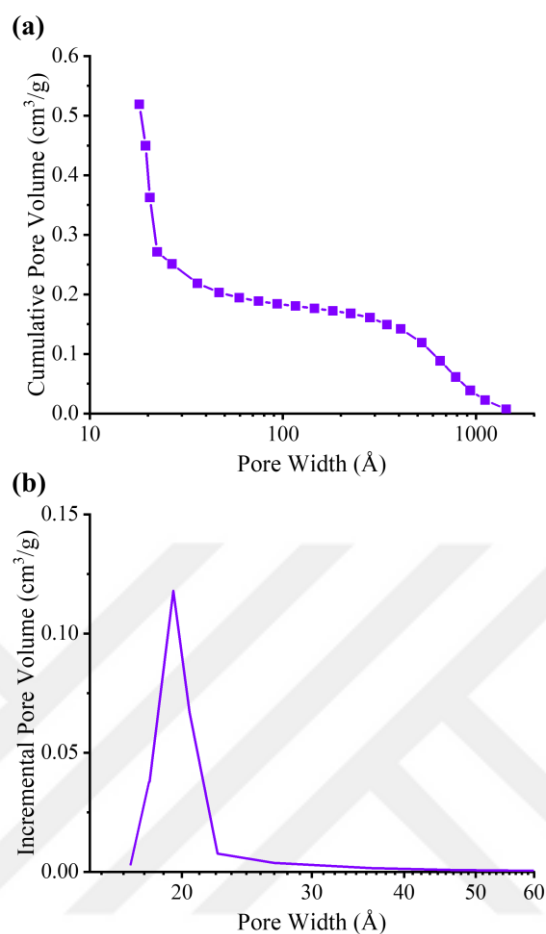


Figure 5A-3. (a) Cumulative and (b) incremental pore volumes of pristine MIL-101(Cr) with respect to the pore width of the porous materials. Pore widths are given in logarithmic scale.

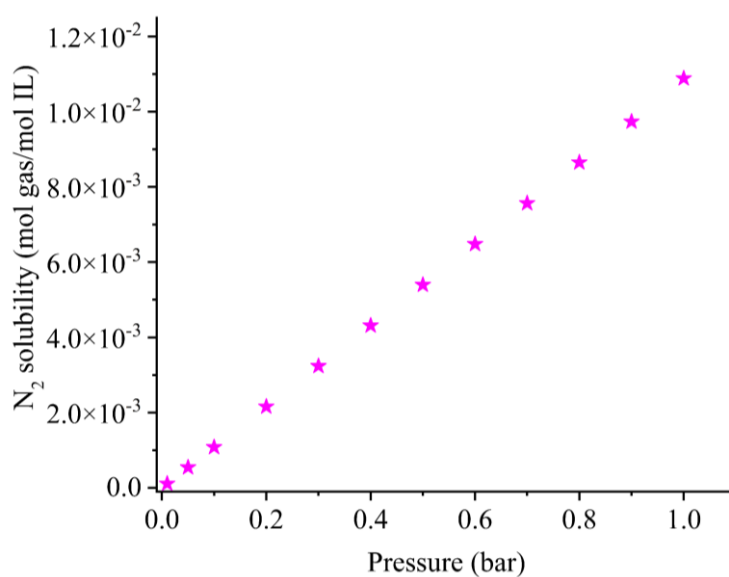


Figure 5A-4. The COSMO-RS solubility data of N₂ in bulk [MPPyr][DCA] calculated at 78 K between 0.1-1 bar.

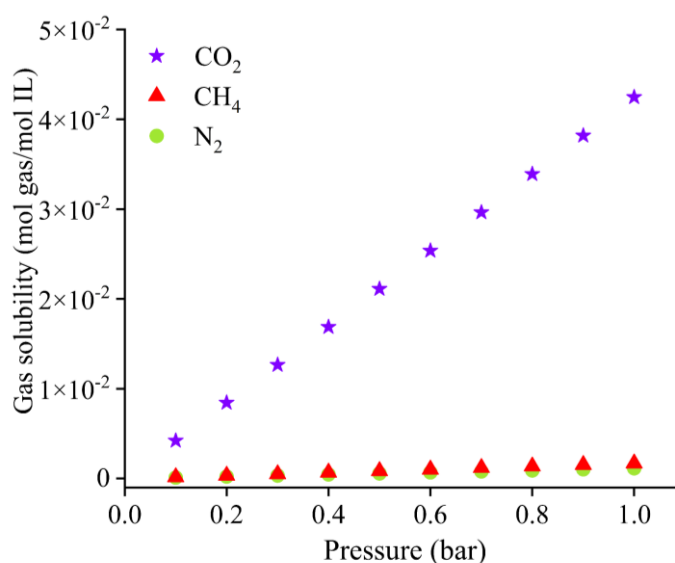


Figure 5A-5. The solubility of CO₂, CH₄, and N₂ in bulk [MPPyr][DCA] was calculated by COSMO-RS calculations at 25 °C between 0.1-1 bar.

Table 5A-1. Dual-site Langmuir-Freundlich fit parameter for pristine in MIL-101(Cr) and [MPPyr][DCA]/MIL-101(Cr) composite.

	Dual-site Langmuir-Freundlich Model							
	Gas	q ₁ (cc/g)	k ₁ (1/mbar)	n ₁ *	q ₂ (cc/g)	k ₂ (1/mbar)	n ₂ *	R ²
MIL-101(Cr)	CO ₂	7.6×10 ⁻¹⁵	1.7×10 ⁻¹⁷	4.1×10 ⁻⁷	157.6	0.21	0.99	0.99
	N ₂	2.55	0.17	0.82	9.30	0.31	1.23	0.99
	CH ₄	33.77	0.16	1.31	16.51	0.40	0.97	0.99
[MPPyr][DCA]/ MIL-101(Cr)	CO ₂	1235.8	0.003	1.54	30.5	0.27	0.96	0.99
	N ₂	0.26	0.73	4.96	0.02	2.60	5.62	0.99
	CH ₄	166.3	0.001	0.96	10 ⁴	0.002	3.00	0.99

Table 5A-2. Comparison of IL/MOF composites reported in the literature for adsorption-based gas separation applications.

IL/MOF composites	Pressure (bar)	Ideal Selectivities		
		CO ₂ /CH ₄	CO ₂ /N ₂	CH ₄ /N ₂
Pristine MIL-101(Cr) (This study)	0.001	5.8	20.62	3.5
	0.01	5.8	19.4	3.3
	1	4.7	13.9	2.9
[MPPyr][DCA]/MIL-101(Cr) (This study)	0.001	34.4	Infinite	Infinite
	0.01	34.7	Infinite	Infinite
	1	28.9	94.4	3.3
Pristine UiO-66[1]	0.01	6.8	28.5	4.3
[BMPyr][DCA]/UiO-66	0.01	8.2	10 ⁶	10 ⁶
[BMPyr][DCA]/UiO-66	1	4.1	32.7	8.1
Pristine ZIF-8[2]	0.001	2.7	7.2	2.8
	0.1	2.2	6.5	2.7
[BMIM][PF ₆]/ZIF-8[2]	0.1	8.9	24.2	2.8
[BMIM][BF ₄]/ZIF-8[3]	0.1	4.3	14.6	3.4
[BMIM][SCN]/ZIF-8[4]	0.01	6.5	21.2	2.2
[BMIM][MeSO ₃]/ZIF-8[5]	0.01	1.7	19.1	11.3
[BMIM][OcSO ₄]/ZIF-8[5]	0.01	4.7	2.6	0.53
[BMIM][OAc]/ZIF-8[6]	0.1		92	
[EMIM][OAc]/ZIF-8[6]	0.1		105	
[HEMIM][DCA]/ZIF-8[6]	0.01	110		
[C ₂ MIM][Ac]/ZIF-8[6]	0.5	3.3		
[C ₁₀ MIM][NTf ₂]/ZIF-8[6]	0.5	3.1		
[C ₆ MIM][NTf ₂]/ZIF-8[6]	0.5	2.6		
[BzMIM][NTf ₂]/ZIF-8[6]	0.5	2.6		
[C ₆ MIM][DCA]/ZIF-8[6]	0.5	3.1		

[C ₆ MIM][C(CN) ₃]/ZIF-8[6]	0.5	2.6		
[C ₆ MIM][Cl]/ZIF-8[6]	0.5	3		
Pristine CuBTC [7]	0.01	4.6	17.6	3.7
[BMMIM][PF ₆]/CuBTC[7]	0.01	5.2	23.1	4.4
[EMIM][DEP]/CuBTC[7]	0.01	7.27	42.3	5.8
[BMIM][NTF ₂]/CuBTC[8]	0.01	3.2	13.1	3.8
[BMIM][CF ₃ SO ₃]/CuBTC[9]	0.01	4.14	19.4	4.5
[BMIM][BF ₄]/CuBTC[9]	0.01	4.6	21.1	4.7
[BMIM][MESO ₄]/CuBTC[9]	0.01	4.4	21.8	4.9
[BMIM][SBF ₆]/CuBTC[9]	0.01	5.5	25.7	4.4
[BMIM][OC(SO ₄)]/CuBTC[9]	0.01	5.4	26.7	5.0
[BMIM][MESO ₃]/CuBTC[9]	0.01	5.6	27.1	4.8
[BMIM][SCN]/CuBTC[9]	0.01	5.7	29.6	5.2
[BMIM][OC(SO ₄)]/CuBTC[9]	0.01	5.4	26.7	5.0
Pristine UiO-66	0.01	6.8	28.5	4.3
[BMPyrr][DCA]/UiO-66	0.01	8.2	10 ⁶	10 ⁶
[BMPyrr][DCA]/UiO-66	1	4.1	32.7	8.1

Table 5A-3. Data of gas permeability and ideal selectivity of membranes having different filler loadings at 35 °C and 1 bar.

Membrane Type	Filler Loading (wt.%)	Permeability (Barrer)			Selectivity CO ₂ /N ₂	Selectivity CO ₂ /CH ₄
		CO ₂	CH ₄	N ₂		
Pure Pebax	0	134.0±2.1	10.9±1.3	4.2±0.5	31.8±1.7	12.3±1.4
MIL-101(Cr)/Pebax MMMs	10	146.0±1.1	6.6±1.3	0.9±0.8	162.2±20.7	22.1±4.6
	15	153.0±8.4	9.6±0.1	0.5±0.02	300±40.5	15.9±0.9
	20	125.0±1.1	15±2.35	1.2±0.06	103±3.9	8.3±1.2
[MPPyr][DCA]/MIL-101(Cr)/Pebax MMMs	10	133.0±11.2	3.6±0.3	1.3±0.2	96.3±21.8	36.9±3.2
	15	148.0±8.4	1.2±0.08	0.1±0.02	1347±134	121.5±11.8
	20	156.0±13.1	2.4±0.04	0.9±0.03	164±7.5	63.4±6.2
[MPPyr][DCA]/Pebax MMM	15	146.1±7.3	2.1±0.41	1.7±0.4	85.9±23.4	69.5±15.8
Free-IL/free-MOF/Pebax MMM	15	129.4±8.1	2.08±0.5	0.4±0.2	322.5±69.7	62.2±10.9

Table 5A-4. Comparison with the literature data plotted on Figure 5.9.

Membrane types	Loading (wt.%)	P _{CO2} (Barrer)	Selectivity CO ₂ /N ₂	Selectivity CO ₂ /CH ₄	Conditions
MOF/Polymer MMMs					
UiO-66/PMMA [10]	15	1.1	55	60	25 °C, 4 bar
UiO-66/Pebax [11]	10	96.3	56.5	-	25 °C, 3 bar
UiO-66/PEI [12]	15	30	-	55	35 °C, 1 bar
UiO-66-NH ₂ /6FDA-durene [13]	20	1540	15.9	16.5	35 °C, 1 bar
UiO-66-NH ₂ /6FDA-DAM [14]	14	1914	-	31	35 °C, 2 bar
UiO-66/PIM-1 [15]	10	6981	16	10	25 °C, 4 bar
UiO-66-NH ₂ /PES [16]	20	28.7	20	-	25 °C, 1 bar
Azo-UiO-66/Matrimid 5218 [17]	20	15	42	-	35 °C, 4 bar
CuBTC/Matrimid [18]	20	20.2	33.8	-	35 °C, 1 bar
NH ₂ -CuBTC/Matrimid [18]	20	13	43	-	35 °C, 1 bar
NH ₂ -MIL101(Cr)/Matrimid [19]	7	17	-	60	35 °C, 10 bar

CuBTC/PPO [20]	10	79	14	13	30 °C, 1 bar
HKUST-1/Pebax [21]	15	128	-	20	30 °C, 3 bar
NH ₂ -CuBTC/Pebax [21]	20	170	-	26	30 °C, 3 bar
CuBTC/PSf [22]	10	8	22.3	25.1	30 °C, 5 bar
ZIF-7/Pebax 1657 [23]	22	137(JPU)	97	30	20 °C, 6 bar
ZIF-90/PI [24]	15	720	-	37	25 °C, 1 bar
MIL-53(Al)/Matrimid [25]	37.5	40	95	90	35 °C, 2 bar
NOTT-300/Pebax 1657 [26]	40	395	61	36.3	35 °C, 5 bar
BIT-72/Pebax 1657 [27]	30	139	56	31	35 °C, 5 bar
CuBTC/Pebax	15	286	128.8	-	35 °C, 1 bar
MIL-101(Cr)/Pebax MMMs (This study)	10	146±0.78	162.2±20	22±4.6	35 °C, 1 bar
	15	153.5±8.4	300±40.5	15.9±0.9	35 °C, 1 bar
	20	125±1.1	103±3.9	8.3±1.2	35 °C, 1 bar
IL/MOF/Polymer MMMs					
[EMIM][NTF ₂]/HKUST-1/6FDA–durene [28]	10	1100	27	29	25 °C, 2 bar
[EMIM][B(CN) ₄]/ZIF-8/[Poly[vbim]][NTf ₂] [29]	25.8	1062	24	12.3	35 °C, 3.5 bar
[BMIM][NTF ₂]/ZIF-8/PSF[30]	6	468	116	40	30 °C, 6 bar
[C ₃ NH ₂ BIM][NTF ₂]/NH ₂ -MIL-101(Cr)/PIM-1 [31]	5	2979	37	-	25 °C, 3 bar
[BMIM][NTF ₂]/ZIF-8/Pebax 1657 [32]	15	105	84	39	25 °C, 1 bar
[BMIM][NTF ₂]/MOF-801/PIM [33]	5	9420	29	-	35 °C, 4 bar
[BMIM][PF ₆]/ZIF-8/Pebax 1657 [34]	30	120	85	-	25 °C, 3-8 bar
[DnBM][Cl]/ZIF-8/Pebax 1657 [35]	32	260	72	39	30 °C, 2 bar
TMGHIM/ZIF-76/PIM-1 [36]	10	12848	13.7	10.5	23 °C, 1 bar
[NH ₂ -PMIM][NTF ₂]/ZIF-76/PIM-1 [37]	5	9536	31.1	-	25 °C, 2bar
[APTMS][Ac]/ZIF-67/PSf [38]	30	22	74	72	25 °C, 10

					bar
[BMIM][NTF ₂]/NH ₂ -MIL101(Cr)/Matrimid [19]	7	19	-	113	35 °C, 10 bar
[BMIM][Br]/MIL101(Cr)/Matrimid [39]	20	9.9	26.9	-	30 °C, 0.7 bar
[TMGA][N ₃]/MOF-5/Matrimid [40]	2	36.9	35.5	-	35 °C, 0.7 bar
[C ₂ MIM][C(CN) ₃]/MOF-74/Matrimid [40]	2	25.9	36.6	-	30 °C, 0.7 bar
[EMIM][OAc]/ZIF-8/Chitosan [41]	10	5431	11.5	-	25 °C
[EMIM][NTF ₂]/ZIF-67/6FDA-durene [42]	20	1400	24		25 °C, 2 bar
[BMIM][NTF ₂]/UiO-66/PEI [12]	15	25		60	35 °C, 1 bar
[HMIM][PF ₆]/NH ₂ -UiO-66/PI [43]	5	4		51	34 °C, 1 bar
[EMIM][OAc]/CuBTC/Pebax	15	335	176		35 °C, 1 bar
[MPPyr][DCA]MIL-101(Cr)/Pebax MMMs (This study)	10	133±11.2	96.3±21.8	36.9±3.2	35 °C, 1 bar
	15	148.2±8.4	1347±134	121.5±11.8	35 °C, 1 bar
	20	156±13.1	164±7.5	63.4±6.2	35 °C, 1 bar

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Chapter 6

IL-modified MOF-177 filler boosts the CO₂/N₂ selectivity of Pebax membrane*

6.1 Abstract

Mixed matrix membranes (MMMs) having ionic liquid (IL) modified metal-organic frameworks (MOF) as fillers present a broad potential for enhancing the separation properties of the polymers. Here, we incorporated an IL, 1-butyl-1-methyl-pyrrolidinium tricyanomethanide [BMPyr][TCM], into MOF-177 and used the modified particles as fillers in Pebax polymer to fabricate IL/MOF-177/Pebax MMMs at different loadings. These MMMs along with those prepared by using pristine MOF-177 as a filler were then tested for CO₂/N₂ separation by measuring their CO₂ and N₂ permeabilities at 35 °C and 1 bar. The [BMPyr][TCM]/MOF-177/Pebax MMM having 10 wt.% filler loading showed remarkable improvements in both CO₂ permeability, 137±2.0 Barrer, and CO₂/N₂ selectivity, 622±105 compared to the neat Pebax membrane having corresponding performance values of 98.0±2.0 Barrer and 64.5±6.0, respectively. This simultaneous improvement in both CO₂ permeability and CO₂/N₂ selectivity breaks the trade-off limitation of polymer membranes. Besides, the MMMs having 10 and 15 wt.% loadings of fillers were located well above the updated Robeson's upper bound, demonstrating the great promise of [BMPyr][TCM]/MOF-177/Pebax MMMs for CO₂/N₂ separation.

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6.2 Introduction

Membrane-based gas separation technology has emerged as a promising alternative to other energy-intensive techniques employed for CO₂ capture thanks to its energy efficiency, environmentally friendly characteristics, ease of processing and scale-up, and reduced carbon footprint [1]. Polymer-based membranes are hindered by the permeability-selectivity trade-off, as demonstrated by the Robeson's upper bound [2]. To overcome this challenge, there have been significant efforts towards the design and development of mixed-matrix membranes (MMMs) combining the superior selectivity of filler materials with the ease of processing and well-established fabrication technology of polymer membranes [3, 4].

Metal-organic frameworks (MOFs), highly porous crystalline materials composed of organic linkers and metal nodes, have been considered as fillers for the fabrication of these MMMs, thanks to their strong affinity for various types of gas molecules [5-7]. Several different types of MOFs have been used as fillers in a well-known polymer, Pebax, to boost its gas separation characteristics. For instance, MMMs formed with Pebax and ZIF-8 (ZIF: zeolitic imidazolate framework) filler at a loading of 35 wt.% showed improved CO₂ permeability of 1287 Barrer at 2 bar (feed pressure), with no significant change in CO₂/N₂ selectivity (32) compared to neat Pebax membrane, offering a CO₂ permeability of 351 Barrer and a CO₂/N₂ selectivity of 33 [8]. ZIF-11/Pebax MMM having a filler loading of 30 wt.%, on the other hand, showed an improved CO₂/N₂ selectivity of 48 at 2 bar (feed pressure), compared to the neat polymer selectivity (40), but the CO₂ permeability (190 Barrer) was lower than the neat polymer membrane (234 Barrer) [9]. These results demonstrate that the type of filler is a key parameter controlling the gas separation characteristics of an MMM, and hence, there is a strong need to identify the MOF fillers that can lead to MOF/polymer MMMs having both enhanced gas permeability and improved selectivity compared to neat polymer membrane.

The interfacial compatibility of polymers and MOFs remains a key challenge to fabricate an efficient MMM [10]. For example, FeBTC (iron-benzene-1,3,5-tricarboxylate) particles were incorporated into Pebax at different filler loadings, and the resulting MOF/polymer MMM having 40 wt.% loading exhibited improved CO₂ permeability (425 Barrer) compared to the neat membranes (70 Barrer) [11]. However,

formation of nonselective voids and particle agglomeration resulted in a decrease in the CO₂/CH₄ selectivity of the MMM (12.3) compared to the neat polymer membrane (18.4). As these examples highlight, it is crucial to find the novel filler materials for making efficient MOF/polymer MMMs that can achieve high permeability and high selectivity simultaneously in addition to offering good polymer-filler compatibility.

To address this need, MOFs have been modified with functional materials, such as metal nanoparticles, metal oxide nanomaterials, graphite oxide, and ionic liquids (IL) to form new composites [12]. Among these, ILs are very promising for gas sorption and separation mainly because of their exceptional characteristics, such as non-volatility, structural tuneability, and high CO₂ solubility [13]. Incorporating ILs into MOFs to synthesize IL/MOF composites has offered high gas separation performance by modulating pore morphology and improving gas affinity and gas transport, thanks to ILs' high affinity for gases, such as CO₂ [12, 14, 15]. Furthermore, introducing ILs into MOFs promotes the preferential interactions among IL/MOF composite and the target gas molecules, such as hydrogen bonding and acid-base interactions. The IL/MOF composites have demonstrated substantial improvement in CO₂/N₂ and CO₂/CH₄ selectivities compared to the separation performance of pristine MOFs [14, 16, 17].

These promising IL/MOF composites have recently been employed as fillers in polymers for the synthesis of IL/MOF/polymer MMMs [18-23]. For instance, [BMIM][NTF₂]/ZIF-8/Pebax MMMs ([BMIM][NTF₂]: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)) were synthesized and the MMM having 15 wt.% filler loading showed improved CO₂ permeability of 100 Barrer and CO₂/N₂ selectivity of 84 [24]. IL addition into MMMs has been also crucial in eliminating the interfacial voids and enhancing the compatibility between polymer and filler. For instance, [BMIM][NTF₂]/ZIF-8/Pebax MMMs [25], [EMIM][NTF₂]/CuBTC/6FDA-durene MMMs [26], and [DnBM][Cl]/ZIF-8/Pebax MMMs ([DnBM][Cl]: 3-Di-n-butyl-2-methylimidazolium chloride) [27] demonstrated improved filler-polymer adhesion and reduced interfacial defects compared to their corresponding MOF/polymer MMMs without the ILs. In these studies, IL improved the polymer-filler compatibility because it was either dispersed in the polymer matrix or was coated outside the MOF surface prior to the MMM synthesis, acting as a wetting agent. To fully gain the advantage of the versatile IL properties in the MMMs, it should be freely dispersed into the membrane and

also incorporated into the MOF pores to enhance selectivities along with the improved polymer-filler interface.

There exist a huge number of ILs [28], alongside with thousands of MOFs [29], resulting in almost unlimited number of unique combinations of IL-MOF pairs to synthesize the composites. Nevertheless, the MMM studies primarily focus on a few widely recognized MOFs, such as ZIF-8/polymer MMMs representing more than 70% of all publications on MOF/polymer MMMs [30]. Therefore, exploration of new MOFs to synthesize IL/MOF composites is strongly required to develop novel IL/MOF/polymer MMMs. MOF-177, having a surface area ranging from 3800 to 4500 m²/g, is among the highly porous MOFs reported [31]. It has ZnO₄ clusters connected by the benzenetribenzoate (BTB) organic linker with open metal sites and offers a high thermal stability. It was recently studied for the post-synthetic modification with ILs for CO₂ adsorption [16, 32]. According to these studies, [EMIM][OAc]/MOF-177 having 10 wt.% IL loading showed enhanced CO₂ adsorption capacity [16]. Besides, amino acid-based ILs, [EMIM][Gly] and [EMIM][Ala] (Gly: glycine, Ala: alanine), were also impregnated at 20 and 30 wt.% loadings into MOF-177. The gas adsorption measurements showed that the CO₂/N₂ selectivity of [EMIM][Gly]/MOF-177 and [EMIM][Ala]/MOF-177 composite were more than doubled and reached 13 and 11, respectively, at 0.2 bar and 30 °C compared to that of pristine MOF-177 (CO₂/N₂ selectivity: 5) [32]. However, further studies are needed to fully comprehend the potential performance of MOF-177 as the MOF component of the composite material to be used as a filler.

Motivated from the favorable properties of MOF-177, such as ultrahigh porosity, excellent thermal and chemical stability, and high CO₂ adsorption capacity [33, 34], here, we first prepared its composite with a pyrrolidinium-based IL and then used the resulting composite as a filler in MMMs. For this purpose, 1-butyl-1-methyl-pyrrolidinium tricyanomethanide, [BMPyr][TCM] was selected because of its high CO₂ solubility and exceptional CO₂/N₂ separation properties demonstrated by the composites of similar pyrrolidinium-based ILs with different MOFs, such as UiO-66 [35]. After the post-synthesis modification of MOF-177 with this highly CO₂-selective pyrrolidinium-based IL, we incorporated the resulting composite into the Pebax to fabricate IL/MOF/polymer MMMs. Pebax was selected as the polymer in our work because of its unique properties that are particularly advantageous for gas separation applications: The rubbery

polyethylene oxide (PEO) component favorably interacts with CO₂, while the glassy polyamide (PA) block provides the necessary mechanical strength for the membrane stability. This combination of crystalline and amorphous structure makes Pebax an optimal choice for achieving high gas separation performance and excellent mechanical strength in membrane applications. Moreover, the presence of polar groups in Pebax ensures high affinity for CO₂ compared to non-polar gases such as N₂, which is essential for efficient membrane performance [25, 36]. The synthesized composite and MMMs, along with those prepared by using pristine MOF-177 as filler, were characterized in detail. Then, the gas adsorption and permeability measurements were performed to determine the corresponding CO₂/N₂ selectivities. Data showed that both MOF-177/Pebax MMMs and [BMPyr][TCM]/MOF-177/Pebax MMMs at different filler loadings offered improvements in both CO₂ permeability and CO₂/N₂ selectivity, exceeding the updated Robeson upper bound [37]. Moreover, improved MOF-polymer compatibility was observed because of the presence of free-IL in the polymer. The experimental findings presented in this work offer opportunities to guide the development of novel IL/MOF/polymer MMMs with enhanced CO₂/N₂ separation performances.

6.3 Results and Discussion

6.3.1 Characterization of the materials

6.3.1.1 Pristine MOF and its composite with [BMPyr][TCM]

To determine the IL loading of the synthesized composite, washing experiments were performed using acetone as the solvent. As shown in **Figure 6A-1**, the characteristic IR peaks of IL were not present in the washed-and-dried composite, confirming the complete removal of the IL molecules. Afterwards, the IL loading was back-calculated as approximately 42 wt.%. This value is slightly lower than the targeted IL loading (45 wt.%). The difference can be ascribed to the loss of some IL molecules on the walls of the sample vial during the synthesis of IL/MOF composite.

The SEM images of pristine MOF-177 and [BMPyr][TCM]/MOF-177 composite presented in **Figure 6.1** were analyzed to study the effects of IL incorporation on the morphology of the pristine MOF-177. **Figures 6.1(a)** and **(b)** demonstrate the crystals of MOF-177 with an undefined geometry, featuring size variations that alternated between small and large aggregates, consistent with the literature [32, 38]. The morphology of the

[BMPyr][TCM]/MOF-177 composite presented in **Figure 6.1(c)** and **(d)** resembles crystalline structure of pristine MOF-177 with no apparent changes.

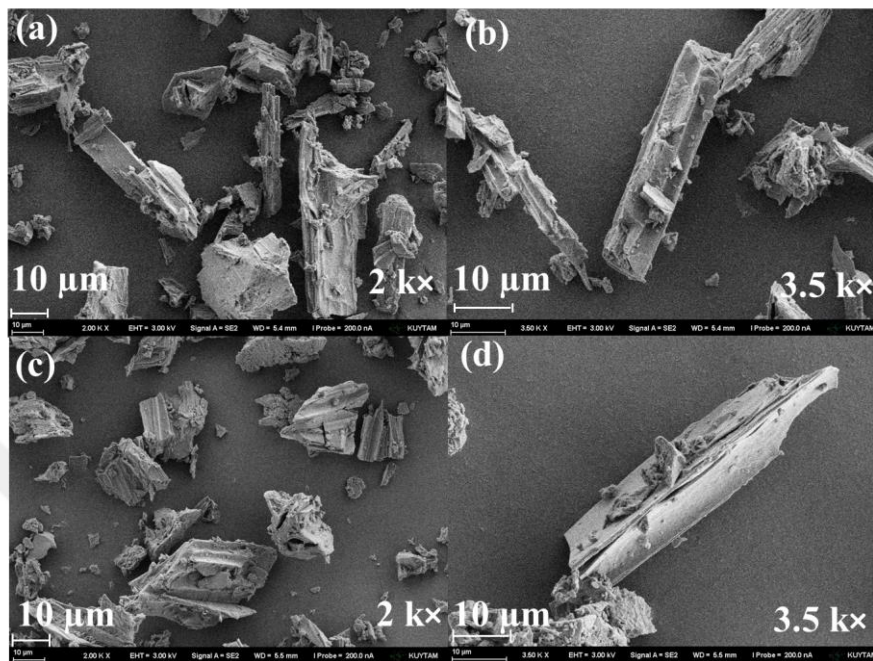


Figure 6.1. SEM images of pristine MOF-177 at (a) 2k $\times$ and (b) 3.5k $\times$ magnifications, and [BMPyr][TCM]/MOF-177 composite at (c) 2k $\times$ and (d) 3.5k $\times$ magnifications.

Crystalline morphology was also examined by performing XRD analysis on the pristine MOF-177 and the IL-incorporated MOF-177. XRD spectra of MOF-177 given in **Figure 6.2(a)** showed a good agreement with the literature, validating the structural integrity of the pristine MOF. The main characteristic peaks present at $2\theta = 5.5, 5.8, 6.0, 6.2, 7.7, 10.5,$ and 11.3° well matched with the literature [33, 48]. In the case of [BMPyr][TCM]/MOF-177 composite, the presence of all the characteristic peaks of pristine MOF revealed that the crystallinity of the MOF-177 was well-maintained upon the IL incorporation. Moreover, presence of a slight shift in some of the 2θ values along with the alteration in the relative intensity of the peaks implies a modification of electronic environment within the crystalline structure. This result is as expected, as the IL molecules occupying the internal pores of MOF-177 induce changes in the electronic structure or shift the atomic orientation in the crystal structure as reported earlier on similar IL/MOF composites [32, 40].

The N₂ adsorption isotherm data collected for the pristine MOF-177 is depicted in **Figure 6A-2**. The BET surface area and pore volume of MOF-177 were measured as 3090 m²/g and 0.26 cm³/g, respectively, consistent with the literature [41]. The IL molecules positioned at the pore entrances of MOF-177 potentially blocks the transport of the probe gas molecule into the pores because of the negligible N₂ solubility in the IL at the BET measurement conditions (liquid nitrogen temperature), resulting in reduced surface area and pore volume values than its pristine counterparts. Consequently, the BET surface area of the composite could not be measured reliably. This phenomenon was also reported previously [35, 42, 43]. Hence, the inherent properties of ILs prevent the solubility of the probe gas, N₂, in [BMPyr][TCM] rather than indicating excessive IL loading. Additional characterization techniques, such as XRD and SEM, confirmed the successful incorporation of IL into the MOF-177 without the structural collapse of the pristine MOF-177.

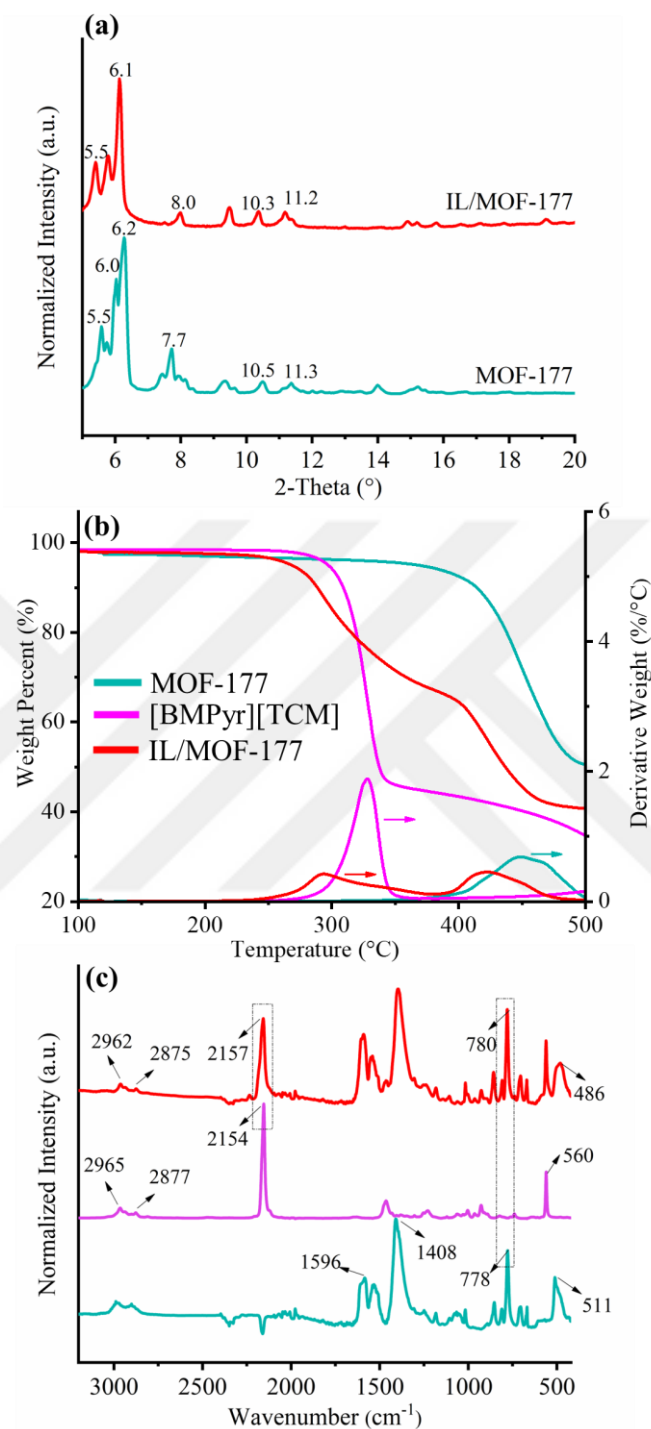


Figure 6.2. (a) XRD diffractogram of MOF-177 and IL/MOF-177 composite, (b) TGA and DTG curves, and (c) IR spectra of MOF-177, [BMPyr][TCM], and [BMPyr][TCM]/MOF-177 composite.

Thermal stability limits of the samples were determined by TGA and the effect of IL incorporation on the thermal stability of pristine MOF-177 was investigated. The

corresponding T'_{onset} values of each sample were estimated from the DTG curves. The TGA data of the pristine MOF-177 given in **Figure 6.2(b)** showed a complete decomposition in a single step at a T'_{onset} temperature of approximately 400 °C, ascribed to the decomposition of the organic linker present in the MOF structure. In the case of bulk IL, the T'_{onset} was measured as approximately 300 °C. The T'_{onset} temperature of the composite, however, was significantly lower (268 °C) from those of both the IL and the MOF. This difference suggests that the decomposition behavior of the IL/MOF composite is completely different than both of its components and indicates the presence of strong interactions, which could be possible only if the majority of the IL molecules positioned inside the MOF pores [14].

To get more insights into these newly formed interactions, IR analysis was conducted for pristine MOF-177, [BMPyr][TCM], and the composite, as shown in **Figure 6.2(c)**. In the IR spectrum of [BMPyr][TCM], the characteristic bands present at 2877 and 2965 cm⁻¹ were attributed to the symmetric and asymmetric $\nu(\text{C-H})$ vibrations of the cation, respectively. The peak located at 2154 cm⁻¹ was ascribed to the $\nu(\text{C}\equiv\text{N})$ of anion. The $\nu(\text{C}\equiv\text{N})$ band of IL demonstrated a blue-shift of 3 cm⁻¹ upon the incorporation of IL into the MOF. This blue-shift suggests a strengthening of C $\equiv$ N bond and a weakening in the interaction strength between the anion and the cation of the IL. In contrast, the peaks present at 2965 and 2877 cm⁻¹ associated with the cation of IL showed red-shifts of 3 and 2 cm⁻¹ (slightly larger than the spectral resolution), respectively. This result suggests the weakening of interionic interactions and the possibility that the cation of IL might be interacting with the MOF.

The characteristic IR peak of pristine MOF-177 located at 511 cm⁻¹ (in **Figure 6.2**) was ascribed to the $\nu(\text{Zn-O})$ band, corresponding to the metal nodes in the MOF. The vibrational peaks at 1596 and 1408 cm⁻¹ were ascribed to $\nu(\text{O-C-O})$ dicarboxylate groups of the BTB linker present in the MOF-177 [33, 44, 45]. The features at 851, 778, and 702 cm⁻¹ were ascribed to the benzene rings [38]. The characteristic peak associated with $\nu(\text{Zn-O})$ band showed a significant red-shift upon the incorporation of IL into the MOF pores with a change from 511 to 480 cm⁻¹. This significant red-shift of 25 cm⁻¹ suggests a weakening of the Zn-O bonds demonstrating changes in the electronic environment surrounding the metal nodes, in the presence of the IL molecules. Hence, we infer that

these shifts are associated with the interactions between the cation of IL and the Zn–O moieties present in the MOF pores.

6.3.1.2 Characterization of MMMs

The cross-sectional morphology of the synthesized MMMs was analyzed by conducting the SEM analysis. It was observed that the MMMs prepared using 4 wt.% of the polymer formed two distinct layers within the membrane, one with polymer-rich phase having the polymer solution with dispersed fillers, and the other one with filler-rich phase having agglomerated inorganic fillers settled at the bottom, as shown in **Figure 6A-3**. It can be inferred that the viscosity of the polymer solution could not sustain the homogenous dispersion of MOF particles in the polymer; therefore, the settling of particles at the bottom of the membrane was observed, resulting in a dual-layer formation in the MMM [46]. To avoid the formation of such dual-layer by improving the viscosity of the polymer solution, the concentration of Pebax was increased to 5 wt.%. Moreover, to further improve the dispersion of the filler particles, the MOF-polymer suspension was sonicated for 30 minutes and stirred continuously for 10 h to ensure the homogeneity of the solution mixture.

Here, we note that one of the primary challenges in fabricating Pebax-based MMMs is the choice of casting solvents, which influences the interaction with the polymer matrix chains and subsequently impacts the membrane's morphology and separation performance. The solvent must completely dissolve the chosen Pebax grade, which varies in polarity and chemical composition. A non-suitable combination can adversely affect the properties of the Pebax membrane and the resulting MMMs [47]. Common solvents include dimethylacetamide (DMAc), dimethylformamide (DMF), n-methyl-2-pyrrolidone (NMP), formic acid, and water/ethanol mixtures, each affecting the membrane's morphology and structure differently. Pebax 1657, used in this study, can dissolve in various solvents but requires specific ones like a water/ethanol mixture to avoid gelation. For instance, Pebax-based MMMs prepared by using NMP and DMF as solvents exhibited poor compatibility and weak interfacial adhesion between the filler and the polymer, resulting in agglomeration of filler particles even at a lower filler loading of 3 wt.%, along with non-homogenous dispersion [48]. The choice of solvent and drying conditions also influences the membrane's crystallinity, for example high-boiling-point

solvents like DMAc tend to create a crystalline structure, while solvents like formic acid lead to amorphous structures [49]. Hence, it is crucial to select the most favorable solvent for the membrane fabrication. Thus, we utilized an ethanol/water solution as the optimum solvent for use with Pebax membrane [50].

However, the MOF-177 is known to be instable in the presence of moisture [42]. To check whether there are any morphological changes on the MOF upon its interaction with the ethanol/water solution, we prepared a sample of MOF-177 by mixing it with ethanol/water solution. The SEM images obtained on this sample after drying are presented in **Figure 6A-4**. These images show that the surface of MOF-177 was partially etched, indicating the presence of surface degradation to some extent. However, the XRD spectra of the MMMs presented in **Figure 6.4** exhibited the presence of characteristic crystalline peaks of MOF-177, suggesting that the degradation of the crystalline structure was limited. Further discussion regarding the integrity of MOF-177 can be found in the XRD section of the MMMs as presented below.

For all the MMMs synthesized in this work using ethanol/water solvent, no apparent cracks or voids in the membrane matrix were observed, ensuring homogenous and defect-free synthesis of the membranes as shown in **Figure 6.3**. The homogeneous morphology may be attributed to the partial etching of the MOF, resulting in its size reduction. This process likely facilitates better dispersion and homogeneity within the MMMs [51, 52]. Furthermore, the prevention of dual-layer formation in all membranes was achieved by increasing the viscosity of the polymer solution, as depicted in **Figure 6A-3**. The cross-sectional images of MOF/polymer MMMs are presented in **Figure 6.3(a-c)**, it was observed that as the MOF loading increases from 10 to 20 wt.%, the structure becomes less smooth, which can be ascribed to the increased crystallinity of the MMMs with the addition of MOF particles. On the other hand, the cross-sectional images of [BMPyr][TCM]/MOF-177/Pebax MMMs shown in **Figure 6.3(d-f)** showed a more homogenous and smooth structure compared to MOF-177/Pebax MMMs. The difference in the morphologies of MMMs can be attributed to the fact that the IL/MOF composite incorporated in IL/MOF/polymer MMMs have less wt.% of MOF particles as compared to the MOF-177/Pebax MMMs for the same filler loading. Another possibility is that during the synthesis process, some of the IL may have leached out of the MOF pores and dispersed in the polymer as free-IL molecules, improving the MOF-polymer adhesion and

interactions [53]. This possibility is further discussed in the IR spectroscopy analysis of the MMMs below.

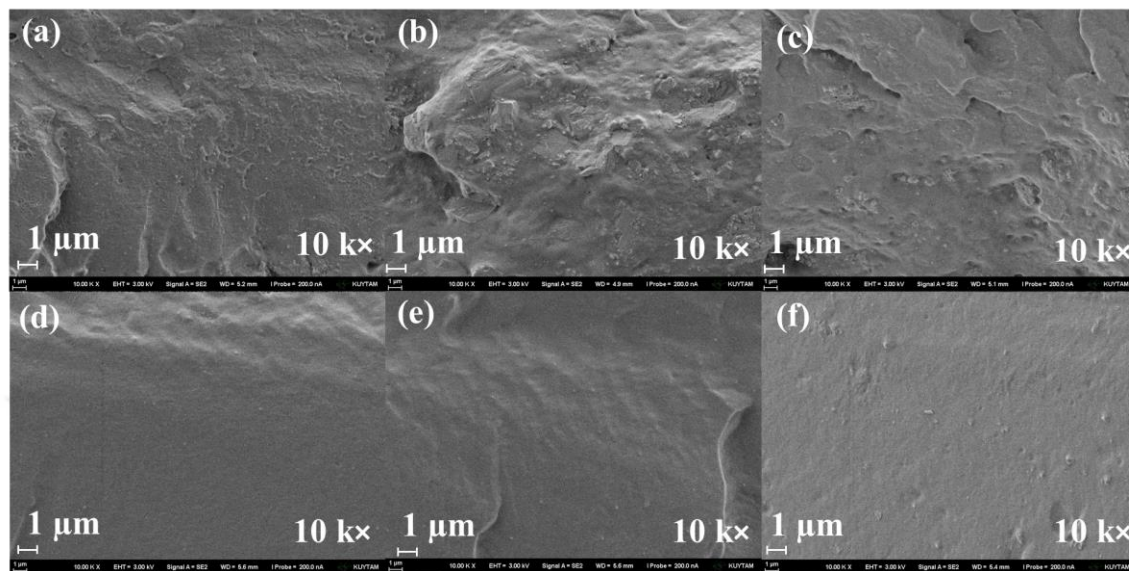


Figure 6.3. SEM images of MOF-177/Pebax MMMs having (a) 10 wt.%, (b) 15 wt.%, and (c) 20 wt.% of MOF-177 loadings and [BMPyr][TCM]/MOF-177/Pebax MMMs with (d) 10 wt.%, (e) 15 wt.%, (f) 20 wt.% of [BMPyr][TCM]/MOF-177 loadings.

The XRD diffraction patterns of Pebax, MOF-177/Pebax MMMs, [BMPyr][TCM]/MOF-177/Pebax MMMs, MOF-177 and, IL/MOF-177 composite are given in **Figure 6.4(a-i)**. The spectra of Pebax membrane presented a broad peak at $2\theta = 12$ to 25° , ascribed to the polyamide (PA) segment of the polymer [54]. The characteristic peak representing the PA functional group was present in all MMMs. The XRD of MMMs presented new peaks at $2\theta = 5.8$ and 10.1° , which were associated with the characteristic peaks of MOF-177, indicating that the structural integrity of the MOF was preserved during MMM synthesis. Moreover, the intensity of the XRD peaks corresponding to MOF-177 was noticeably increased as the filler loading was increased from 10 to 20 wt.% as shown in **Figure 6.4(b-d)**. This phenomenon can be ascribed to the increase in the crystallinity of the MOF/polymer MMMs with the increasing MOF loading. In the spectra of [BMPyr][TCM]/MOF-177/Pebax MMMs, the decrease in relative intensity of the peaks was observed in **Figure 6.4(e-g)**, which is attributed to having a less loading of the MOF-177 in the composite, dispersed into Pebax to synthesize IL/MOF/polymer MMMs.

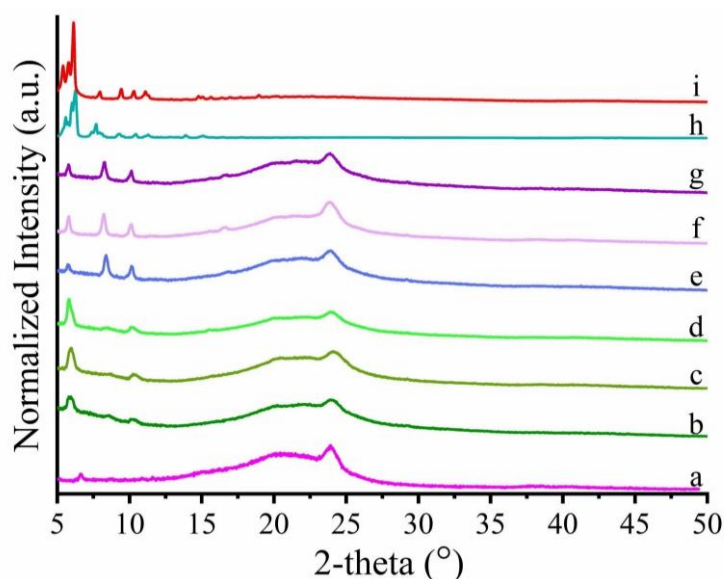


Figure 6.4. XRD spectra of neat Pebax (a), MOF-177/Pebax MMMs having MOF-177 loadings of 10 wt.% (b), 15 wt.% (c), 20 wt.% (d), and [BMPyr][TCM]/MOF-177/Pebax MMMs with a filler loading of 10 wt.% (e), 15 wt.% (f), 20 wt.% (g). The data for pristine MOF-177 (h) and IL/MOF-177 composite (i) are provided for comparison.

The IR spectra of neat Pebax, MOF-177/Pebax MMMs, and [BMPyr][TCM]/MOF177/Pebax MMMs having filler loadings of 10, 15, and 20 wt.% are presented in **Figure 6.5(a-g)**. The IR spectrum of the Pebax membrane exhibited a characteristic peak at 1095 cm⁻¹, corresponding to $\nu(\text{C}-\text{O}-\text{C})$ vibrations of PEO segment present in the polymer [55]. The IR bands located at 1636 and 1729 cm⁻¹ were attributed to the $\nu(\text{O}-\text{C}-\text{O})$, and $\nu(\text{H}-\text{N}-\text{C}=\text{O})$ vibrations, respectively [56], while the peaks present at 1539 and 3296 cm⁻¹ were ascribed to the $\nu(\text{N}-\text{H})$ group [57], present in PA segment. The IR spectra of MOF/polymer MMMs shown in **Figure 6.5(b-d)**, demonstrated that the $\nu(\text{C}-\text{O}-\text{C})$ vibrations peak present at 1095 cm⁻¹ attributed to the PEO segment, showed a slight blue-shift (slightly above the spectral resolution of 2 cm⁻¹) compared to its location in the neat Pebax. The new IR bands observed at 792 cm⁻¹ were attributed to the BTB linker of MOF-177 exhibited a blue shift of 14 cm⁻¹ compared to its location in the pristine MOF-177 spectra, suggesting MOF-polymer interactions through PEO of the polymer and organic linker of MOF. Moreover, the peak associated with the MOF-177 was intensified with increase in the MOF loading from 10 to 20 wt.%.

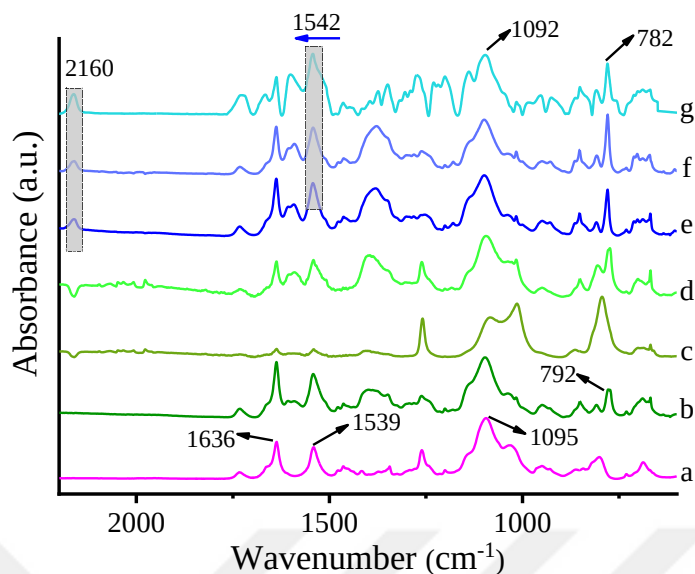


Figure 6.5. IR spectra of neat Pebax (a), MOF-177/Pebax MMMs having a MOF-177 loading of 10 wt.% (b), 15 wt.% (c), 20 wt.% (d), and [BMPyr][TCM]/MOF-177/Pebax MMMs having a [BMPyr][TCM]/MOF-177 loading of 10 wt.% (e), 15 wt.% (f), 20 wt.% (g).

In the case of [BMPyr][TCM]/MOF-177/Pebax MMMs shown in **Figure 6.5(e-g)**, the IR band at 1095 cm⁻¹ (PEO) presented a red-shift of 3 cm⁻¹ suggesting that the bond strength among the PEO segment was weakened. Moreover, the characteristic peak associated with the BTB linker of MOF-177 exhibited a red-shift of 8 cm⁻¹ compared to its location in the MOF/polymer MMMs. The observed red-shifts suggest the interactions between the of PEO of the polymer and the organic ligand of the MOF. Furthermore, the presence of a new IR peak located at 2160 cm⁻¹ was attributed to $\nu(\text{C}\equiv\text{N})$, anion of the IL, which showed a blue-shift of 3 cm⁻¹ as compared to its position in the [BMPyr][TCM]/MOF-177 composite spectra. If all IL molecules were encapsulated within the MOF cages, no shifts in their IR bands would be expected upon the fabrication of the MMM, because of the lack of interactions with the polymer. Thus, the slight shift in the characteristic peak of the IL's anion might indicate that some of the IL molecules leached out from the MOF's pores during the fabrication of the MMM.

To verify this possibility, the [BMPyr][TCM]/MOF-177 composite was mixed in ethanol-water solution. The IR spectra of the mixed-and-dried composite is presented in **Figure 6A-6**. The characteristic IR peaks of the IL are still present in the spectrum of IL/MOF composite. However, the peaks' intensity is lower than the as-synthesized

[BMPyr][TCM]/MOF-177 composite confirming that some of the IL molecules were leached out of the MOF cages during the MMM synthesis. The presence of IL in the polymer matrix in the form of the free molecules can enhance the polymer-MOF interfacial compatibility, resulting in improved gas separation performance, which will be discussed below [53].

The thermal stability limits of neat Pebax, MOF-177/Pebax MMMs, and IL/MOF-177/Pebax MMMs were determined by TGA, the results are presented in **Figure 6.6**. All the MMMs showed one-step decomposition mechanism. The data demonstrated that decomposition of all MMMs initiated at approximately T'_{onset} of 355 °C, attributed to the degradation of the polymer backbone. Moreover, no significant changes were observed in the decomposition temperature of the MMMs as the filler loadings were varied. Overall, all the MMMs showed stability up to 350 °C, attributed to their high thermal stability.

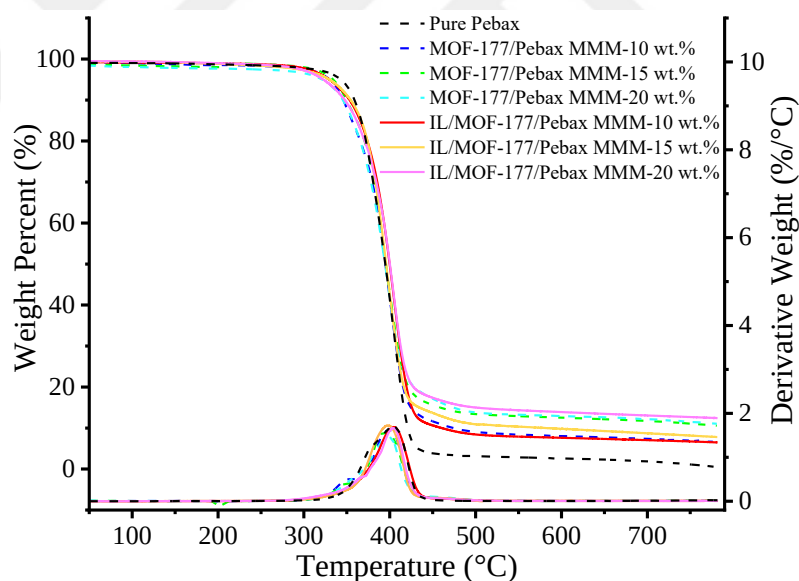


Figure 6.6. TGA curves of neat Pebax, MOF-177/Pebax MMMs and [BMPyr][TCM]/MOF-177/Pebax MMMs having 10, 15, and 20 wt.% of filler loadings.

Additionally, to assess the glass transition temperature (T_g) and melting temperature (T_m) of the polymer, DSC analyses were conducted. The related results are presented in **Table 6A-2** and **Figure 6A-7**. Neat Pebax membrane showed a T_g of -48.3 °C along with two T_m of 21.4 and 205.4 °C for PEO and PA segment, respectively, in line with the literature [25, 58]. **Figure 6A-7** shows slight, stepwise, and nearly composition independent transition around 118 °C associated with the amorphous PA. The occurrence

of two distinct melting temperatures in the Pebax indicates the microphase separated structure of the copolymer.

In the case of MOF-177/Pebax MMMs, a slight increase in T_m and enthalpy of melting of PA segment was observed compared to the neat Pebax membrane as shown in **Table 6A-2**. This change can be ascribed to enhanced crystallinity and stronger intermolecular interactions within the polymer matrix. In contrast, for IL/MOF/Pebax membrane having an IL/MOF composite loading of 10 wt.%, the T_m of both PA and PEO segment the T_g decreased to 17.6, 200.3, and -50.9 °C, respectively, compared to the neat polymer membrane. As the composite loading was increased to 20 wt.%, T_m of PA segment and T_g further decreased to 197 and -53.4 °C, respectively. This decrease may result from an increase in the chain mobility within the MMM associated with the IL contribution [59]. In addition, it can be related to the increase in the interaction of polymer and IL as explained in the IR results. Note that a similar trend can be also observed from the enthalpy values of individual polymer segments. For IL/MOF/Pebax MMM with an IL/MOF loading of 10 wt.%, the enthalpies of PEO and PA decreased to 13.9 and 12.4 J/g, respectively, compared to neat Pebax. Further increase in the IL/MOF loading to 20 wt.% decreased the enthalpies for IL/MOF/Pebax MMMs compared to neat Pebax membrane. This result can be attributed to the reduction in the crystallinity of polymer chains in the presence of IL [59], which results in an overall increase in polymer segmental mobility. Moreover, the decrease in T_g also suggests that IL/MOF composite has a stronger effect on the packing of polymer chains resulting in higher FFV within MMMs [60]. This phenomenon has the potential to impact the gas separation performance of the MMM, as presented below.

6.3.2 Gas separation performances of materials

6.3.2.1 Adsorption-based gas separation with the IL/MOF composite

Volumetric single-component CO₂ and N₂ adsorption measurements were performed for pristine MOF-177 and [BMPyr][TCM]/MOF-177 composite at 1 bar and 25 °C, the results are presented in **Figure 6.7(a)**. The CO₂ and N₂ uptakes of pristine MOF-177 were measured as 15.9 and 2.7 cm³/g, respectively, consistent with the reported literature [45]. In the case of the IL/MOF composite, the CO₂ and N₂ uptakes were decreased to 4.6 and 0.3 cm³/g, respectively. The decrease in the gas adsorption capacity

of [BMPyr][TCM]/MOF-177 was attributed to the incorporation of the IL molecules within the pores of MOF-177, resulting in decreased surface area and pore volume of the material. Moreover, below 0.01 bar pressure, the composite showed critically low N₂ uptakes. The COSMO-RS calculations performed at 25 °C and 0.1 to 1 bar are shown in **Figure 6A-8**, revealed that the solubility of N₂ in [BMPyr][TCM] is insignificant at low pressures compared to the considerably higher solubility of CO₂. Consequently, the N₂ uptake of the [BMPyr][TCM]/MOF-177 composite at low pressures was non-detectable.

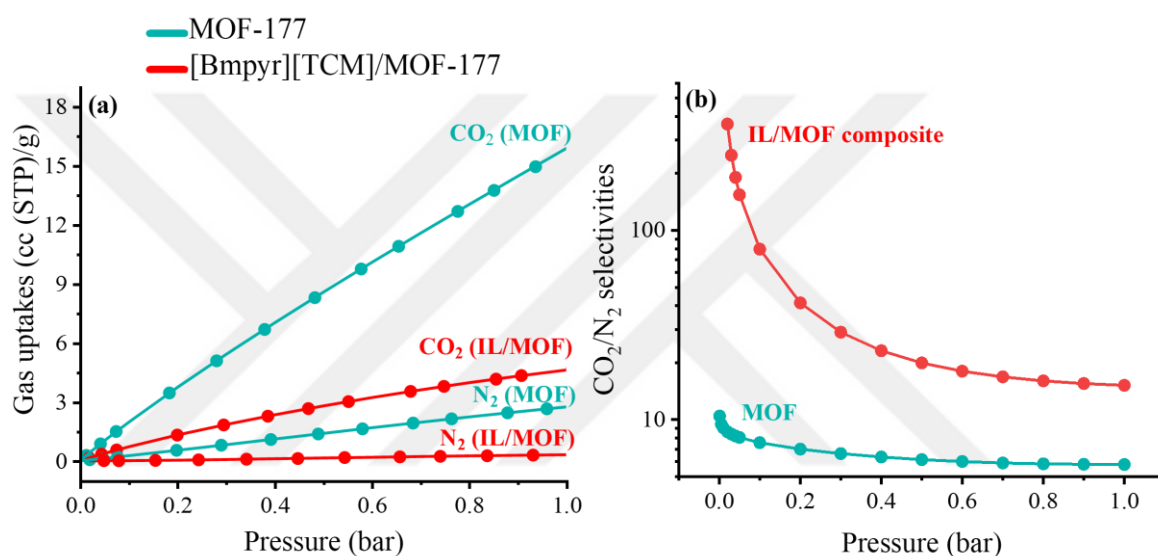


Figure 6.7. (a) CO₂ and N₂ volumetric gas uptakes, (b) CO₂/N₂ selectivity of MOF-177 and [BMPyr][TCM]/MOF-177 composite measured up to 1 bar and 25 °C. In (a), circles represent the experimental data, and the lines represent the fitted data. Selectivities on the y-axis are given in a logarithmic scale.

The CO₂/N₂ selectivity of pristine MOF-177 and [BMPyr][TCM]/MOF-177 composite was calculated by fitting the gas adsorption isotherms up to 1 bar as represented in **Figure 6.7(b)**. The data demonstrated that the CO₂/N₂ selectivity of the [BMPyr][TCM]/MOF-177 composite is higher than that of the pristine MOF. For instance, [BMPyr][TCM]/MOF-177 composite showed improved selectivity of 364 and 15.1 at 0.02 and 1 bar, respectively. Such improvement in selectivity corresponding to 42- and 2.6-times, at 0.02 and 1 bar, respectively, compared to that of pristine MOF can be ascribed to the remarkable solubility of pyrrolidinium-based ILs for CO₂ [35], promoting the diffusion of CO₂ molecules into the IL/MOF composite, while hindering the N₂ molecules, resulting in a N₂-phobic and highly CO₂ selective composite. Literature

comparison demonstrated that the separation performance of this [BMPyr][TCM]/MOF-177 composite is 3.1-times higher than that of [EMIM][Gly]/MOF177 (compared to 13 at 0.2 bar and 30 °C), and 3.7-times higher compared to [EMIM][Ala]/MOF177 (compared 11 at 0.2 bar and 30 °C) [32], demonstrating the high potential of the newly synthesized composite. Moreover, the composite showed non-detectable N₂ uptakes up to 0.01 bar, making it completely selective for CO₂ over N₂ up to that pressure.

As demonstrated in **Figure 6.7(b)**, the CO₂/N₂ selectivity is decreased with increasing pressure. This behavior is ascribed to a change in the driving forces for surface adsorption. For instance, at high pressures, the gas adsorption is dominated by the available pore volume of the material; conversely, in the low-pressure region, adsorbent-adsorbate (gas molecules) interactions become predominant [42, 61]. Therefore, with an increase in pressure, the gas adsorption mechanism shifts towards pore availability, leading to a decrease in the selectivity.

6.3.2.1 Membrane-based gas separation

Based on the superior gas adsorption and separation performance, IL/MOF/polymer MMMs were tested for gas separation. The CO₂ and N₂ permeabilities were measured at 1 bar and 35 °C, for neat Pebax, MOF-177/Pebax MMMs, and [BMPyr][TCM]/MOF-177/Pebax MMMs. **Figures 6.8(a)** and **(b)** show the CO₂ permeability of the synthesized membranes at different filler loadings of MOF-177 and [BMPyr][TCM]/MOF-177 composite, along with the corresponding membrane selectivities, respectively. The permeability and selectivity data presented in **Figure 6.8** are also given in the tabulated form in **Table 6A-3**.

Neat Pebax showed CO₂ and N₂ permeabilities of 98±2.0 and 1.5±0.2 Barrer, respectively, with a corresponding CO₂/N₂ selectivity of 64.5±6.0, consistent with the reported literature [62]. In the case of MOF/polymer MMMs, the data exhibited an enhancement in CO₂ permeability and CO₂/N₂ selectivity compared to the neat Pebax membrane. For instance, the CO₂ permeabilities of MOF-177/Pebax MMM having 10 and 15 wt.% loading were determined as 154±6.0 and 176±16.2 Barrer, along with N₂ permeabilities of 1.42±0.1 and 1.35±0.07 Barrer, respectively. Accordingly, the CO₂/N₂ selectivities were calculated as 108±12.6 and 130±11.6 for MMMs having 10 and 15 wt.% of MOF loading, respectively, as shown in **Figures 6.8(a)** and **6.8(b)**. These results

showed that the incorporation of MOF-177 into Pebax improved the CO₂ permeability of the membrane and decreased the N₂ permeability, leading to an enhanced gas separation performance. Overall, the MOF-177/Pebax MMM having a filler loading of 10 and 15 wt.% showed 1.7- and 2-times enhancement in CO₂/N₂ selectivity compared to the neat Pebax membrane, respectively. This improvement can be ascribed to the improved free volume in the polymer matrix with the incorporation of MOF-177 [3].

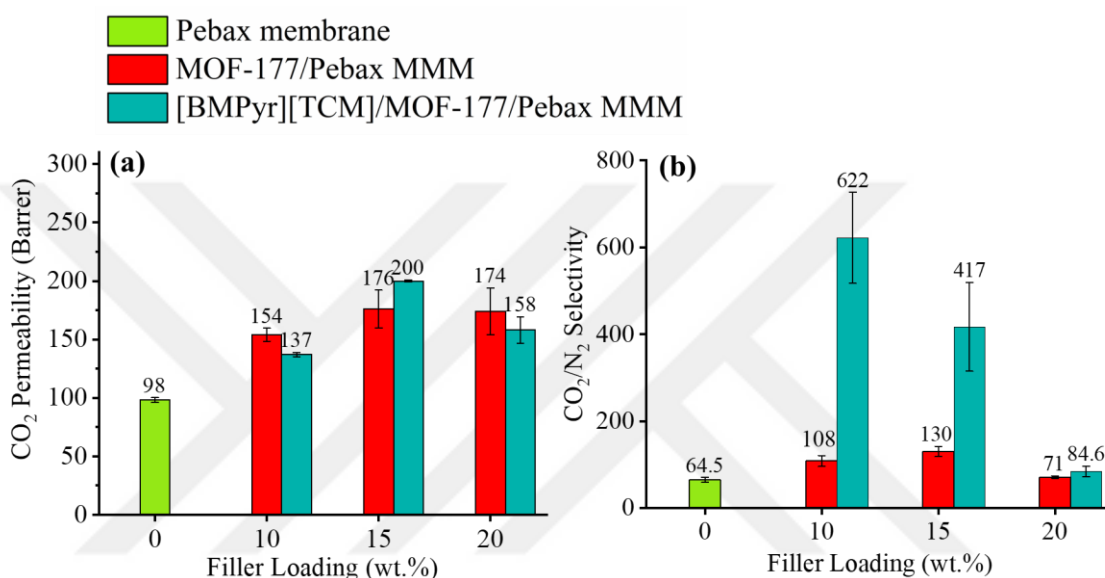


Figure 6.8. (a) CO₂ permeability and (b) CO₂/N₂ selectivity of MOF-177/Pebax and [BMPyr][TCM]/MOF-177/Pebax MMMs, in comparison with those of neat Pebax, measured at 35 °C and at a feed pressure of 1 bar.

Next, the gas separation performance of IL/MOF/polymer MMMs was evaluated. The data presented in **Figure 6.8(a)** and **(b)** demonstrated that addition of IL/MOF composite in the polymer significantly improved the gas separation performance. For instance, the IL/MOF-177/Pebax MMMs having an IL/MOF composite loading of 10 and 15 wt.% showed CO₂ permeabilities of 137±2.0 and 200±0.7 Barrer, along with N₂ permeabilities of 0.2±0.04 and 0.5±0.1 Barrer, respectively. The corresponding CO₂/N₂ selectivities of these MMMs were calculated as 622±105 and 417±102, the relatively large error bar is originated from the very low N₂ permeability in the denominator, for an IL/MOF loading of 10 and 15 wt.%, respectively. Overall, these [BMPyr][TCM]/MOF-177/Pebax MMMs showed 9.6- and 6.5-times improvement in CO₂/N₂ selectivity of Pebax membrane, respectively. As the IL/MOF composite loading was increased to 20 wt.%, a notable decrease in both CO₂ permeability and CO₂/N₂ selectivity was observed

for MOF/polymer MMM and IL/MOF/polymer MMM, as illustrated in **Figure 6.8(a)** and **(b)**. This decrease can be attributed to the reduced compatibility between the filler and the polymer at higher loadings, as well as the agglomeration of filler particles, as discussed in previous studies [63, 64].

To check whether the synergistic effect of IL and MOF in an IL/MOF composite is important for gas separation performance, we synthesized another membrane having IL and MOF-177 freely dispersed in the polymer matrix with the similar loadings corresponding to a total filler loading of 10 wt.%. The CO₂ and N₂ permeabilities of this membrane were measured as 171.3±5.0 and 0.5±0.07 Barrer, respectively, and the CO₂/N₂ selectivity was calculated as 329±56. The MMM having 10 wt.% IL/MOF-177 composite showed 1.9-times higher CO₂/N₂ selectivity compared to the corresponding values of this MMM having IL and MOF freely dispersed in the polymer matrix. Furthermore, we also synthesized a [BMPyr][TCM]/Pebax MMM having equivalent loading of IL present in 10 wt.% IL/MOF/Pebax MMM, and the results showed that the MMM exhibited CO₂ and N₂ permeabilities of 125±3.0 and 1.4±0.2 Barrer, respectively, resulting in a CO₂/N₂ selectivity of 92±17. We observed that the [BMPyr][TCM]/Pebax MMM performance did not significantly differ from that of neat Pebax at this IL loading. This can be attributed to the inherent properties of the Pebax matrix, which already provides a certain level of CO₂ permeability and selectivity. In contrast, IL/MOF-177/Pebax MMM having IL/MOF composite as a filler benefit from the increased free volume in the polymer matrix, the presence of Zn⁺² metal sites in MOF-177, and the favorable interactions between IL, MOF, and polymer which enhance the overall membrane performance. Hence, we infer that having an IL/MOF composite with IL molecules present mostly inside MOF pores is crucial in reaching remarkable separation performance.

Next, the CO₂ permeability and CO₂/N₂ selectivity data of the synthesized MMMs were compared with the reported literature and plotted on the Robeson's upper bound (2008) along with the updated upper bound 2019 [37] as illustrated in **Table 6A-4** and **Figure 6.9**, respectively. The temperature and pressure of the collected literature data are in the range of 25-35 °C and 1-6 bar, respectively. The MMMs having Pebax as the polymer are represented with different symbols in **Figure 6.9** for clarity. It was observed that both MOF-177/Pebax MMMs and [BMPyr][TCM]/MOF-177/Pebax MMMs having

a filler loading of 10 and 15 wt.% surpassed the updated upper bound, while those with 20 wt.% filler loading crossing the upper bound 2008. The data also showed that the CO₂ permeabilities and the CO₂/N₂ selectivities of IL/MOF/polymer Pebax MMMs presented in this study, especially with 10 wt.% IL/MOF composite has superior gas separation performance, demonstrating the broad potential of [BMPyr][TCM]/MOF-177 composite as a filler in MMMs.

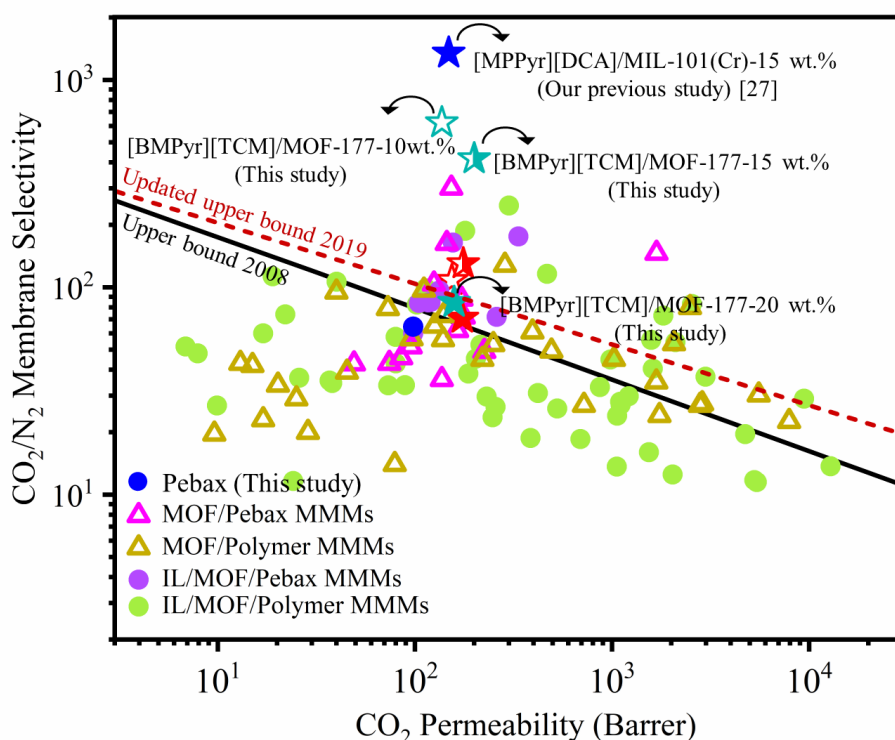


Figure 6.9. Comparison of CO₂/N₂ selectivity and CO₂ permeability of MMMs synthesized in this study with the literature data. The red stars represent MOF-177/Pebax MMMs synthesized in this study. The black line represents the Robeson's upper bound (2008) [2] and the maroon dotted line represents the updated upper bound (2019) [37].

Next, the separation performance of IL/MOF-177/Pebax MMM having 10 wt.% MOF loading was compared with other reported IL/MOF/Pebax MMMs under the same temperature and pressure conditions. For instance, the CO₂/N₂ selectivity of [BMPyr][TCM]/MOF-177/Pebax MMM having 10 wt.% IL/MOF-177 loading was 8.4-times higher compared to the [EMIM][OAc]/CuBTC/Pebax MMM having 10 wt.% IL/MOF loading [21]. Another comparison showed that the IL/MOF-177/Pebax MMM has 1.2- and 7.3-times higher CO₂ permeability and CO₂/N₂ selectivity, respectively,

compared to [BMIM][PF₆]/ZIF-8/Pebax MMM which exhibited CO₂ permeability and CO₂/N₂ selectivity of 120 Barrer and 85, respectively [65].

In this study, we have successfully achieved improvements in both CO₂/N₂ selectivity and in CO₂ permeability of MMMs, overcoming the trade-off limitation. This notable improvement demonstrates the superiority of our modified material in facilitating more efficient gas separation. Moreover, the incorporation of MOF-177 into the MMMs offers a significant environmental advantage because of the non-toxic nature of zinc metal, contrasting with the toxicity associated with several other metals such as MIL-101(Cr). This substitution enhances the eco-friendliness of our MMMs, reducing the potential environmental impact associated with toxic metal usage. Thus, by utilizing a Zn-based MOF, we contribute to the development of environmentally sustainable separation, aligning with modern ecological principles and regulations. A more comprehensive comparison of the synthesized IL/MOF-177/Pebax MMM with the reported literature is provided in **Table 6A-4**.

The superior gas separation performance of the IL/MOF-177/Pebax MMMs can be ascribed to the incorporation of IL into the MOF cages, tailoring the pore openings of MOF-177. Moreover, the superior CO₂ solubility of [BMPyr][TCM] also enhanced the selectivity of MMMs compared to the neat polymer membrane. The presence of IL molecules has proven to be effective in enhancing the MOF-polymer interfacial interactions, which is the ultimate hindrance in the separation performance of MMMs. In the characterization section, it has been mentioned that some of the IL molecules leached out of the large pore openings of MOF-177 during the synthesis procedure and dispersed as free molecules in the polymer matrix. Those free-IL molecules might act as a wetting-agent to improve the interfacial adhesion between the polymer and MOF particles, thus, leading to a defect-free interface and ultimately resulting in improved CO₂ permeability as well as CO₂/N₂ selectivity of the resultant MMMs.

Next, the long-term stability of the [BMPyr][TCM]/MOF-177/Pebax MMM having 10 wt.% IL/MOF-177 loading was tested up to 75 hours under the same operating conditions, as shown in **Figure 6.10**. The data fluctuated within a narrow error range with the corresponding average values of 141±5 Barrer for CO₂ permeability and 705±78 for CO₂/N₂ selectivity, indicating the stability of the MMM under continuous operational

conditions. While some fluctuations in performance were observed, which can be attributed to the significantly low N₂ permeability, these deviations do not detract from the overall performance characteristics of the membrane, as the observed values remain consistent within an error margin of approximately $\pm 10\%$. This stability underscores the potential of synthesized membranes for sustained performance and reliability in practical applications over extended periods of time.

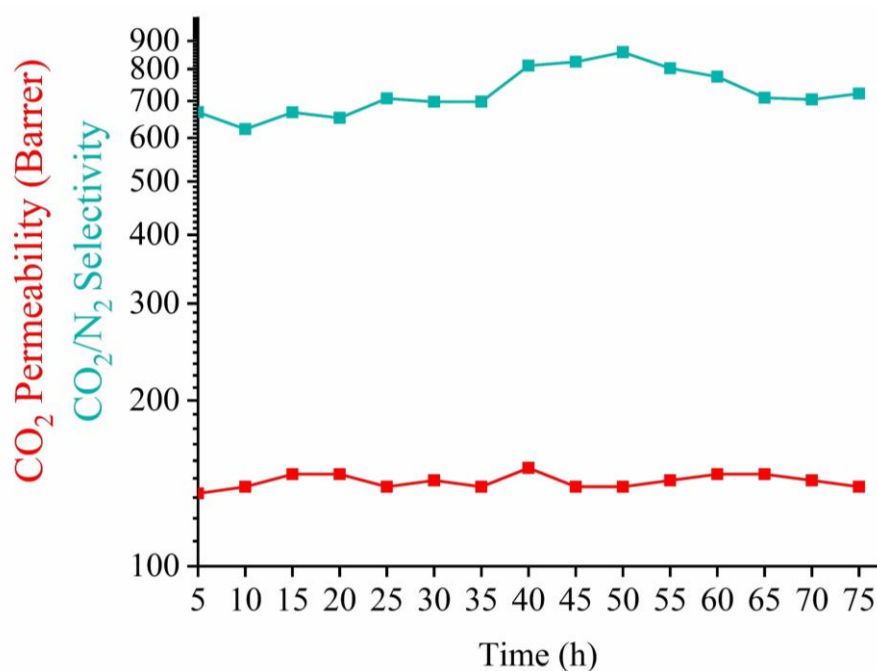


Figure 6.10. Long-term stability measurements of [BMPyr][TCM]/MOF-177/Pebax MMM having 10 wt.% IL/MOF-177 loading.

6.4 Conclusion

In this chapter, we combined a pyrrolidinium-based IL, [BMPyr][TCM], and MOF-177 to design a CO₂-selective [BMPyr][TCM]/MOF-177 composite. The synthesized composite was then incorporated into the polymer matrix to prepare a novel [BMPyr][TCM]/MOF177/Pebax MMMs for CO₂/N₂ separation. For comparison, a MOF177/Pebax MMMs was also synthesized. The uniform morphology of all MMMs was confirmed by the SEM images with no detectable interfacial voids, indicating the presence of well-dispersed fillers in the polymer matrix. The gas permeability measurements revealed that the MMM having a [BMPyr][TCM]/MOF177 composite with a loading of 10 wt.% showed a CO₂ permeability of 137 ± 2.0 Barrer and a CO₂/N₂

selectivity of 622 ± 105 , corresponding to 1.4- and 9.6-times improvements, respectively, compared to the neat Pebax membrane (CO₂ permeability: 98.0 ± 2.0 Barrer and CO₂/N₂ selectivity: 64.5 ± 6.0). The simultaneous increase in the CO₂ permeability and the CO₂/N₂ selectivity of MMMs breaks the trade-off limitation of the polymer membranes. The CO₂/N₂ selectivities of MMMs having 10 and 15 wt.% filler loadings presented in this study outperformed the updated upper bound, demonstrating superior gas separation performance of the synthesized MMMs.



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APPENDIX 6A

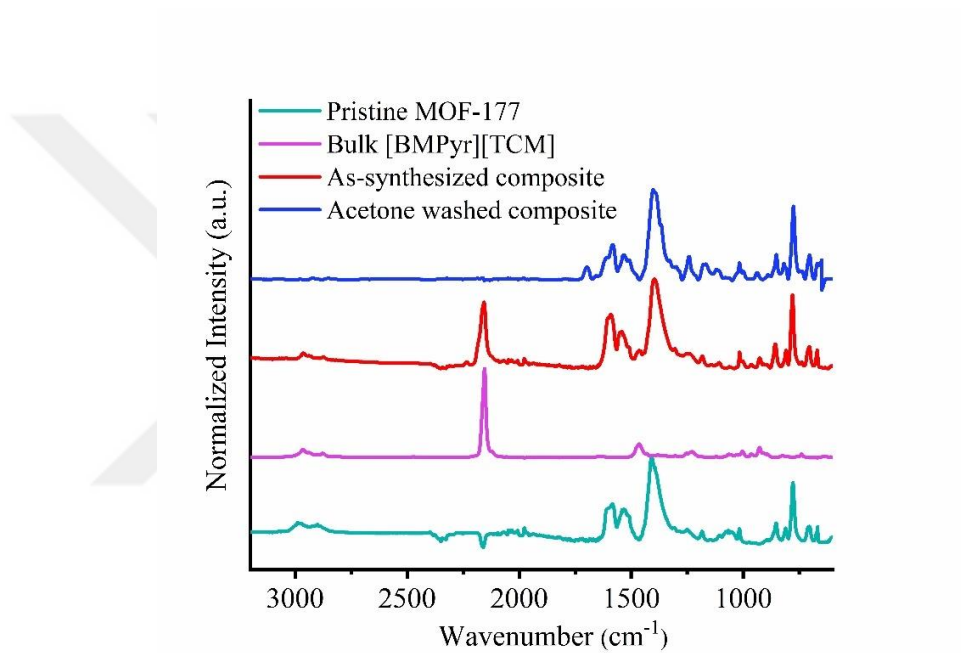


Figure 6A-1. IR spectra of MOF-177, bulk [BMPyr][TCM], [BMPyr][TCM]/MOF-177 before and after washing with acetone.

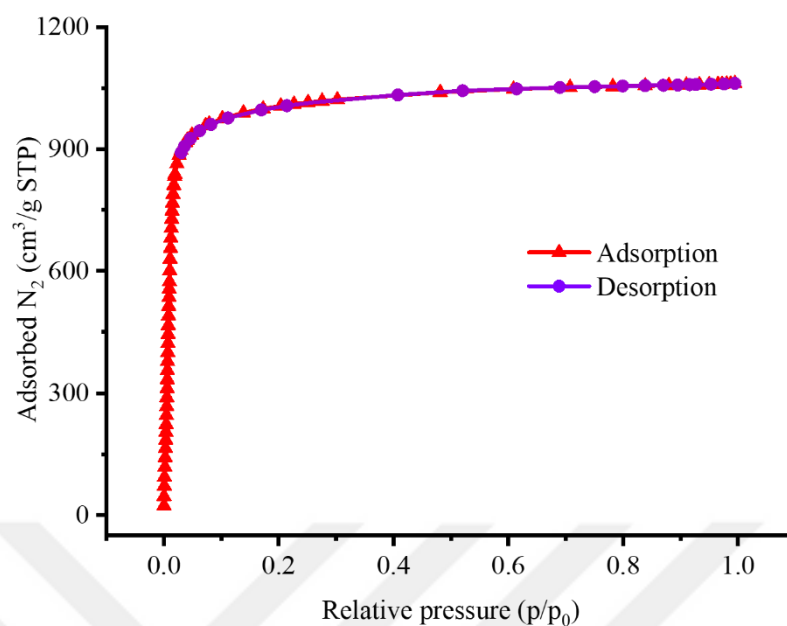


Figure 6A-2. N₂ adsorption-desorption isotherms of pristine MOF-177.

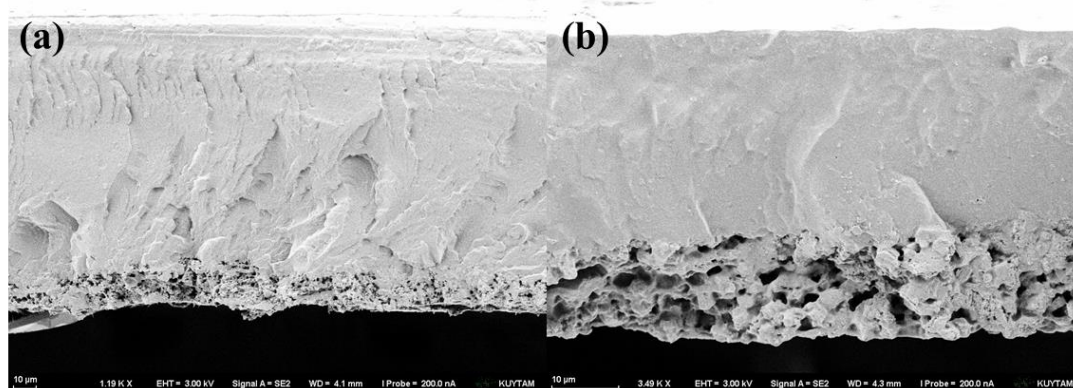


Figure 6A-3. SEM images of MOF-177/polymer MMMs having 4 wt.% polymer loading and dried at room temperature after casting procedure at (a) 1.1k× and (b) 3.49k× magnifications.

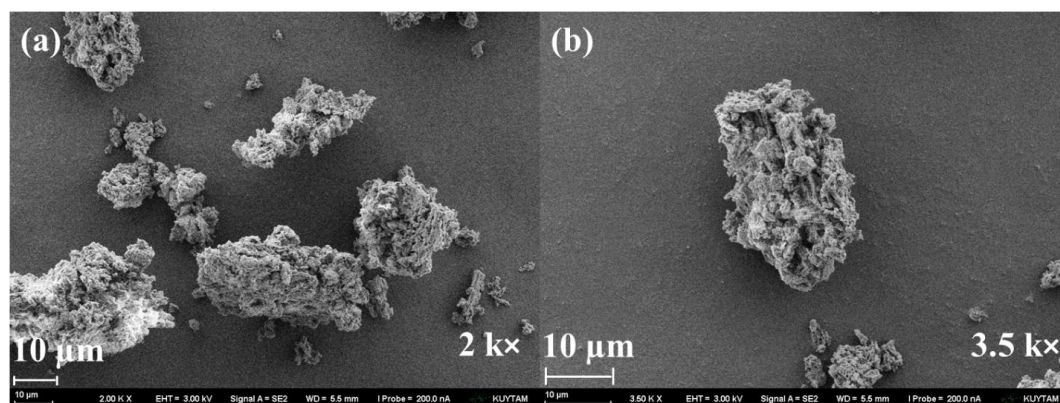


Figure 6A-4 SEM images of MOF-177 after mixing in ethanol/water mixture at (a) 2k×

and (b) 3.5k $\times$ magnifications.

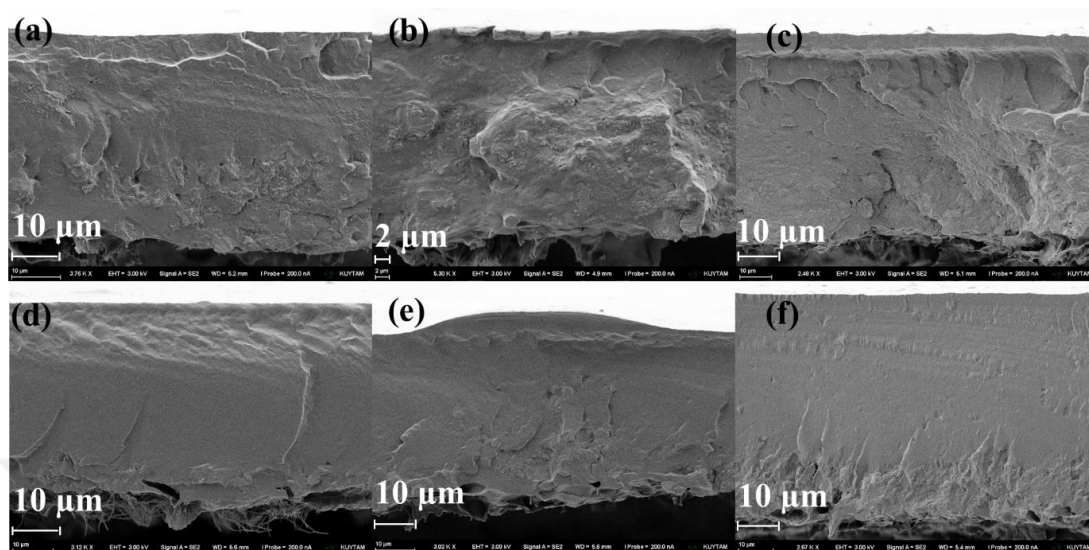


Figure 6A-5. SEM images of MOF-177/Pebax MMMs have (a) 10 wt.%, (b) 15 wt.%, and (c) 20 wt.% MOF-177 loadings and [BMPyr][TCM]/MOF-177/Pebax MMMs with (d) 10 wt.%, (e) 15 wt.%, (f) 20 wt.% [BMPyr][TCM]/MOF-177 loadings.

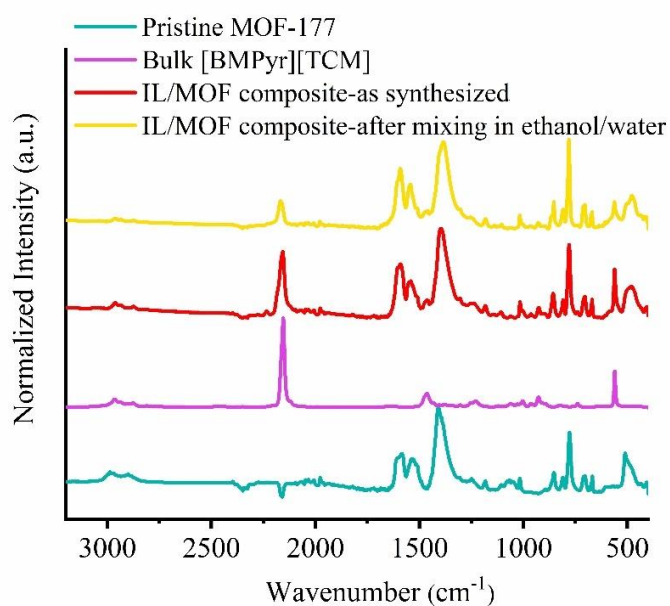


Figure 6A-6. IR spectra IL/MOF-177 composite before and after mixing in ethanol/water solution during the synthesis procedure.

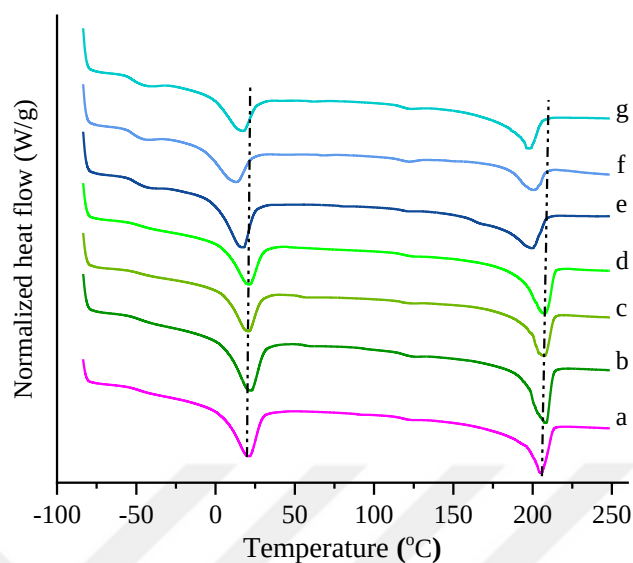


Figure 6A-7. Heat flow curves of (a) pure Pebax, MOF-177/Pebax MMMs having (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.% MOF-177 loadings and [BMPyr][TCM]/MOF-177/Pebax MMMs with (e) 10 wt.%, (f) 15 wt.%, (g) 20 wt.% [BMPyr][TCM]/MOF-177 loadings.

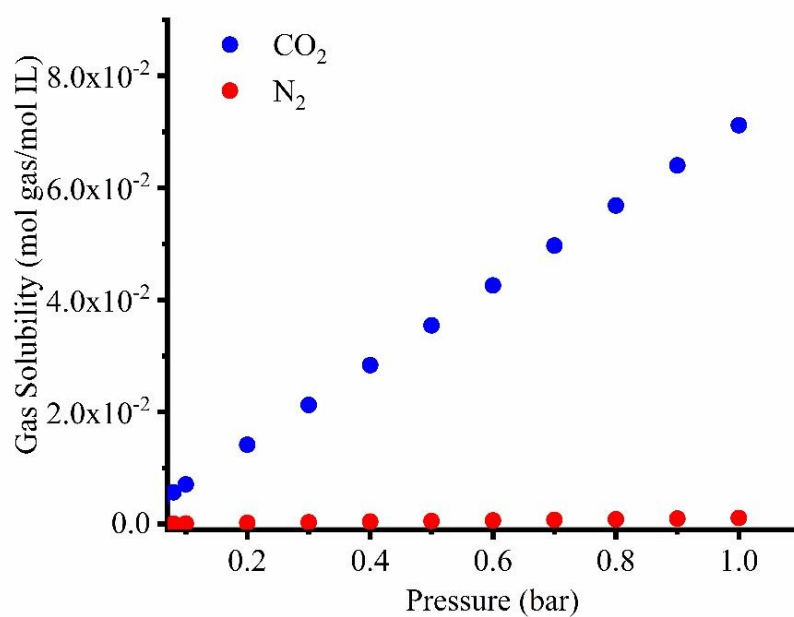


Figure 6A-8. The solubility of CO₂, and N₂ in bulk [BMPyr][TCM] calculated by COSMO-RS calculations at 35 °C.

Table 6A-1. Dual-site Langmuir-Freundlich fit parameter for pristine MOF-177 and [BMPyr][TCM]/MOF-177 composite.

	Dual-site Langmuir-Freundlich Model							
	Gas	q ₁ (cc/g)	k ₁ (1/mbar)	n ₁ *	q ₂ (cc/g)	k ₂ (1/mbar)	n ₂ *	R ²
Pristine MOF-177	CO ₂	8.80	1.6498	0.92	115.95	0.16	1.28	0.99
	N ₂	4.32	0.63	1.76	3.32	0.72	0.99	0.99
[BMPyr][TCM]/MOF-177	CO ₂	3.40	2.09	0.96	5.87	0.76	1.59	1
	N ₂	0.54	1.14	1.88	1.1×10 ⁻⁵	4.16	523.3	0.99

Table 6A-2. Glass transition temperatures (T_g) and specific enthalpies (ΔH, normalized by mass fraction of Pebax (φ) in the MMMs) pure Pebax, MOF-177/Pebax MMMs and [BMPyr][TCM]/MOF-177/Pebax MMMs.

Membrane Type	Filler loading (wt. %)	T _g (°C)	T _m (PEO) (°C)	ΔH _{PEO} /φ (J/g)	T _m (PA) (°C)	ΔH _{PA} /φ (J/g)
Pure Pebax	0	-48.3	21.4	14.5	205.5	13.8
MOF-177/Pebax MMMs	10	-48.5	22.3	18.0	208.6	16.1
	15	-48.4	20.8	13.9	207.6	14.2
	20	-48.9	21.6	15.9	206.7	17.8
[BMPyr][TCM]/MOF-177/Pebax MMMs	10	-50.9	17.6	13.9	200.3	12.4
	15	-52.8	13.1	11.6	200.7	8.1
	20	-53.4	17.5	10.0	197.8	11.0

Table 6A-3. CO₂ and N₂ permeability and CO₂/N₂ ideal selectivity of MMMs having different filler loadings at 35 °C and 1 bar.

Membrane Type	Filler Loading (wt.%)	Permeability (Barrer)		Selectivity (CO ₂ /N ₂)
		CO ₂	N ₂	
Pure Pebax	0	98.0±2.0	1.5±0.2	64.5±6.0
MOF-177/Pebax MMMs	10	154.0±6.0	1.42±0.1	108±12.6
	15	176±16.2	1.35±0.07	130±11.6
	20	174±20	2.5±1.1	71±3.0
[BMPyr][TCM]/MOF-177/Pebax MMMs	10	137.0±2.0	0.2±0.04	622±105
	15	200.0±0.7	0.5±0.1	417±102
	20	158±11.0	1.9±0.4	84.6±12.0
Free-IL/free-MOF/Pebax MMM	10	171.3±5.0	0.5±0.07	329±56.0
[BMPyr][TCM]/Pebax MMMs	10	125±3.0	1.4±0.2	92±17

Table 6A-4. Comparison with the literature data plotted on Robeson's upper bound in Figure 6.9.

Membrane types	Loading (wt.%)	P _{CO2} (Barrer)	Selectivity (CO ₂ /N ₂)	Conditions
MOF/Polymer MMMs				
UiO-66/PMMA [1]	15	1.1	55	25 °C, 4 bar
UiO-66/Pebax [2]	10	96.3	56	25 °C, 3 bar
UiO-66-NH ₂ /6FDA-durene [3]	20	1540	15.9	35 °C, 1 bar
UiO-66/PIM-1 [4]	10	6981	16	25 °C, 4 bar
UiO-66-NH ₂ /PES [5]	20	28.7	20	25 °C, 1 bar
Azo-UiO-66/Matrimid 5218 [6]	20	15	42	35 °C, 4 bar
CuBTC/Matrimid [7]	20	20.2	34	35 °C, 1 bar
NH ₂ -CuBTC/Matrimid [7]	20	13	43	35 °C, 1 bar
CuBTC/PPO [8]	10	79	14	30 °C, 1 bar
CuBTC/PSf [9]	10	8	22.3	30 °C, 5 bar

ZIF-7/Pebax 1657 [10]	22	137	97	20 °C, 6 bar
COF@PEI/6FDA-DAM [11]	7	1023	45	1 bar
SNW-1/PSf [12]	12	25.04	29	3.5 bar
ZIF-67/PIM-1 [13]	15	2800	27	2 bar
NH ₂ -UiO-66/PIM-1[14]	5	1740	24.1	1 bar
PDASS/PIM-1 [15]	24	1678	35	1 bar
MIL-53(Al)/Matrimid [16]	37.5	40	95	35 °C, 2 bar
NOTT-300/Pebax 1657 [17]	40	395	61	35 °C, 5 bar
BIT-72/Pebax 1657 [18]	30	139	56	35 °C, 5 bar
MOF-177/Pebax MMMs (This Study)	10	154.0±6	108±12.6	35 °C, 1 bar
	15	176±16.2	130±11.6	35 °C, 1 bar
	20	174±20	71±3.0	35 °C, 1 bar
IL/MOF/Polymer MMMs				
[EMIM][B(CN) ₄]/ZIF-8/[Poly(vbim)][NTf ₂] [19]	25.8	1062	24	35 °C, 3.5 bar
[BMIM][NTF ₂]/ZIF-8/PSF [20]	6	468	116	30 °C, 6 bar
[C ₃ NH ₂ BIM][NTF ₂]/NH ₂ -MIL-101(Cr)/PIM-1 [21]	5	2979	37	25 °C, 3 bar
[BMIM][NTF ₂]/ZIF-8/Pebax 1657 [22]	15	105	84	25 °C, 1 bar
[BMIM][NTF ₂]/MOF-801/PIM [23]	5	9420	29	35 °C, 4 bar
[BMIM][PF ₆]/ZIF-8/Pebax 1657 [24]	30	120	85	25 °C, 3-8 bar
[DnBM][Cl]/ZIF-8/Pebax 1657 [25]	32	260	72	30 °C, 2 bar
TMGHIM/ZIF-76/PIM-1 [26]	10	12848	14	23 °C, 1 bar
[NH ₂ -PMIM][NTF ₂]/ZIF-76/PIM-1 [27]	5	9536	31	25 °C, 2bar
[APTMS][Ac]/ZIF-67/PSf [28]	30	22	74	25 °C, 10 bar
[BMIM][Br]/MIL101(Cr)/Matrimid [29]	20	10	27	30 °C, 0.7 bar
[TMGA][N ₃]/MOF-5/Matrimid [30]	2	37	36	35 °C, 0.7 bar
[C ₂ MIM][C(CN) ₃]/MOF-74/Matrimid [30]	2	26	37	30 °C, 0.7 bar
[EMIM][OAc]/ZIF-8/Chitosan [31]	10	5431	12	25 °C

[EMIM][NTF ₂]/ZIF-67/6FDA-durene [32]	20	1400	24	25 °C, 2 bar
TSIL@NH ₂ -MIL-101(Cr)/PIM-1 [21]	5	2979	37	25 °C, 3 bar
[EMIM][NTF ₂]/HKUST/6FDA-Durene [33]	10	1106	27.1	25 °C, 2 bar
[BMPyr][TCM]/MOF-177/Pebax MMMs (This Study)	10	137.0±2.0	622±105	35 °C, 1 bar
	15	200.0±0.7	417±102	35 °C, 1 bar
	20	158±11.0	84.6±12.0	35 °C, 1 bar

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Chapter 7

A novel IL/MOF/polymer mixed matrix membrane having superior CO₂/N₂ selectivity*

7.1 Abstract

In this chapter, we synthesized an ionic liquid (IL)/metal organic framework (MOF) composite, 1-ethyl-3-methylimidazolium acetate/copper-1,3,5-benzenetricarboxylate ([EMIM][OAc]/CuBTC) and used it as a filler in a polymer, Pebax, to fabricate novel IL/MOF/polymer mixed matrix membranes (MMMs). CuBTC/Pebax and [EMIM][OAc]/CuBTC/Pebax MMMs having different filler loadings of 10, 15, and 20 wt.% were prepared by solution casting method. Uniform dispersion of MOF and IL/MOF fillers in the MMMs were observed. Incorporation of IL/MOF composite into Pebax significantly improved CO₂ permeability and CO₂/N₂ selectivity of the polymer by 2.5- and 5.5-times, respectively. Gas permeability measurements showed that the MMM having 15 wt.% IL/MOF loading exhibits significantly higher CO₂ permeability of 335 Barrer and CO₂/N₂ selectivity of 176 than the Pebax membrane having CO₂ permeability of 135 Barrer and CO₂/N₂ selectivity of 32. CO₂/N₂ selectivity of the [EMIM][OAc]/CuBTC/Pebax MMM with 15 wt.% [EMIM][OAc]/CuBTC filler loading was the highest among the values reported for other types of IL/MOF/polymer MMMs in the literature. All the CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC/Pebax MMMs that we fabricated in this work exceeded the Robeson's updated upper bound, showing the excellent potential of these novel membranes for CO₂/N₂ separation.

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7.2 Introduction

Membrane technology has been proven to be promising due to its low installation cost, operational simplicity, high-energy efficiency, and environmental friendliness. Polymer membranes can be easily fabricated [1], however their gas separation performances are restricted by the well-known Robeson's upper bound [2] which represents the trade-off between the gas permeability and selectivity for a target gas separation. Mixed matrix membranes (MMMs), composed of inorganic fillers dispersed in the polymer matrix, have received significant interest in the last decade since they combine easy processability of polymers with the good gas separation performance of inorganic fillers. Traditionally, zeolites have been used as fillers for the fabrication of zeolite/polymer MMMs, however difficulty of preparing defect-free zeolite crystals and poor adhesion between the polymer and zeolite particles limit the applicability of these MMMs [3].

Metal-organic frameworks (MOFs), a relatively new family of novel organic-inorganic materials, have been recently used as fillers in MMMs to enhance the gas separation performance of polymer membranes [4-8]. MOFs have high surface areas, large porosities, controllable pore sizes, good mechanical and thermal stabilities. The most important advantage of MOFs over other traditional fillers is that their physical and chemical properties can be easily tuned by choosing the proper metal-ligand pair for a target application [9, 10]. A large number of experimental studies has been reported on MOF/polymer MMMs for various gas separation applications including CO₂/CH₄, CO₂/N₂, H₂/CO₂ [11-15]. Incorporation of MOFs into polymers generally improve either the gas permeability or the selectivity of the polymer membrane [16]. For instance, Nafisi et al. [17] fabricated ZIF-8/Pebax MMMs and the MMM with 35 wt.% ZIF-8 loading showed significantly higher CO₂ permeability (1287 Barrer) compared to pure polymer (351 Barrer) whereas CO₂/CH₄ (32) and CO₂/N₂ (9) selectivities of the membrane remained unchanged. On the other hand, incorporation of a MOF could increase the selectivity of a polymer at the expense of decreased gas permeabilities. For example, Ordonez et al. [18] reported improved H₂/CO₂ and CO₂/CH₄ selectivities with increasing ZIF-8 loading for ZIF-8/Matrimid MMMs, from 121 to 472 and from 40 to 124, respectively, compared to the pure Matrimid membrane. Whereas, the CO₂, H₂ and CH₄

permeabilities were decreased from 12 to 7, 29 to 20, and 0.3 to 0.1 Barrer, respectively. Therefore, improving both the gas permeability and selectivity of the polymer membranes simultaneously by addition of new and novel filler materials is still highly desired.

Ionic liquids (ILs) can enhance the separation performance of MOFs due to their high affinity towards various gasses, such as CO₂, in addition to modifying the MOFs' pore structure. Incorporation of ILs into MOFs to prepare IL/MOF composites can combine the advantages of both constituents, such as high affinity of ILs towards desired gas molecules and tunable structure of both materials [19, 20]. IL/MOF composites have proven to be highly CO₂ selective over N₂ and CH₄ gasses through adsorption studies which leads to improved selectivities compared to pristine MOFs [21-26]. Therefore, utilization of IL/MOF composites in MMM applications has been examined and recent studies showed that IL/MOF composites can significantly improve the selectivity of the membranes depending on the well-controlled location of IL molecules [27, 28].

Introduction of ILs into MMMs via confining them into the pores of MOFs modifies the pore structures and chemical properties of the designed composite filler. For instance, Ban et al. [29] incorporated [BMIM][Tf₂N]/ZIF-8 composite ([BMIM][Tf₂N]:1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) into polysulfone (PSF) and the resulting MMM having a volume fraction of 6 % IL/ZIF-8 showed increased CO₂/CH₄ and CO₂/N₂ selectivities (from 19 to 38 and from 29 to 116, respectively) compare to pure PSF. Li et al. [30] incorporated a similar composite, [BMIM][Tf₂N]/ZIF-8, into Pebax and the resulting MMM with 15 wt.% IL/ZIF-8 loading showed significant increase in CO₂/CH₄ and CO₂/N₂ selectivities (from 20 to 34 and from 48 to 84, respectively). Yasmeeen et al. [31] investigated the separation performance of [APTMS][Ac]/ZIF-67/PSf MMM ([APTMS][Ac]: 3-(trimethoxysilyl)propan-1-aminium acetate) and showed that CO₂/CH₄ and CO₂/N₂ selectivities of the MMM with 30 wt.% IL/MOF filler loading are higher (72.1 and 74.5, respectively) than the selectivities of the pure PSf membrane (25.1 and 27.2, respectively).

IL/MOF composites have been incorporated into highly permeable polymers such as polymers of intrinsic microporosity (PIM-1) and less permeable polymers such as Matrimid, to synthesize IL/MOF/polymer MMMs with improved gas separation performance. Chen et al. [27] incorporated [BMIM][TF₂N]/MOF-801 composite into

PIM-1. The CO₂ permeability of IL/MOF/PIM-1 MMM with 5 wt.% IL/MOF loading was 2.2-times higher (9420 Barrer) than that of PIM-1 membrane (4110 Barrer) and CO₂/N₂ selectivity (29) was 1.4-times higher compared to that of PIM-1 membrane (20). Ferreira et al. [28] incorporated, 1-propyl-3-methylimidazolium bromide, [PMIM][Br]/MIL101(Cr) composite into Matrimid and the IL/MOF/polymer MMMs exhibited CO₂ permeability of 44 Barrer, which was 4-times higher than that of pure Matrimid (9.8 Barrer). Lin et al. [32] synthesized [EMIM][Tf₂N]/CuBTC composite ([EMIM][Tf₂N]:1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) and prepared IL/MOF/polymer MMMs by incorporating the composite into 6FDA polymer. Results showed that CO₂ permeability of IL/CuBTC/polymer MMM was significantly higher, 1200 Barrer, than the pure polymer membrane, 790 Barrer. However, CO₂/N₂ and CO₂/CH₄ selectivities of the MMM were only slightly improved compared to that of the pure polymer. These results highlight that IL/MOF composites can be highly promising filler particles for MMM applications due to their high CO₂ affinities. Thus, the synthesis of new IL/MOF composites and their use in polymers to generate MMMs can lead to new membranes with exceptional CO₂ separation performances. Accordingly, extending the list of such filler materials having different components, ILs and MOFs, is highly desired to understand how their structures should be tuned for improved separation performance of the MMMs. Besides, these initial studies have also shown that using fillers improved the gas permeability and/or the gas selectivity of the polymer membrane. Enhancing both the gas permeability and selectivity to exceed the Robeson's upper bound has been the main target of all the MMM studies for a very long time.

In this work, we reported a novel IL/MOF/polymer MMM offering an exceptionally high performance for CO₂/N₂ separation. Considering the very large variety and number of possible IL/MOF/polymer combinations, this work will significantly contribute into the design and development of new MMMs having different types of IL/MOF fillers. 1-ethyl-3-methylimidazolium acetate, [EMIM][OAc], was incorporated in CuBTC by wet impregnation method to synthesize [EMIM][OAc]/CuBTC composite. [EMIM][OAc] was selected as the IL due to its high CO₂ solubility associated with its Lewis basic acetate anion [20]. CuBTC was chosen as the porous support for the newly synthesized IL/MOF composite filler considering the limited number of studies on IL/CuBTC/polymer MMMs

[32]. These selected IL and CuBTC were used to prepare a novel [EMIM][OAc]/CuBTC composite for utilizing the potential of these individual constituents in CO₂/N₂ separation. Then, [EMIM][OAc]/CuBTC composite was dispersed as a filler in Pebax at the loadings of 10, 15, and 20 wt.% to prepare [EMIM][OAc]/CuBTC/Pebax MMMs. Pebax was selected as a polymer matrix for its well-known affinity for polar gases [33], with the aim of fabricating highly CO₂ selective MMMs demonstrating enhanced filler-composite compatibility. Synthesized [EMIM][OAc]/CuBTC composite, CuBTC/Pebax MMMs, and [EMIM][OAc]/CuBTC/Pebax MMMs were characterized in deep detail using various characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Infrared spectroscopy (IR), and thermogravimetric analysis (TGA) and corresponding structural changes were discussed. Single-component adsorption isotherms of CO₂ and N₂ for pristine CuBTC and [EMIM][OAc]/CuBTC composite were experimentally measured using volumetric adsorption method whereas single-component CO₂ and N₂ permeability of all MMMs were measured using a custom-built constant pressure/variable volume setup. Consequently, we evaluated the gas permeability and selectivity of the MMMs containing CuBTC and [EMIM][OAc]/CuBTC fillers by comparing their results with other reported MOF/polymer and IL/MOF/polymer MMMs. Based on these, the results of this work will significantly contribute into the literature of MMMs and accelerate the design and development of new IL/MOF/polymer MMMs in near future.

7.3 Results and Discussion

7.3.1 Characterization of the materials

7.3.1.1 Pristine MOF and its composite

Surface area and pore volume of the pristine CuBTC and the [EMIM][OAc]/CuBTC composite were determined by the N₂ adsorption isotherms presented in **Figure 7A-1**. Results demonstrated that both pristine CuBTC and [EMIM][OAc]/CuBTC composite have typical type-I adsorption isotherms, a characteristic feature of microporous materials. Thus, we inferred that CuBTC maintains its microporosity upon the IL incorporation. Results further showed that the BET surface area and pore volume of CuBTC decreased from 1152 m²/g and 0.13 cm³/g to 9.12 m²/g and 0.03 cm³/g upon the incorporation of [EMIM][OAc], respectively. These significant

decreases indicated that the pores of CuBTC were mostly occupied by the [EMIM][OAc] molecules, confirming the successful incorporation of IL into MOF, consistent with the literature [19, 41]. However, it is noteworthy that overall N₂ uptake is also dependent on the solubility of N₂ in the ILs. To address this issue, additional COSMO-RS calculations were conducted to compute the solubility of N₂ in bulk [EMIM][OAc] at the BET measurement conditions as given in **Figure 7A-2**. Results demonstrated that N₂ has almost negligible solubility in [EMIM][OAc] at the BET measurement conditions. Therefore, it can be inferred that some IL molecules located at the gate openings of the CuBTC might restrict the accessibility of N₂ into the completely/partially available pores [42, 43]. Therefore, BET analysis can be quantitatively misleading in terms of providing reliable data for IL/CuBTC composite.

XRD diffraction patterns of pristine CuBTC and [EMIM][OAc]/CuBTC composite are presented in **Figure 7.1**. The presence of main diffraction peaks at 6.7, 9.4, and 11.6° in both diffraction data confirmed that IL incorporation did not affect the crystalline structure of CuBTC. However, some minor differences in the peak intensities were observed in XRD patterns of CuBTC and [EMIM][OAc]/CuBTC composite, which are likely associated with the changes in the electronic environment of the crystals or their preferential orientation due to the presence of IL molecules inside the pores [29, 44]. Moreover, morphology of the pristine CuBTC and [EMIM][OAc]/CuBTC composite was investigated using the SEM images and **Figure 7A-3** demonstrated that the surface morphology of CuBTC remained mostly intact upon the incorporation of [EMIM][OAc], consistent with an earlier report presenting a composite of CuBTC with 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄] [45].

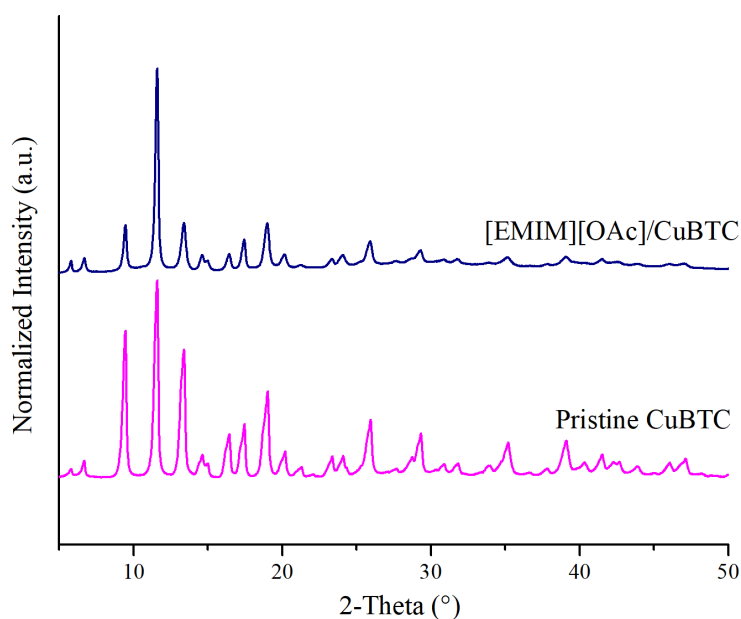


Figure 7.1. XRD diffractogram of pristine CuBTC and [EMIM][OAc]/CuBTC composite.

Figure 7.2 represents the TGA analysis of CuBTC, [EMIM][OAc], and [EMIM][OAc]/CuBTC. In the TGA curves, two weight loss steps were observed for CuBTC and bulk IL. The initial weight loss between 80 and 100 °C is associated with the moisture content of the structure. Accordingly, CuBTC decomposed approximately at T'_{onset} value of 320 °C, which may be attributed to the removal of the organic linker and decomposition of CuBTC structure [46]. The bulk IL decomposed through a typical one-step decomposition mechanism with T'_{onset} value of approximately 190 °C, whereas the IL/MOF composite showed a T'_{onset} of approximately 260 °C. These results demonstrated that synthesized IL/MOF composite has a higher T'_{onset} compared to the bulk IL. This change in T'_{onset} can be attributed to the presence of direct IL-MOF interactions in the composite offering a completely different behavior of the IL when incorporated into CuBTC, consistent with the previous reports [47].

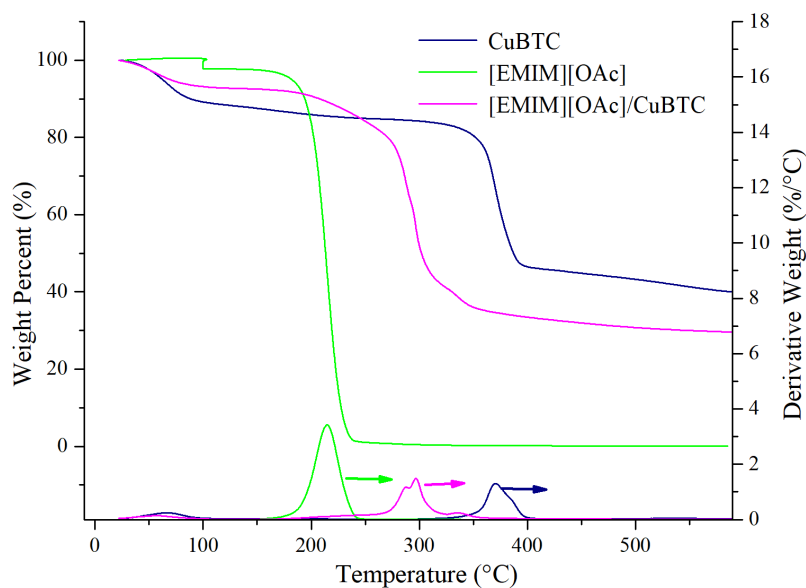


Figure 7.2. TGA and DTG curves of CuBTC, [EMIM][OAc]/CuBTC, and bulk [EMIM][OAc].

To have further insight into the interactions between IL and CuBTC, IR analysis was performed. The IR spectra of pristine CuBTC, bulk [EMIM][OAc], and [EMIM][OAc]/CuBTC composite are shown in **Figure 7.3**. The peaks were deconvoluted, and then the shifts in the peak positions were determined compared to the corresponding characteristic peak positions in the bulk [Emim][OAc] and pristine CuBTC. In [Emim][OAc] spectrum, the peaks located at 1570, 1429 and 1232 cm^{-1} represented the $\nu(\text{C}=\text{O})$, $\delta(\text{CH}_3)$ and $\nu(\text{C}-\text{CH}_3)$ vibrational modes due to the presence of acetate ion in the IL, whereas the peaks at 1185 and 1377 cm^{-1} were attributed to $\nu(\text{C}-\text{N})$ and $\nu(\text{C}-\text{O})$ vibrations of the imidazolium ring present in [Emim]⁺ cation [48]. It was observed that $\nu(\text{C}-\text{N})$ and $\nu(\text{C}-\text{O})$ characteristic vibrations of the imidazolium ring exhibited red-shifts of 11 and 6 cm^{-1} , respectively, in the IR spectra of IL/CuBTC suggesting a molecular interaction between CuBTC and the cation of IL [49]. The presence of shifts in the IL band positions indicated that the IL was successfully incorporated inside the CuBTC cages.

In pristine CuBTC, bands from 1300 to 1700 cm^{-1} can be associated with the carboxylate linker and were attributed to the coordination of benzenetricarboxylate (BTC) linker to the copper sites. Accordingly, the peaks located at 1648, 1450 and 1374 cm^{-1}

¹ correspond to the $\nu(\text{C}=\text{C})$, the asymmetric $\nu(\text{COOH})$ and $\nu(\text{C}-\text{O})$ vibrations, respectively, of benzene groups in the BTC linker [50]. The characteristic $\nu(\text{C}-\text{O}-\text{Cu})$ and $\nu(\text{C}-\text{C})$ peaks of CuBTC, located at 1117 and 1450 cm^{-1} [35], slightly red shifted to lower wavenumbers with 2 cm^{-1} , upon the incorporation of IL, similar with the previously reported IL/CuBTC studies [45, 51]. These red shifts in the characteristic $\nu(\text{C}-\text{O}-\text{Cu})$ and $\nu(\text{C}-\text{C})$ bands of pristine CuBTC imply a possible change in the electronic environment of existing pores and can be attributed the presence of IL molecules which may weakened the Cu–O bond of CuBTC. Hence, observed changes in the characteristic peak positions of bulk IL and pristine CuBTC can be inferred to the electron sharing between the cation of IL and the open metal sites of CuBTC, confirming the presence of direct interactions between IL and MOF in the composite material. Moreover, IR results were consistent with the TGA analysis confirming the presence of interactions between IL and CuBTC.

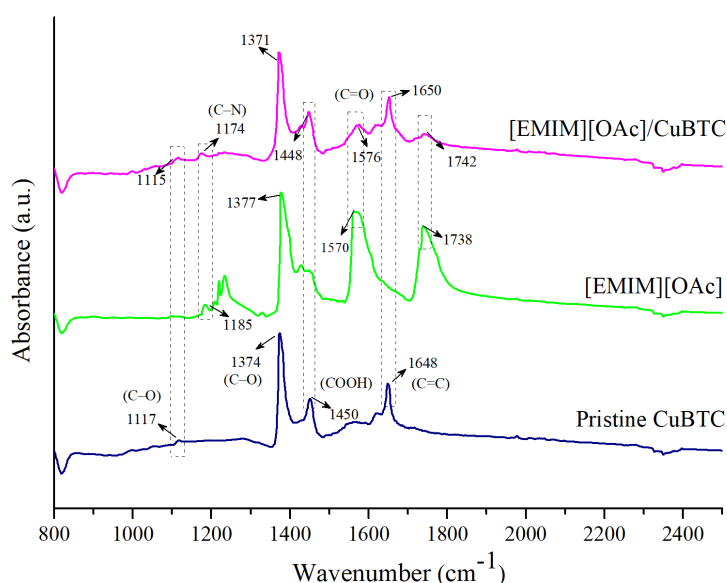


Figure 7.3 FTIR spectra of pristine CuBTC, [EMIM][OAc]/CuBTC, and bulk [EMIM][OAc].

7.3.1.1 Characterization of MMMs

MOF/polymer MMMs and IL/MOF/polymer MMMs were synthesized by incorporating 10, 15, and 20 wt.% loadings of pristine CuBTC and [EMIM][OAc]/CuBTC as fillers into Pebax. SEM analysis was used to investigate the

[illegible]

Figure 7.4. Cross-sectional SEM images of MMMs at magnifications of 10 k $\times$. CuBTC/Pebax MMMs (given in (a), (b), and (c)) and [EMIM][OAc]/CuBTC/Pebax MMMs (given in (d), (e), and (f)) with corresponding filler amounts for both types of MMMs are (a, d) 10 wt.%, (b, e) 15 wt.%, (c, f) 20 wt.%.

The EDS results of Cu mapping also proved the uniform dispersion of the filler particles represented in **Figure 7A-4**. The Cu distribution in CuBTC/Pebax MMMs became more prominent as the CuBTC loading was increased from 10 to 20 wt.%, shown in **Figure 7A-6(a-c)**. In the case of [EMIM][OAc]/CuBTC/Pebax MMMs shown in **Figure 7A-6(d-f)**, it was observed that IL addition leads to more dense and smooth membranes compared to MOF/polymer MMMs, which may be attributed to the reduction in the crystallinity of the membranes [52].

XRD patterns of pure Pebax, CuBTC/Pebax MMMs, and [EMIM][OAc]/CuBTC/Pebax MMMs with 10, 15, and 20 wt.% fillers are represented in **Figure 7.5**. A broad peak at 13-23° and a narrow peak at 24.2° were observed in the pure polymer as shown in **Figure 7.5(a)**, which were attributed to the polyamide (PA) group, representing the semicrystalline structure of Pebax [53]. For all the MMMs, the positions of these peaks remain almost the same, indicating that the intersegmental spacing of Pebax did not change with the filler incorporation. Furthermore, XRD spectra presented in **Figure 7.5(b-g)** showed new peaks at 6.7, 9.4, and 11.7° corresponding to the characteristic peaks of CuBTC in all MMMs [54]. It was also observed that as the CuBTC loading was increased from 10 to 20 wt.%, the intensities of the corresponding CuBTC peaks were also increased as shown in **Figure 7.5(b-d)**, indicating that the crystal structure of CuBTC remains intact in the polymer. However, in the case of IL/CuBTC/Pebax MMMs shown in **Figure 7.5(e-g)**, the intensity of PA peaks of the polymer was decreased as the [EMIM][OAc]/CuBTC loading was increased, which can be ascribed to the disruption of polymer chains packing and reduced crystallinity of the membranes [55].

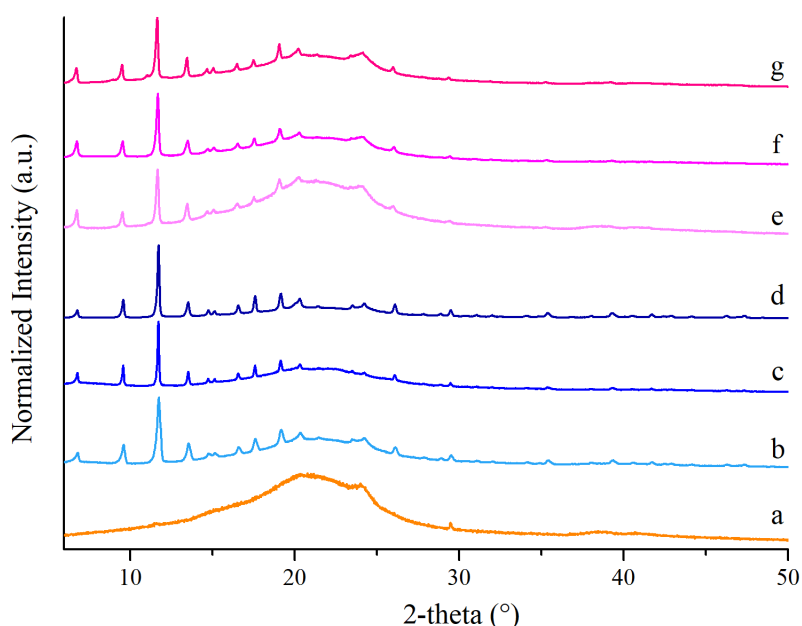


Figure 7.5. XRD spectra of membranes. (a) Pure Pebax, CuBTC/Pebax MMMs with (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.% CuBTC loadings. [EMIM][OAc]/CuBTC/Pebax MMMs with (e) 10 wt.%, (f) 15 wt.%, (g) 20 wt.% [EMIM][OAc]/CuBTC loadings.

The TGA curves of CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC/Pebax MMMs at different filler loadings are shown in **Figure 7.6(a-c)** and (d-f), respectively. The decomposition temperatures did not significantly change with the increase in the filler loadings. The first stage of the weight loss was observed around 80-90 °C, caused by the desorption of water and the residual solvent. At the second stage, the mass loss around 260-270 °C indicated the decomposition of organic ligands of CuBTC and [EMIM][OAc]/CuBTC composite present in CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC MMMs, respectively. The third stage of weight loss was primarily due to the decomposition of the polymer backbone, which is at the range of 300±5 °C for CuBTC/Pebax MMMs and at the range of 360±5 °C for [EMIM][OAc]/CuBTC/Pebax MMMs. The decomposition temperature of [EMIM][OAc]/CuBTC/Pebax MMMs was observed to be slightly higher than that of CuBTC/Pebax MMMs, which was attributed to the high thermal stability of [EMIM][OAc]/CuBTC composite, consistent with the literature [56]. In general, all the MMMs are stable up to 300 °C, indicating that they can withstand high temperatures.

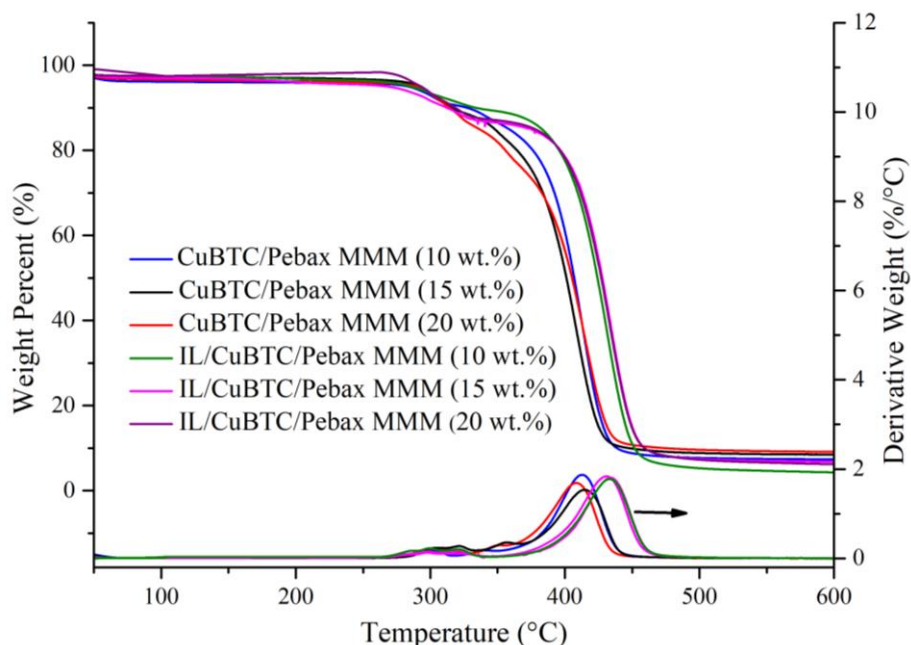


Figure 7.6. TGA and DTG curves of CuBTC/Pebax MMMs with (a) 10 wt.%, (b) 15 wt.%, (c) 20 wt.% CuBTC loadings and [EMIM][OAc]/CuBTC/Pebax MMMs with (d) 10 wt.%, (e) 15 wt.%, (f) 20 wt.% [EMIM][OAc]/CuBTC loadings.

FTIR spectra of pure Pebax, CuBTC/Pebax MMMs, and [EMIM][OAc]/CuBTC/Pebax MMMs with 10, 15, and 20 wt.% loadings of CuBTC and [EMIM][OAc]/CuBTC, respectively, are represented in **Figure 7.7(a-g)**. In the IR spectra of Pebax as shown in **Figure 7.7(a)**, the characteristic peaks of PA group located at 3297, 1637, and 1732 cm^{-1} were attributed to the hydrogen bonded $\nu(\text{N-H})$ group [57, 58], (O-C-O) group, and (H-N-C=O) group [59], respectively. The peak observed near 1100 cm^{-1} related to the (C-O-C) group was attributed to the (PEO) part of the Pebax [60]. Moreover, the $\delta(\text{C-H})$ and $\nu(\text{C-H})$ vibrations at 2864-2942 cm^{-1} and 1440 cm^{-1} represented the aliphatic groups present in Pebax. Similar characteristic peaks of Pebax were observed in all MMMs as shown in **Figure 7.7(b-g)**. CuBTC/Pebax MMMs with 10 wt.% CuBTC loading given in **Figure 7.7(b)** showed characteristic peaks of Pebax, located at 1116 cm^{-1} (C-O-C), 1636 cm^{-1} (O-C-O), 1738 cm^{-1} (H-N-C=O), 3298 cm^{-1} (N-H) and 2866-2942 cm^{-1} (C-H). As the loading of CuBTC was increased to 15 and 20 wt.%, (O-C-O) exhibited blue-shifts of 3 and 6 cm^{-1} and, (C-O-C) exhibited red-shifts of 6 and 5 cm^{-1} , respectively. These shifts suggested an interaction present between the

CuBTC and Pebax. Moreover, the new peaks observed at 729 cm⁻¹ (C–H bending vibrations) and 1377 cm⁻¹ (COO symmetric vibrations) can be associated with the characteristic peaks of CuBTC and consistently, the peak intensities were increased with the increasing CuBTC loading.

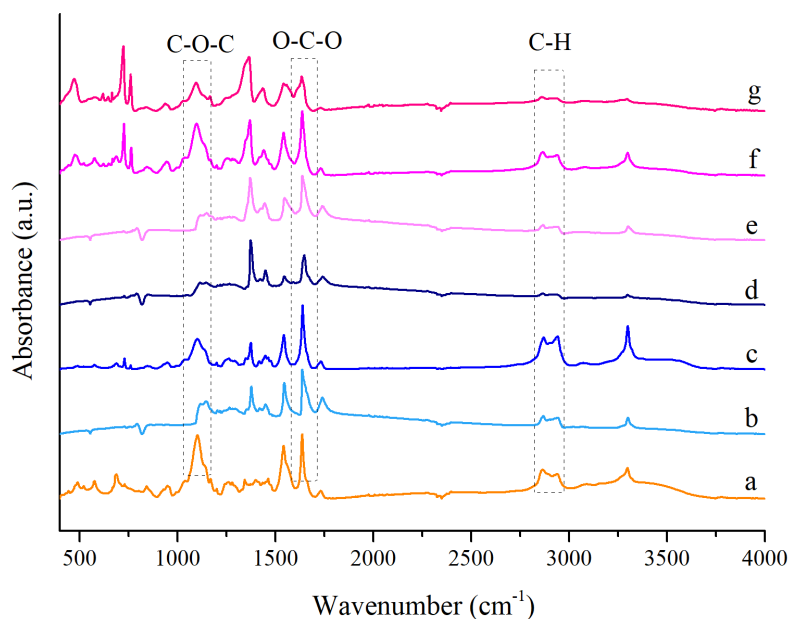


Figure 7.7. IR spectra of the membranes. (a) Pure Pebax, CuBTC/Pebax MMMs with (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.% CuBTC loadings, and [EMIM][OAc]/CuBTC/Pebax MMMs with (e) 10 wt.%, (f) 15 wt.%, (g) 20 wt.% [EMIM][OAc]/CuBTC loadings.

The IR spectra of [EMIM][OAc]/CuBTC/Pebax MMMs are represented in **Figure 7.7(e-g)**. At 10 wt.% IL/CuBTC loading, in **Figure 7.7(e)**, the spectra showed characteristic peaks of Pebax located at 1107 cm⁻¹ (C–O–C), 1640 cm⁻¹ (O–C–O), 1738 cm⁻¹ (H–N–C=O), 3301 cm⁻¹ (N–H) and 2866–2936 cm⁻¹ (C–H). As the loading of IL/CuBTC composite was increased to 15 and 20 wt.%, it was observed that (O–C–O) exhibited red-shifts of 4 and 5 cm⁻¹ and, (C–O–C) exhibited red-shifts of 10 and 11 cm⁻¹, respectively. These shifts suggested the interaction present between IL/CuBTC composite and Pebax. Moreover, the peaks located at 727 cm⁻¹ (C–H bending vibrations) and 1370 cm⁻¹ (COO symmetric vibrations) corresponding to the characteristic peaks of CuBTC were observed to be intensified with the increase in IL/CuBTC loadings and this could be explained by the increase in CuBTC concentration. In contrast, as the CuBTC and IL/CuBTC loadings were increased from 10 to 20 wt.%, the intensity of IR bands

corresponding to (C–H) and (C–O–C) groups of Pebax was observed to decrease as shown in **Figure 7.7**(c, d, f, g), indicating agglomeration of the filler particles and polymer chain rigidification at high loadings [61].

7.3.2 Gas separation performances of materials

7.3.2.1 IL/MOF composite

Single-component volumetric adsorption measurements of CO₂ and N₂ gases in CuBTC and [EMIM][OAc]/CuBTC composite were performed up to 1 bar at 25 °C as shown in **Figure 7.8**(a). Results showed that both CO₂ and N₂ uptakes decreased upon IL incorporation into CuBTC. For instance, CO₂ and N₂ uptakes of CuBTC at 1 bar, corresponding to 91.3 and 5.8 cm³/g, decreased to 11.4 and 0.9 cm³/g, respectively, in the case of IL/CuBTC composite. The decrease in the gas uptakes was attributed to the reduced surface area and pore volume of the [EMIM][OAc]/CuBTC composite considering the occupation of pores of CuBTC by the IL molecules.

The corresponding ideal CO₂/N₂ selectivities of pristine CuBTC and IL/CuBTC composite were calculated from the single-component gas adsorption data and shown in **Figure 7.8**(b). Data illustrated that IL/CuBTC composite is more CO₂ selective than its CuBTC counterpart, at low-pressure region up to 0.2 bar. Upon the incorporation of [EMIM][OAc], the ideal CO₂/N₂ selectivity of CuBTC was increased to 122.6 (67.3) from 20.3 (20.2) at 0.001 (0.01) bar yielding 6-times (3.3-times) improvement. **Table 7A-1** compares [EMIM][OAc]/CuBTC adsorption selectivity results with those reported for other IL/CuBTC composites in the literature. The ideal CO₂/N₂ selectivity of [EMIM][OAc]/CuBTC composite that we synthesized is 1.6-times higher (67.3 at 0.01 bar and 25 °C) than that of 1-ethyl-3-methylimidazolium diethyl phosphate, [EMIM][DEP]/CuBTC composite (42.3 at 0.01 bar and 25 °C), showing the high potential of [EMIM][OAc]/CuBTC composite for selective CO₂ separation of from N₂ [51]. As demonstrated in **Figure 7.8**(b), above 0.2 bar, a decrease in the selectivity of the composite was observed compared to the pristine material. This can be explained by the change in the driving forces of surface adsorption with increasing pressure. In the low-pressure range, gas adsorption is significantly determined by the adsorbent's affinity towards the guest molecules [26, 62], however, with increasing pressure, the adsorption

mechanism mostly depends on the available pore volume of the material. Therefore, the reduced selectivity of the composite observed above 0.2 bar can be attributed to the change in the adsorption mechanism, from surface affinity to pore availability. Overall, these results illustrated that the [EMIM][OAc]/CuBTC composite is highly CO₂ selective at low pressures and can have a huge potential as a filler material for MMMs to achieve CO₂/N₂ separation with high selectivity.

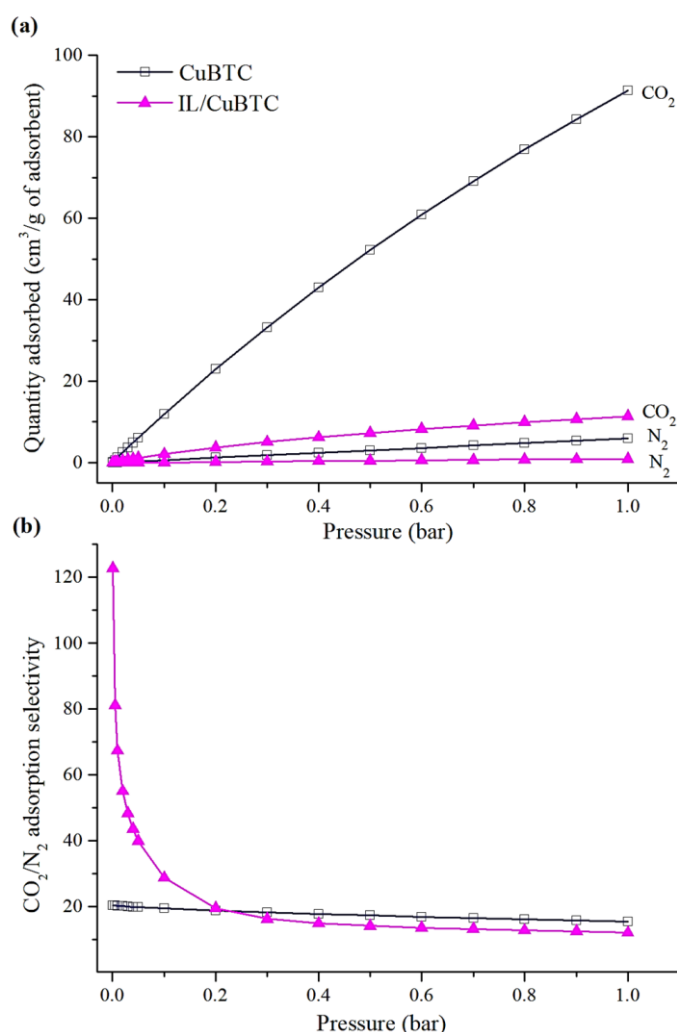


Figure 7.8. (a) CO₂ and N₂ adsorption isotherms, (b) ideal CO₂/N₂ selectivity of pristine CuBTC and [EMIM][OAc]/CuBTC composite at 25 °C.

6.3.2.1 Membrane-based gas separation

We examined gas permeabilities and selectivities of CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC/Pebax MMMs. Single-component gas permeation tests were conducted at 35°C and 1 bar for both MMMs. **Figure 7.9**(a) and (b) show CO₂

permeabilities and CO₂/N₂ permeation selectivities of CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC/Pebax MMMs with different CuBTC and IL/CuBTC loadings, respectively. The data for CO₂ and N₂ permeability and CO₂/N₂ selectivity is also presented in **Table 7A-3**. For pure Pebax membrane, CO₂ and N₂ permeabilities were measured as 134.6±2 and 4.2±0.5 Barrer, respectively and CO₂/N₂ selectivity was calculated as 31.8±1.7. For CuBTC/Pebax MMMs having 10 wt.% CuBTC loading, CO₂ and N₂ permeabilities were measured as 190±4 and 2.67±1.1 Barrer, respectively, leading to a CO₂/N₂ selectivity of 71±11. This data shows that upon the incorporation of CuBTC at a filler loading of 10 wt.%, CO₂ permeability of the membrane increased whereas N₂ permeability decreased, resulting in an improved CO₂/N₂ selectivity. CO₂ permeability was further increased to 286±9 Barrer and N₂ permeability was decreased to 2.22±0.4 Barrer as the CuBTC loading was increased to 15 wt.%. As a result, CuBTC/Pebax MMMs having 15 wt.% CuBTC loading exhibited a CO₂/N₂ selectivity of 128±11. Overall, CO₂ permeabilities of CuBTC/Pebax MMMs with 10 and 15 wt.% CuBTC loadings were 1.4- and 2.1-times higher than the pure Pebax membrane. Moreover, CO₂/N₂ selectivities of CuBTC/Pebax MMMs with 10 and 15 wt.% CuBTC loadings were also 2.2- and 4-times higher compared to the selectivity of the pure polymer membrane. These results showed that incorporation of CuBTC as a filler into Pebax to synthesize CuBTC/Pebax MMMs resulted in a significantly improved CO₂/N₂ selectivity.

We then compared CO₂/N₂ separation performance of CuBTC/Pebax MMM with the other MOF/Pebax MMMs reported in the literature. For example, UiO-66/Pebax MMM having 10 wt.% UiO-66 loading was reported to have CO₂ permeability of 96 Barrer at 25 °C and 3 bar [63]. Thus, CuBTC/Pebax MMM that we synthesized in this work has 2-times higher permeability than UiO-66/Pebax MMM. The CO₂/N₂ selectivity of CuBTC/Pebax MMM was 1.2-times higher (71) than the highest reported CO₂/N₂ selectivity (56.5) of UiO-66/Pebax MMM. We also compared the separation performance of CuBTC/Pebax MMM with the data reported at 23 °C and 1 bar for ZIF-8/Pebax MMM having various ZIF-8 loading [52]. CO₂ permeability and CO₂/N₂ selectivity of CuBTC/Pebax MMM having 15 wt.% CuBTC loading were 2.8- and 3.6-times higher, respectively, compared to the highest CO₂ permeability (100 Barrer) and CO₂/N₂ selectivity (35) of ZIF-8/Pebax MMM having 15 wt.% ZIF-8 loading. A more detailed

comparison of CuBTC/Pebax MMMs with the other MMMs reported in the literature is given in **Table 7A-4**. Results illustrated that the CO₂ permeabilities and CO₂/N₂ selectivities of CuBTC/Pebax MMMs presented in this study are superior compared to the literature. Overall, the significant enhancement we observed in CO₂ permeability of the MMM upon the CuBTC addition can be attributed to the increased free volume in the polymer matrix due to increased CuBTC loading [64], and the strong CO₂ affinity of open Cu⁺² sites of CuBTC framework [8].

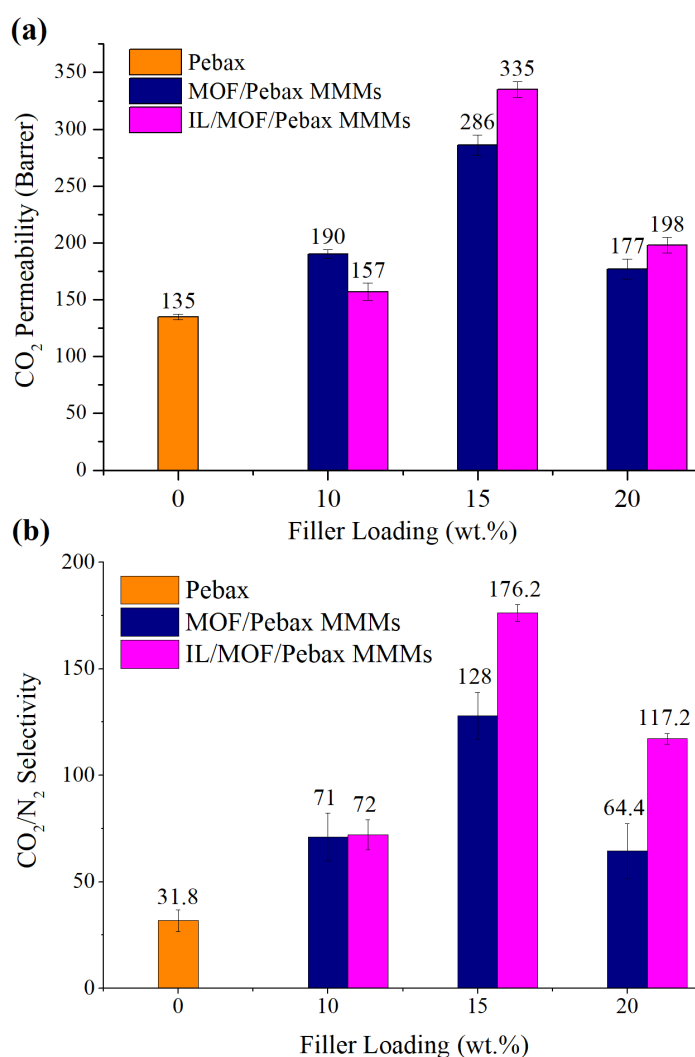


Figure 7.9. (a) CO₂ permeability, (b) CO₂/N₂ selectivity of CuBTC/Pebax MMMs with 10, 15, and 20 wt.% CuBTC loadings, and [EMIM][OAc]/CuBTC/Pebax MMMs with 10, 15, and 20 wt.% [EMIM][OAc]/CuBTC loadings measured at 35°C and 1 bar.

Separation performance of the polymer membrane was further improved when the [EMIM][OAc]/CuBTC composite was used as the filler. For IL/MOF/polymer MMMs with 10 wt.% IL/CuBTC loading, CO₂ and N₂ permeabilities were measured as 157.5±7.5 and 2.19±0.2 Barrer, respectively, leading to a CO₂/N₂ selectivity of 71.9±7. The CO₂ permeability was further increased to 335±7 Barrer and the N₂ permeability was decreased to 1.90±0.3 Barrer as the IL/CuBTC loading was increased to 15 wt.%. As a result, IL/CuBTC/Pebax MMMs having 15 wt.% IL/CuBTC loading exhibited a CO₂/N₂ selectivity of 176.3±4. This data shows that upon the incorporation of IL/CuBTC at a loading of 10 wt.% and 15 wt.%, CO₂ permeability of the membrane increased whereas N₂ permeability decreased, resulting in an improved CO₂/N₂ selectivity. Overall, CO₂ permeabilities of IL/CuBTC/Pebax MMMs with 10 and 15 wt.% CuBTC loadings were 1.1- and 2.5-times higher than the Pebax membrane. Moreover, CO₂/N₂ selectivities of IL/CuBTC/Pebax MMMs with 10 and 15 wt.% IL/CuBTC loadings were also 2.2- and 5.5-times higher compared to the selectivity of the pure polymer membrane.

These improvements in the gas separation performance of IL/MOF/polymer MMMs synthesized in this study was mainly attributed to high CO₂ affinity of the acetate ion present in IL, which significantly enhances the CO₂/N₂ selectivity [65]. Furthermore, the introduction of IL into the pores of CuBTC prior to membrane fabrication resulted in significant reduction in the pore volume of composite and improved its molecular sieving effect [30]. Since CO₂ has a smaller kinetic diameter (3.3 Å) compared to the that of N₂ (3.64 Å), preferential permeation of CO₂ over N₂ was favored in IL/MOF/polymer MMMs, leading to improved CO₂/N₂ selectivities. When the excessive amount of filler, 20 wt.%, was incorporated into polymer, a dramatic decrease in both CO₂ permeability and CO₂/N₂ selectivity was observed as shown in **Figure 7.9**(a, b), which can be attributed to the reduced compatibility between the filler and the polymer at higher loadings and agglomeration of the filler particles [18, 27, 66]. These changes (i.e., agglomeration) in the morphology of the IL/MOF/polymer MMMs and MOF/polymer MMMs at higher filler loadings were also observed in the SEM images given in **Figure 7.4**. Despite this, no large aggregates were observed in the membrane, helping to avoid the interfacial defects between filler and polymer. These changes in the morphology of the IL/MOF/polymer MMMs at higher filler loadings were observed in the SEM images and

despite this, no large aggregates were observed in the membrane, helping to avoid the interfacial defects between filler and polymer.

CO₂ permeability and CO₂/N₂ selectivity data of the CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC/Pebax MMMs are shown in **Figure 7.10** together with the Robeson's upper bound [10]. To make a comprehensive evaluation of the MMMs that we introduced in this work, we collected the data for other MOF/polymer MMMs and IL/MOF/polymer MMMs for CO₂/N₂ separation from the literature and showed them in **Figure 7.10** and listed in **Table 7A-4**. The literature data was collected in the pressure and temperature range of 1 to 6 bar and 20 to 35 °C, respectively. CuBTC/Pebax MMMs with 10, 15, and 20 wt.% CuBTC loadings and [EMIM][OAc]/CuBTC/Pebax MMMs with 10, 15, and 20 wt.% [EMIM][OAc]/CuBTC loadings surpassed the upper bound by outperforming many other MMMs for CO₂/N₂ separation.

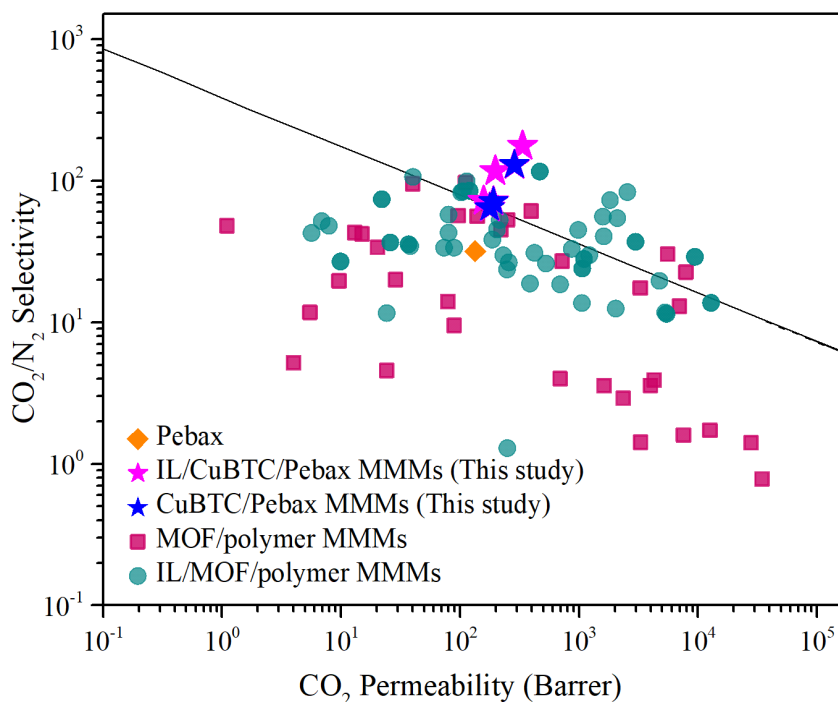


Figure 7.10. Comparison of CO₂/N₂ selectivity and CO₂ permeability of MMMs synthesized in this study with the literature data. The line represents the Robeson's upper bound [2].

We compared the separation performance of [EMIM][OAc]/CuBTC/Pebax MMM

that we fabricated, with [BMIM][TF₂N]/ZIF-8/Pebax MMM having an IL/MOF loading of 15 wt.% [30]. CO₂ permeability of [EMIM][OAc]/CuBTC/Pebax MMM (335 Barrer) was 3-times higher than that of [BMIM][TF₂N]/ZIF-8/Pebax MMM (105 Barrer), under the same temperature (35 °C) and pressure conditions (1 bar). Moreover, the CO₂/N₂ selectivity of [EMIM][OAc]/CuBTC/Pebax MMM (176.2) was also 2-times higher than the reported CO₂/N₂ selectivity (84.5) of [BMIM][TF₂N]/ZIF-8/Pebax MMM. We also compared the separation performance of [EMIM][OAc]/CuBTC/Pebax MMM with 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF₆]/ZIF-8/Pebax MMMs, reported at 3 bar and 35 °C [67]. CO₂ permeability of [EMIM][OAc]/CuBTC/Pebax MMM was 2.9-times higher than that of [BMIM][PF₆]/ZIF-8/Pebax MMM (120 Barrer), and CO₂/N₂ selectivity was also 2.2-times higher, compared to the best reported selectivity (85) of [BMIM][PF₆]/ZIF-8/Pebax MMM. A more detailed comparison of [EMIM][OAc]/CuBTC/Pebax MMMs with the other IL/MOF/polymer MMMs reported in the literature is given in **Table 7A-4** and results showed that the CO₂ permeabilities and CO₂/N₂ selectivities of [EMIM][OAc]/CuBTC/Pebax MMMs presented in this study are superior to the literature data reported to-date. To the best of our knowledge, CO₂ permeability of the [EMIM][OAc]/CuBTC/Pebax MMM with 15 wt.% [EMIM][OAc]/CuBTC filler loading was the highest among the values reported for other types of IL/MOF/Pebax MMMs while CO₂/N₂ selectivity was the highest among all IL/MOF/polymer MMMs reported in the literature as shown in **Figure 7.10**. Hence, these results underscore the huge potential of IL-modified CuBTC composite for the fabrication of high-performance IL/MOF/polymer MMMs for CO₂/N₂ separation.

It is important for a membrane to maintain performance stability under continuous operating conditions, especially for industrial applications. Therefore, we tested the stability of [EMIM][OAc]/CuBTC/Pebax MMM with 15 wt.% [EMIM][OAc]/CuBTC loading under continuous operating conditions for up to 72 h. As shown in **Figure 7.11**, CO₂ permeability and CO₂/N₂ selectivity fluctuated within a narrow range during this test. The test results demonstrated that good long-term working stability, indicating the structural stability of the synthesized [EMIM][OAc]/CuBTC/Pebax MMMs for gas separations. Furthermore, to validate the obtained results, another batch of IL/MOF/polymer MMM with 15 wt.% loading was prepared from scratch and tested for

CO₂/N₂ gas separation. The obtained results (**Figure 7A-5**), CO₂ permeability of 301±3.7 Barrer and CO₂/N₂ selectivity of 160±10, were within ±5% error range, indicating the reproducibility of the MMMs. Overall, the results demonstrate the potential of IL/CuBTC/Pebax MMMs synthesized in this study, for continuous and extended operations.

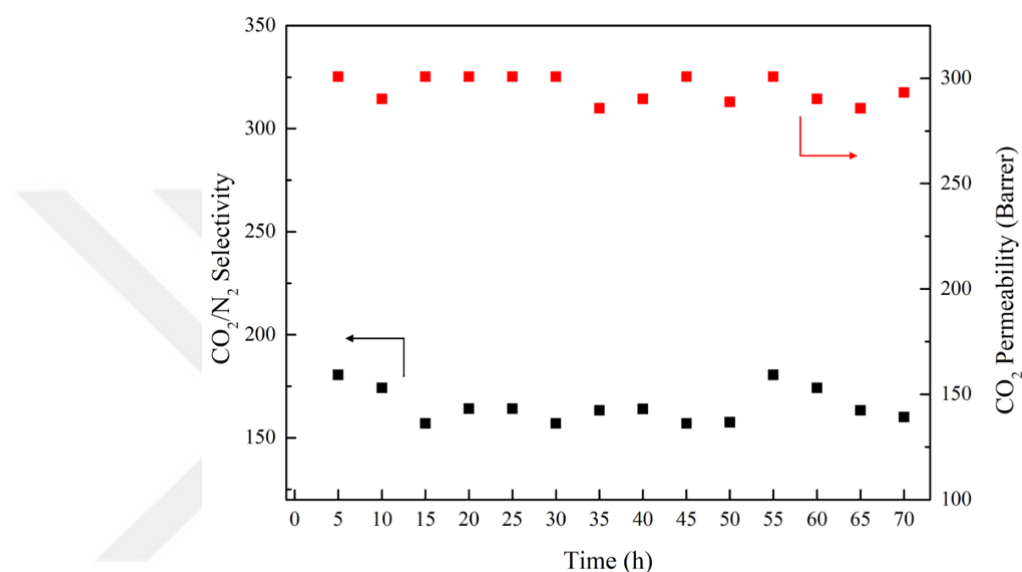


Figure 7.11. Long-term stability of [EMIM][OAc]/CuBTC/Pebax MMM with 15 wt.% [EMIM][OAc]/CuBTC loading

7.4 Conclusion

In this chapter, CuBTC/Pebax MMMs and [EMIM][OAc]/CuBTC/Pebax MMMs were synthesized with 10, 15 and 20 wt.% loadings of CuBTC and [EMIM][OAc]/CuBTC fillers, respectively. Various experimental analysis showed that morphology of all the MMMs was homogenous, and no apparent interfacial voids were observed, which can be ascribed to the well dispersion of CuBTC and [EMIM][OAc]/CuBTC fillers in the polymer matrix. At 15 wt.% [EMIM][OAc]/CuBTC loading, the MMM showed significantly higher CO₂ permeability of 335 Barrer and CO₂/N₂ selectivity of 176 compared to pure Pebax having a CO₂ permeability of 135 Barrer and CO₂/N₂ selectivity of 32. The CO₂ permeability and CO₂/N₂ selectivity of [EMIM][OAc]/CuBTC/Pebax MMM was 2.5- and 5.6-times higher than the pure Pebax membrane. and significantly superior to the other IL/MOF/polymer MMMs reported in the literature under the same temperature and pressure conditions. All the MMMs that we

synthesized in this work were found to be located above the Robeson's upper bound, indicating their exceptional performance for CO₂/N₂ separation. Considering the existence of a large number and variety of ILs, MOFs, and polymers, our results will contribute into the design and fabrication of new IL/MOF/polymer MMMs for various gas separations.



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APPENDIX 7A

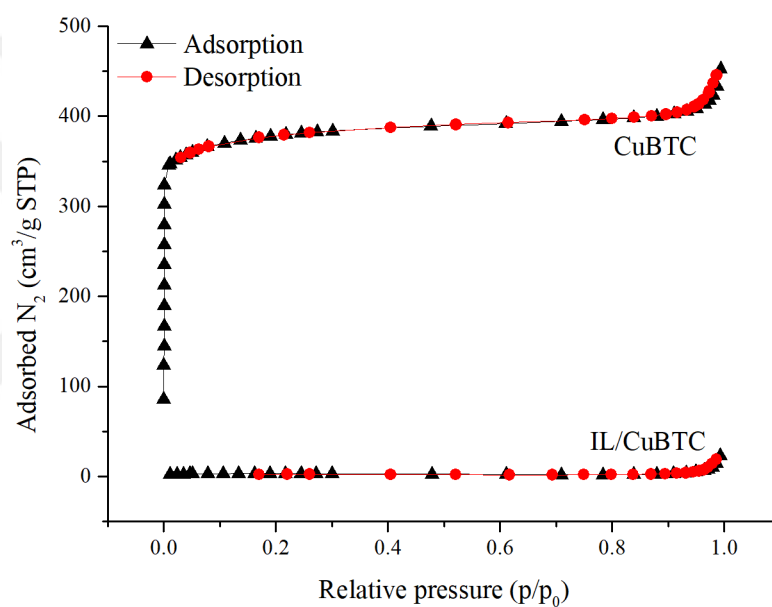


Figure 7A-1. Physical N_2 adsorption-desorption isotherms of pristine CuBTC and [EMIM][OAc]/CuBTC composite.

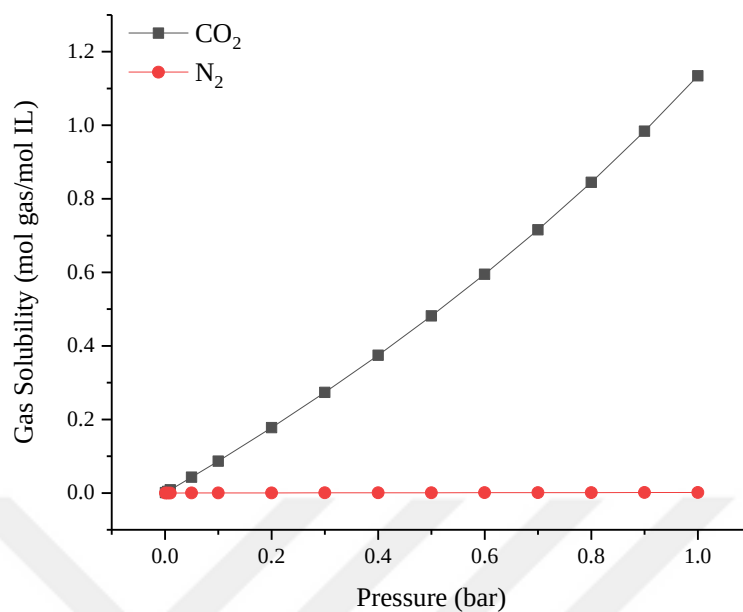


Figure 7A-2. CO₂ and N₂ solubility in [EMIM][OAc] calculated using COSMO-RS at 196 K.

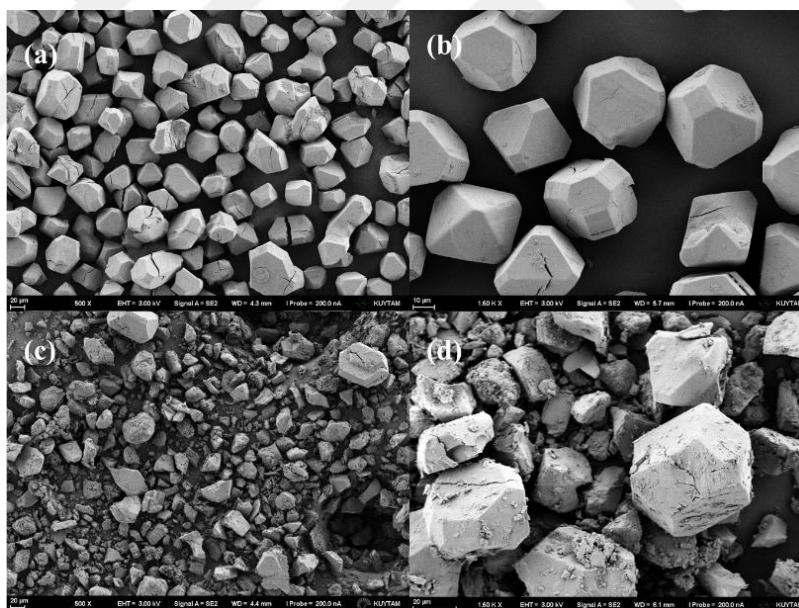


Figure 7A-3. Morphology of (a, b) CuBTC and (c, d) [EMIM][OAc]/CuBTC composite obtained at magnifications of 500 × and 1.5 k×, respectively.

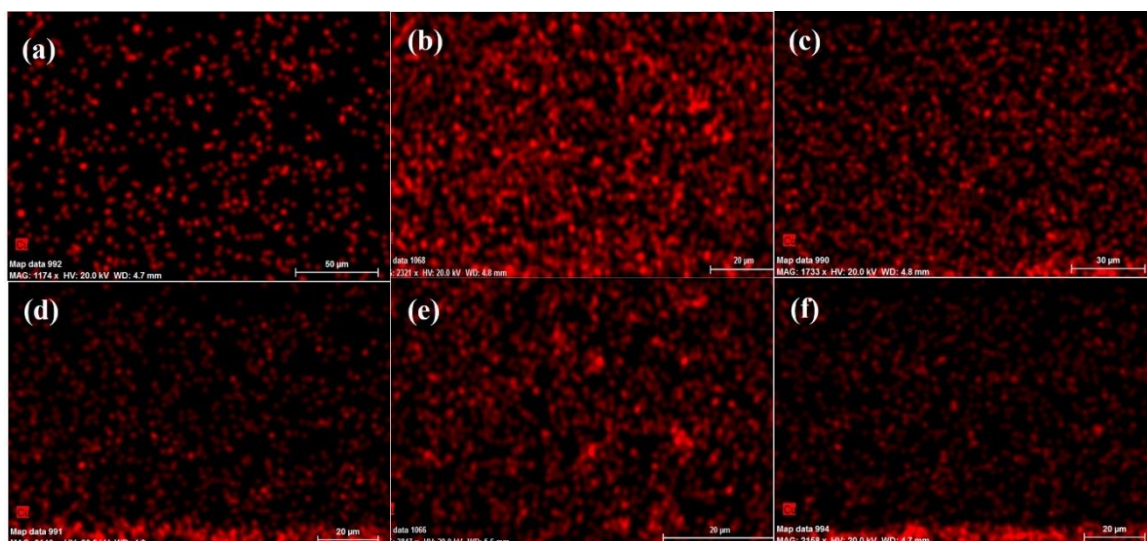


Figure 7A-4. EDS mapping of Cu in CuBTC/Pebax MMMs with (a) 10 wt.%, (b) 15 wt.%, (c) 20 wt.% CuBTC loadings and [EMIM][OAc]/CuBTC/Pebax MMMs with (d) 10 wt.%, (e) 15 wt.%, (f) 20 wt.% [EMIM][OAc]/CuBTC loadings in the polymer.

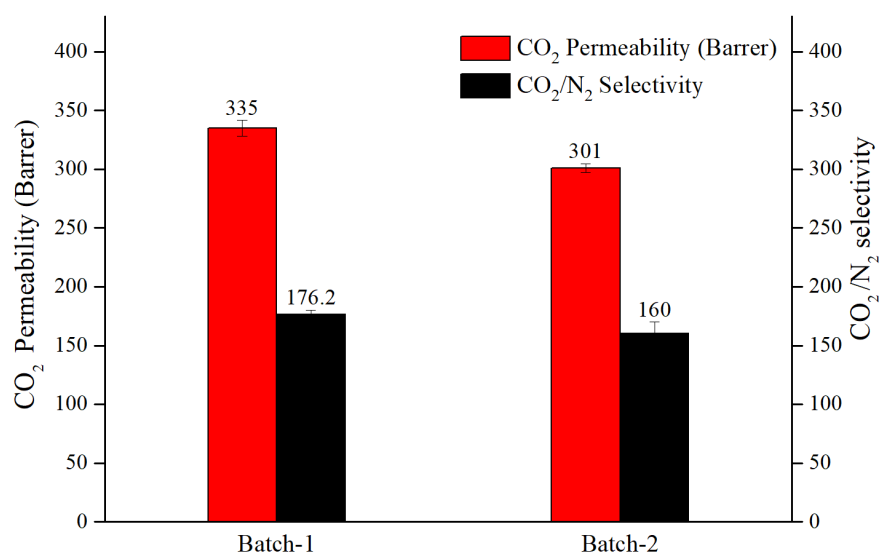


Figure 7A-5. Reproducibility of IL/MOF/polymer MMM with 15 wt.% IL/MOF loading.

Table 7A-1. Langmuir-Freundlich and Dual-site Langmuir-Freundlich fit parameter for pristine CuBTC and [EMIM][OAc]/CuBTC composite.

Langmuir-Freundlich Model								
CuBTC	Gas		q (cc/g)		k (1/mbar)		n*	R ²
	CO ₂		305.99		0.42		1.01	0.99
	Dual-site Langmuir-Freundlich Model							
	Gas	q ₁ (cc/g)	k ₁ (1/mbar)	n ₁ *	q ₂ (cc/g)	k ₂ (1/mbar)	n ₂ *	R ²
	N ₂	16.99	0.17	0.97	168.9	0.02	1.09	0.99
[EMIM][OAc]/ CuBTC	CO ₂	53.78	0.25	1.01	4.45	3.31	0.98	0.99
	N ₂	2.36	1.49	1.83	1.59	0.81	1.02	0.99

Table 7A-2. Data of gas permeability and ideal selectivity of membranes having different filler loadings at 35 °C and 1 bar.

Membrane Type	Filler Loading (wt. %)	Permeability (Barrer)		Selectivity (CO ₂ /N ₂)
		CO ₂	N ₂	
Pure Pebax	0	134.6 ± 2	4.2 ± 0.5	31.8
CuBTC/Pebax MMMs	10	190 ± 4	2.67 ± 1.1	71.2 ± 11
	15	286 ± 9	2.22 ± 0.4	128.8 ± 11
	20	177 ± 8	2.75 ± 0.3	64.4 ± 12
IL/CuBTC/Pebax MMMs	10	157.5 ± 7.5	2.19 ± 0.2	71.9 ± 7
	15	335 ± 7	1.90 ± 0.3	176.3 ± 4
	20	198 ± 6.2	1.69 ± 0.3	117.2 ± 3

Table 7A-3. Comparison with the literature data plotted on **Figure 7.11**.

Membrane types	Loading (wt. %)	P _{CO2} (Barrer)	Selectivity (CO ₂ /N ₂)	Conditions
MOF/Polymer MMMs				
UiO-66/PMMA[1]	15	1.1	55	25 °C, 4 bar
UiO-66/Pebax[2]	10	96.3	56.5	25 °C, 3 bar
Azo-UiO-66/Matrimid [3]	20	15	42	35 °C, 4 bar
UiO-66/PIM-1[4]	10	6981	16	25 °C, 4 bar
UiO-66-NH ₂ /PES[5]	20	28.7	20	25 °C, 1 bar
CuBTC/Matrimid[6]	20	20.2	33.8	35 °C, 1 bar
NH ₂ -CuBTC/Matrimid[6]	20	13	43	35 °C, 1 bar
CuBTC/PPO[7]	10	79	14	30 °C, 1 bar
HKUST-1/Pebax[8]	15	128	20	30 °C, 3 bar
NH ₂ -CuBTC/Pebax[8]	20	170	26	30 °C, 3 bar
CuBTC/PSf[9]	10	8	22.3	30 °C, 5 bar
ZIF-7/Pebax 1657[10]	22	111	97	20 °C, 6.5 bar
ZIF-90/PI[11]	15	720	27	25 °C, 1 bar
MIL-53(Al)/Matrimid[12]	37.5	40	95	35 °C, 2 bar
NOTT-300/Pebax 1657[13]	40	395	61	35 °C, 5 bar
BIT-72/Pebax 1657[14]	30	139	56	35 °C, 5 bar
CuBTC/Pebax MMMs (This Study)	10	190 ± 4	71.2 ± 11	35 °C, 1 bar
	15	286 ± 9	128.8 ± 11	35 °C, 1 bar
	20	177 ± 8	64.4 ± 12	35 °C, 1 bar
IL/MOF/Polymer MMMs				
[EMIM][NTf ₂]/HKUST-1/6FDA-durene[15]	10	1100	28	25 °C, 2 bar
[EMIM][B(CN) ₄]/ZIF-8/[Poly(vbim)][NTf ₂][16]	25.8	1062	24	35 °C, 3.5 bar
[BMIM][NTf ₂]/ZIF-8/PSF[17]	6	468	116	30 °C, 6 bar

[C ₃ NH ₂ BIM][NTF ₂]/NH ₂ -MIL-101(Cr)/PIM-1[18]	5	2979	37	25 °C, 3 bar
[BMIM][NTF ₂]/ZIF-8/Pebax 1657[19]	15	105	84	25 °C, 1 bar
[BMIM][NTF ₂]/MOF-801/PIM[20]	5	9420	29	35 °C, 4 bar
[BMIM][PF ₆]/ZIF-8/Pebax 1657[21]	30	120	85	25 °C, 3-8 bar
TMGHIM/ZIF-76/PIM1[22]	10	12848	13.7	23 °C, 1 bar
[APTMS][Ac]/ZIF-67/PSf[23]	30	22	74	25 °C, 10 bar
[BMIM][Br]/ /MIL101(Cr)/[Matrimid[24]	20	9.9	26.9	30 °C, 0.7 bar
[TMGA][N ₃]/MOF-5/Matrimid[25]	2	36.9	35.5	35 °C, 0.7 bar
[C ₂ MIM][C(CN) ₃]/MOF-74/Matrimid[25]	2	25.9	36.6	30 °C, 0.7 bar
[EMIM][OAc]/ZIF-8/Chitosan[26]	10	5431	11.5	25 °C
[EMIM][OAc]/CuBTC/Pebax (This Study)	10	157 ± 7.5	71.9 ± 7	35 °C, 1 bar
	15	335 ± 7	176.3 ± 4	35 °C, 1 bar
	20	198 ± 6.2	117.2 ± 3	35 °C, 1 bar

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Chapter 8

Selective Separation of Acetylene from Ethylene Using Mixed Matrix Membranes with MIL-100(Fe) as a Filler

8.1 Abstract

Separation of acetylene from ethylene is challenging due to the similar physicochemical properties of these two gases. In this regard, the potential of mixed matrix membranes (MMMs) has remained mostly unexplored. Herein, we synthesized MOF/polymer MMMs by incorporating an iron-based metal-organic framework (MOF), MIL-100(Fe), into a Pebax polymer matrix at different filler loadings of 10, 15, and 17 wt.%. The synthesized MMMs were characterized in detail and tested for C₂H₂/C₂H₄ separation. Gas permeation measurements showed that the neat Pebax membrane has C₂H₂ and C₂H₄ permeabilities of 434.8±19.0 and 29.6±0.5 Barrer, respectively, at 1 bar and 35 °C, along with the corresponding C₂H₂/C₂H₄ of 14.7±1. Incorporation of MIL-100(Fe) into the Pebax led to a significant improvement in C₂H₂ permeability and C₂H₂/C₂H₄ selectivity: The MMMs having 15 and 17 wt.% MIL-100(Fe) exhibited C₂H₂ permeabilities of 624.1±5.4 and 509.3±7.3 Barrer, respectively, corresponding to C₂H₂/C₂H₄ selectivities of 23.4±2.3 and 35.6±1.0. Long-term stability tests indicated that the MMMs maintained their separation performance under continuous operation for at least three days, underscoring their robustness and industrial application potential. These results set a benchmark for effectively separating C₂H₂ from C₂H₄ with the synthesized MMMs, offering valuable insights for future acetylene separation applications.

8.2 Introduction

Acetylene is a critical feedstock in the chemical industry, widely used for the synthesis of high-value chemicals such as vinyl chloride, acrylonitrile, and various polymers [1]. However, the presence of ethylene in acetylene streams can lead to unwanted side reactions and reduce the yield of desired products. Therefore, ensuring the purity of acetylene is essential for maintaining product quality and optimizing the process. The separation of C_2H_2 from C_2H_4 is particularly challenging due to their similar molecular size and physicochemical properties [2]. Furthermore, due to its high reactivity, C_2H_2 poses significant safety risks, including the potential for explosive mixtures [3]. As a result, efficient separation technologies are crucial for isolating C_2H_2 from C_2H_4 , ensuring the safe handling of these gases while enhancing the production efficiency and the purity of the final products.

Cryogenic distillation and catalytic hydrogenation are conventional methods used for C_2H_2/C_2H_4 separation in the industry [4] however, they require intensive energy and have high operational costs. Membrane-based gas separation technology is more advantageous thanks to its energy-saving characteristics, superior separation properties, and small carbon footprint [5-7]. However, polymeric membranes suffer from an inherent tradeoff between gas selectivity and permeability, which limits their performance. Mixed matrix membranes (MMMs) combine the easy processibility of polymeric membranes along with the good separation performance of the inorganic fillers [8, 9]. In the last two decades, metal-organic frameworks (MOFs) have emerged as promising filler materials in MMMs, thanks to their high surface area, good thermal and mechanical strength, tunable properties, and superior gas separation performance [10, 11].

Several MOFs have been studied for C_2H_2/C_2H_4 separation; however, the membrane separation process of light hydrocarbons is still underdeveloped, and only a few MMMs have been studied for the removal of acetylene from ethylene [12]. For instance, Xu et al. incorporated three different MOFs (MOF-87, -88, and -89) into 6FDA-ODA, a polyimide-based polymer [13]. Among synthesized MMMs, MOF89/6FDA-ODA with a filler loading of 15 wt.% exhibited the best performance, achieving the permeabilities of 36.2 Barrer for C_2H_2 and 6.4 Barrer for C_2H_4 , corresponding to a C_2H_2/C_2H_4 selectivity of 5.6. These values were superior to the neat membrane having C_2H_2 and C_2H_4 permeabilities of 8 and 3.4 Barrer, respectively, corresponding to

C₂H₂/C₂H₄ selectivity of 2.4.

Zhang et al. functionalized a COF (COF: covalent organic framework) with OH anion followed by MMM synthesis, employing the same polymer (6FDA-ODA) and tested them for C₂H₂/C₂H₄ separation [14]. The C₂H₂ and C₂H₄ permeability of the MMM having 15 wt.% filler loading was increased to 55.6 and 4.6 Barrer, respectively, and the corresponding C₂H₂/C₂H₄ selectivity improved to 12.1. Similarly, the COF nanosheet was incorporated into 6FDA-ODA, and the resulting MMM having 15 wt.% loading showed improved C₂H₂ permeability (10 Barrer) and C₂H₂/C₂H₄ selectivity (6.7) but reduced C₂H₄ permeability (1.5 Barrer) compared to the neat membranes [15]. It is noteworthy that all these reported MMM studies have utilized only one type of polymer, polyimide (PI). This leaves a significant gap in exploring other polymer matrices and fillers for C₂H₂/C₂H₄ separation. Therefore, our research aims to investigate alternative MMM formulations for pushing the boundaries of current knowledge and enhancing the efficiency of C₂H₂/C₂H₄ separation.

Motivated by this aim, we incorporated an iron-based MOF, iron (III) trimeric known as MIL-100(Fe), into the Pebax to synthesize MOF/polymer MMMs. MIL-100(Fe) was selected because it demonstrates selective sorption characteristics for C₂H₂ over C₂H₄, which is attributed to the strong interactions between acetylene and the Fe³⁺ and surface OH sites [16]. Pebax was selected as the polymer because it has not been previously explored for C₂H₂/C₂H₄ separation, unlike the more extensively studied polyimide. The combination of crystalline and amorphous structures in Pebax has the potential to offer high gas permeability, mechanical stability, and the robustness needed for effective gas separation, making it a promising polymer for the MMM application [17]. Our results demonstrated improved separation performance of the resulting MMMs, showcasing significant advancements in membrane-based C₂H₂/C₂H₄ separation. This study provides valuable insights and sets a new benchmark for future research in this challenging field.

8.3 Results and Discussion

8.3.1 Characterization of the materials

The surface area and pore volume of MIL-100(Fe) was determined by measuring N₂ adsorption isotherms presented in **Figure 8A-1**. The BET surface area and pore

volume were calculated as $1258 \text{ cm}^2/\text{g}$ and $0.67 \text{ cm}^3/\text{g}$, respectively, which are comparable to the literature [18-20]. The SEM images of the MIL-100(Fe) are presented in **Figure 1(a)** and **(b)** at magnifications of $2 \text{ k}\times$ and $6.9 \text{ k}\times$, respectively. The images demonstrated some degree of agglomeration, with the crystals lacking perfect geometric uniformity [21]. Despite the presence of irregular shapes and sizes, which deviate from the ideal octahedral structure typically associated with MIL-100(Fe), the crystals still exhibit distinct characteristics of the MOF.

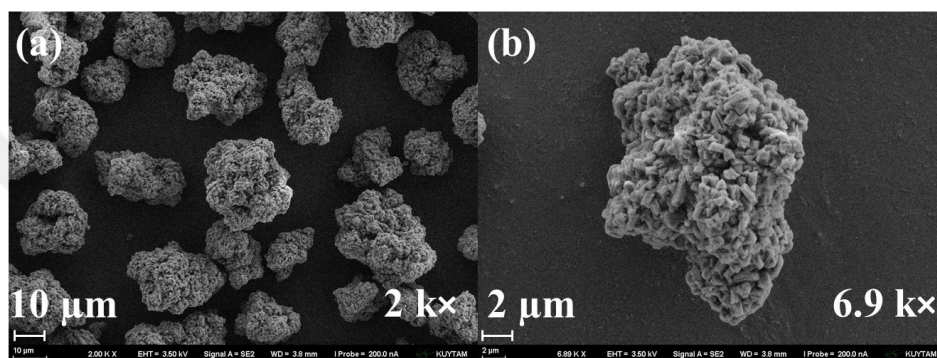


Figure 8.1. SEM images of pristine MIL-100(Fe) at (a) $2 \text{ k}\times$ and (b) $6.9 \text{ k}\times$ magnifications.

Similarly, the cross-sectional morphology of synthesized MIL-100(Fe)/Pebax MMMs having 10, 15, and 17 wt.% filler loading was also analyzed. The corresponding SEM images collected at different positions are presented in **Figures 8.2(a), (b), and (c)** (at a magnification of $10 \text{ k}\times$) and in **Figure 8.2(d), (e), and (f)** (at a magnification of $20 \text{ k}\times$). It was observed that at all filler loadings, MIL-100(Fe) particles are uniformly distributed within the polymer matrix with no evidence of phase separation or dual-layer formation. This homogenous dispersion highlights the membrane's structural integrity. The SEM analysis further revealed that at a filler loading of 17 wt.% shown in **Figure 8.2(c)** and **8.2(f)**, the MMM exhibits a slight roughness associated with the relatively high concentration of MIL-100(Fe) particles. Despite this observation, the membrane maintained its structural integrity, with no cracks, agglomeration or defects observed. However, as the filler loading was increased to 20 wt.%, the membrane exhibited significant cracking, likely due to the excessive crystallinity and the challenges of uniform dispersion of filler particles at such a high concentration of filler [22, 23]. Therefore, in this study, 17 wt.% loading was selected as the highest filler loading to achieve a defect-free MMM along with the improved separation performance.

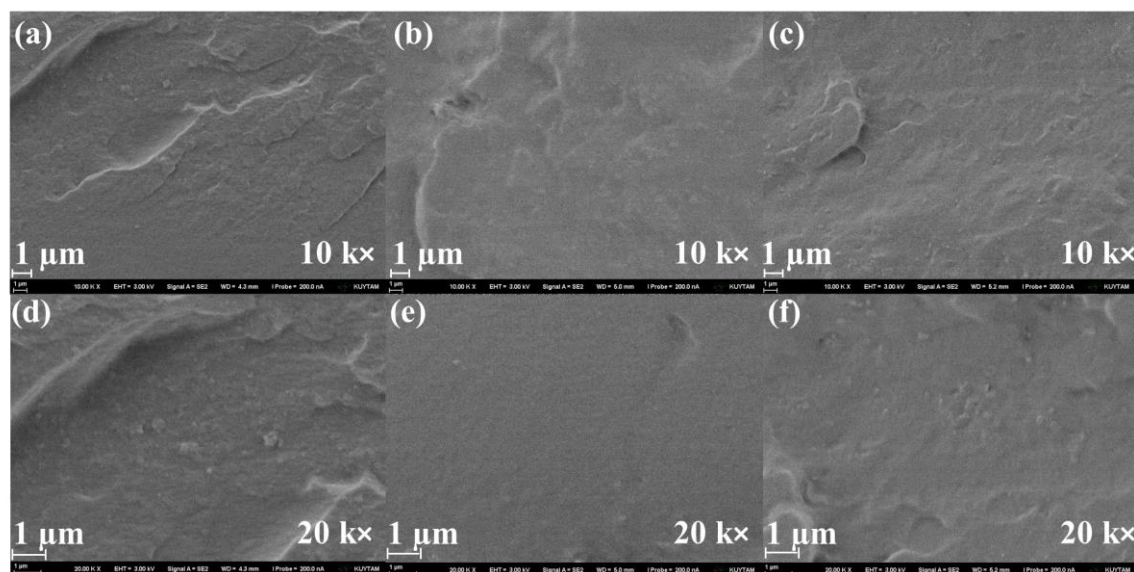


Figure 8.2. SEM images of MIL-100(Fe)/Pebax MMMs having a MIL-100(Fe) loading of (a) 10 wt.%, (b) 15 wt.%, (c) 17 wt.% at a magnification of 10 k $\times$ and (d) 10 wt.%, (e) 15 wt.%, and (f) 17 wt.% at a magnification of 20 k $\times$.

The XRD diffractograms of pristine MIL-100(Fe), neat Pebax, and MOF-100(Fe)/Pebax MMMs are shown in **Figure 8.3(a)**. The characteristic XRD peaks of pristine MIL100(Fe) located at $2\theta = 5.8, 6.2, 6.7, 10.1, 10.9$, and 20° are well-matched with the reported literature [24, 25], confirming the structural integrity of the MOF. In the XRD patterns of membranes, the neat Pebax showed a broad peak around $2\theta = 12-24^\circ$, which can be ascribed to the polyamide (PA) group present in the polymer [26]. The characteristic peak associated with the PA group was also observed in all the MMMs. In the case of MOF-100(Fe)/Pebax MMMs, new peaks were observed at $2\theta = 10.1, 10.9$, and 20° , which were associated with the pristine MIL-100(Fe), with no apparent shifts in their peak positions. Additionally, as the MOF loading was increased from 10 to 17 wt.%, the intensity of the peaks associated with MIL-100(Fe) peaks was observed to increase as the crystallinity of the resulting MMMs increased, as expected.

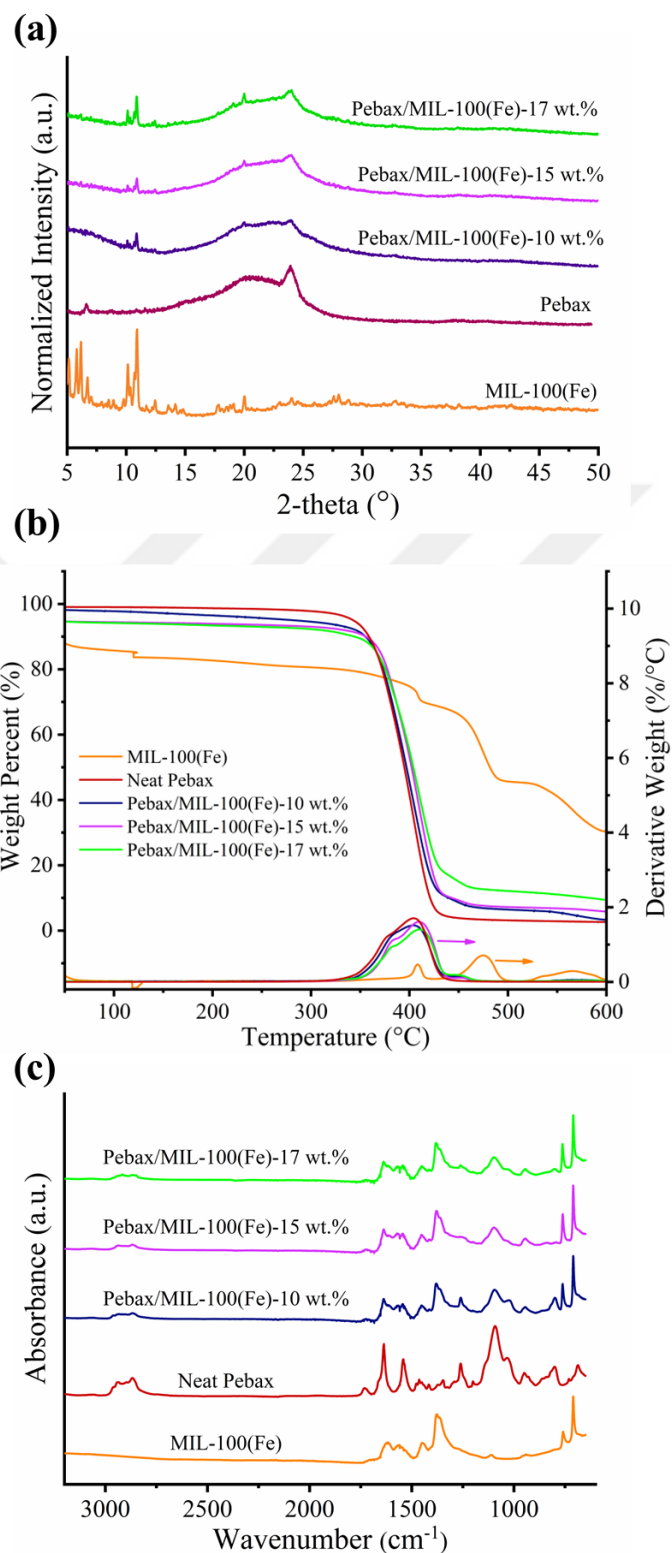


Figure 8.3. (a) XRD diffractogram, (b) TGA and DTG curves, and (c) IR spectra of MIL-100(Fe), neat Pebax, and MIL-100(Fe)/Pebax MMMs at 10, 15, and 17 wt.% loadings.

TGA analysis was conducted on MIL-100(Fe), neat Pebax, and the synthesized MOF/polymer MMMs as shown in **Figure 8.3(b)**, to determine the thermal stability limits of the samples. The TGA profile of pristine MIL-100(Fe) showed a three-step decomposition profile matching well with the literature [27, 28]. First weight loss up to T'_{onset} of 395 °C corresponds to the removal of water molecules that are coordinated with the MIL-100(Fe) structure. The second weight loss occurs at a T'_{onset} value of approximately 440 °C, which was attributed to the decomposition of the organic ligand. Finally, the third and final stage, with a T'_{onset} temperature between 515 and 600 °C, is ascribed to the complete collapse of the MIL-100(Fe) framework [19, 29]. In contrast, the neat Pebax membrane and the MMMs presented in **Figure 8.3(b)**, exhibited a single-step decomposition mechanism, with initial degradation starting at T'_{onset} temperature of 350 °C, and the complete collapse of polymer backbone at T'_{onset} of 420 °C. All MMMs displayed a similar decomposition pattern, and thermal stability up to 350 °C, demonstrating high thermal resilience. Moreover, with the addition of MIL-100 in Pebax, a slight change was observed in the DTG curves, possibly indicating some interactions between the MOF and the polymer.

To gain insights into these interactions, an analysis based on IR spectroscopy was conducted. The IR spectra of pristine MIL-100(Fe), neat Pebax, and synthesized MMMs were analyzed to investigate the interactions between the MOF and the polymer, as shown in **Figure 8.3(c)**. In the IR spectra of MIL-100(Fe), the peaks located at 710 and 760 cm^{-1} were ascribed to $\nu[\text{C-H}]$ stretching vibration of the benzene ring. Moreover, the characteristic peaks present at 1380, 1450, and 1560 cm^{-1} were associated with the $\nu[\text{C-O}]$ stretching vibrations. The band located at 1630 cm^{-1} was ascribed to the C=O of the benzene-1,3,5-tricarboxylate (BTC) linker present in the MIL-100(Fe). The broad peak located around 2900 to 3600 cm^{-1} representing $\nu[\text{O-H}]$ stretching vibrations was ascribed to the coordination of water molecules with open metal sites of MIL-100(Fe) [30].

In the IR spectra of neat Pebax membrane presented in **Figure 8.3(c)**, the characteristic peaks located at wavenumber 1097, 1636, and 1731 cm^{-1} corresponded to $\nu(\text{C-O-C})$ vibrations, $\nu(\text{O-C-O})$, and $\nu(\text{H-N-C=O})$ vibrations, of PEO segment, respectively. The peaks located at 1541 and 2948 cm^{-1} were ascribed to the $\nu(\text{N-H})$

vibrations of the polyamide (PA) groups within the polymer structure [37]. All the characteristic peaks of Pebax polymer were present in the MMMs; however, a change in the intensity of the peaks was observed, which can be ascribed to the interaction between the polymer and the MOF particles, affecting the overall polymer membrane structure. Besides, new peaks were observed at wavenumbers 710, 762, 1381, and 1573 cm^{-1} in the IR spectra the MMMs, compared to the spectrum of the neat Pebax. These new bands were associated with the characteristic IR peaks of the pristine MIL-100(Fe) as described above. A slight blue shift of 2 cm^{-1} to 762 cm^{-1} was observed in the position of the $\nu(\text{C-H})$ compared to its corresponding position in the pristine MIL-100(Fe) spectrum. Moreover, the peak at 1573 cm^{-1} associated with $\nu(\text{C-O})$ stretching vibrations in the MIL-100(Fe) structure presented a blue shift of 13 cm^{-1} compared to its position in the IR spectrum of the pure MOF. This shift indicates that the ligand present in the MOF structure is interacting with the polymer. Moreover, the peak corresponded to the PEO group of the polymer present at 1639 cm^{-1} also showed a blue shift of 3 cm^{-1} (slightly higher than the spectral resolution) in the MMMs. These shifts in the position of the IR features associated with the polymer functional groups and the linker of the MOF likely indicate the presence of weak Van der Waals interactions between the MOF and polymer within the membrane structure.

8.3.2 Gas separation performances of materials

8.3.2.1 Adsorption-based gas separation

Volumetric gas adsorption isotherms for single-component C_2H_2 and C_2H_4 for MIL-100(Fe) were measured at pressures ranging from 0.01 to 1 bar and at 25 °C, as illustrated in **Figure 8.4(a)**. The C_2H_2 and C_2H_4 isotherms were fitted using the Dual-Site Langmuir (DSL) employing the IAST++ software, the corresponding fitting parameters are given in **Table 8A-1**. The C_2H_2 and C_2H_4 uptakes of MIL-100(Fe) were measured as 1.7 and 0.8 cm^3/g , respectively, at 0.01 bar. As the pressure was increased to 1 bar, gas uptakes were increased to 36 and 30 cm^3/g for C_2H_2 and C_2H_4 , respectively, which are consistent with values reported in the literature [31].

The corresponding $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ adsorption selectivities at different pressures were computed for MIL-100(Fe) based on fitting parameters, as shown in **Figure 8.4(b)**. MIL-100(Fe) demonstrated the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ selectivity of 2.2 at 0.01 bar. However, as the

pressure was increased to 1 bar, the selectivities decreased to 1.2. The reduction in selectivity can be attributed to the transition in the gas adsorption mechanism. At low pressures, adsorption is predominantly influenced by specific interactions between the gas molecules and the active sites on the surface of MIL-100(Fe), which enhances the selectivity. In contrast, at higher pressures, the adsorption mechanism shifts, and the process is primarily governed by the availability of pore volume rather than specific interactions [32, 33], resulting in a decrease in selectivity. Comparative analysis indicates that the C_2H_2 uptake and C_2H_2/C_2H_4 selectivity values for MIL-100(Fe) align well with those reported for other C_2H_2 selective MOFs in the literature, as detailed in **Table 8A-2**.

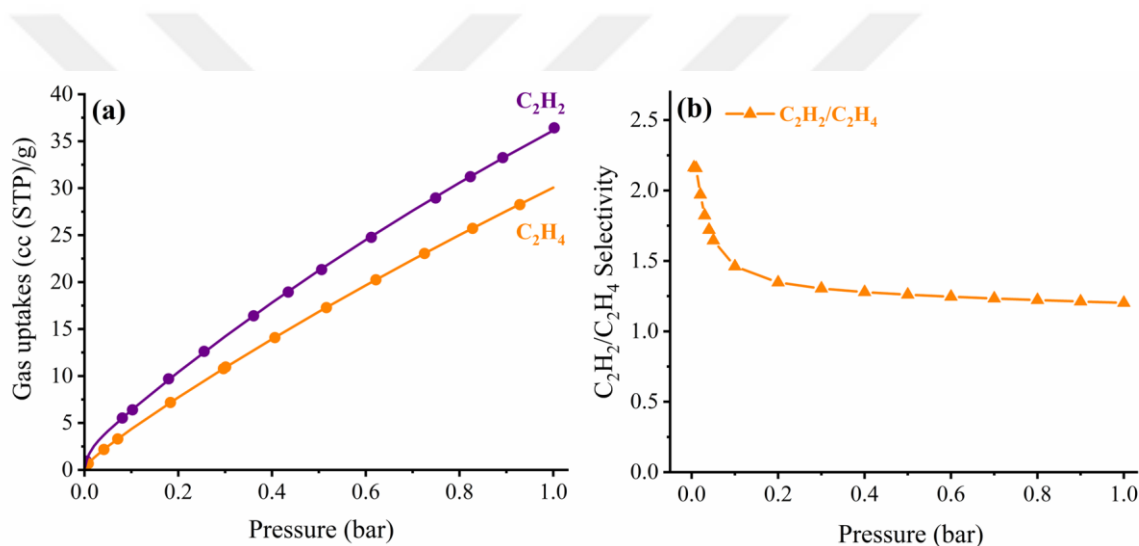


Figure 8.4. (a) Volumetric C_2H_2 and C_2H_4 uptakes measured at 25 °C and up to 1 bar. (b) C_2H_2/C_2H_4 adsorption selectivity of MIL-100(Fe). In (a), circles indicate the experimental data, while the lines represent the fitted isotherms.

8.3.2.1 Membrane-based gas separation

Pure gas permeability measurements for C_2H_2 and C_2H_4 were conducted for neat Pebax and the MIL-100(Fe)/Pebax MMMs at 1 bar and 35 °C, as depicted in **Figure 8.5(a)**. Based on permeability data, the corresponding C_2H_2/C_2H_4 selectivities of membranes were calculated as presented in **Figure 8.5(b)**. The data are also provided in tabular form in **Table 8A-3**. For the neat Pebax membrane, C_2H_2 and C_2H_4 permeabilities were measured as 434.8 ± 19.0 and 29.6 ± 0.5 Barrer, respectively, with the corresponding C_2H_2/C_2H_4 selectivities of 14.7 ± 1.0 .

In the case of MIL-100(Fe)/Pebax MMMs, it was observed that the addition of MIL-100(Fe) improved the C_2H_2 permeabilities along with the C_2H_2/C_2H_4 selectivities, as shown in **Figure 8.5**. For instance, the MMM having 10 wt.% MIL-100(Fe) loading exhibited C_2H_2 and C_2H_4 permeabilities of 528.0 ± 26 and 30.5 ± 4.5 Barrer, respectively, along with the corresponding C_2H_2/C_2H_4 selectivity of 17.3 ± 1.7 . As the MIL-100(Fe) loading was increased to 15 wt.%, C_2H_2 permeability was further increased to 624.1 ± 5.4 Barrer, along with the C_2H_4 permeability of 26.7 ± 3.0 Barrer, corresponding to a C_2H_2/C_2H_4 selectivity of 23.4 ± 2.3 . Thus, the MMM having 15 wt.% filler loading demonstrated a 1.4-times improvement in C_2H_2 permeability and 1.6-times higher C_2H_2/C_2H_4 selectivity, compared to the neat Pebax membrane.

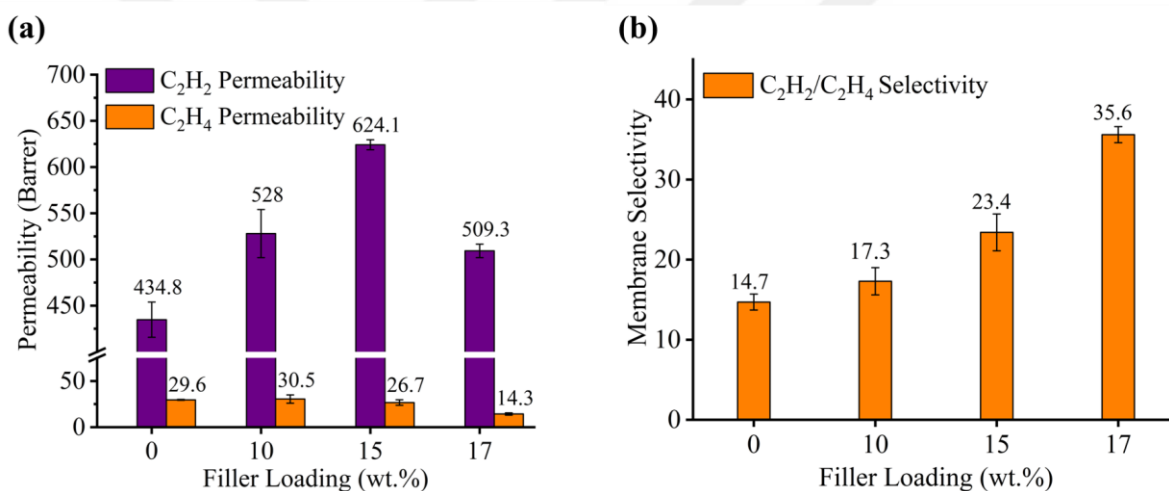


Figure 8.5. (a) C_2H_2 and C_2H_4 permeabilities, (b) C_2H_2/C_2H_4 selectivities of MIL-100(Fe)/Pebax MMMs compared to neat Pebax, measured at 35 °C and a feed pressure of 1 bar.

The C_2H_2/C_2H_4 selectivity of the MMM was further improved to 35.6 ± 1 with an increase in filler loading to 17 wt.%. This selectivity corresponds to a 2.4-times improvement compared to that of the neat Pebax. This improvement can be attributed to several factors, primarily associated with the differences in the interaction strengths of the two gases with the MIL-100(Fe) structure. C_2H_2 molecules exhibit stronger van der Waals and Lewis acid-base interactions with the unsaturated Fe^{3+} centers and surface hydroxyl (OH) groups present in MIL-100(Fe) compared to C_2H_4 molecules. This difference facilitates the enhanced adsorption of C_2H_2 , which is crucial for improving the

membrane's C_2H_2 selectivity over C_2H_4 [16]. However, the improvement in selectivity at high filler loading occurs at the expense of reduction in permeabilities (to 509.3 ± 7.3 and 14.3 ± 1.2 Barrer for C_2H_2 and C_2H_4 , respectively). These changes in permeabilities can be attributed to agglomeration and potential pore blocking within the membrane matrix [25]. Therefore, we posit that the optimal balance of filler loading is crucial to maximize the performance of the MMM in gas separation applications.

Next, we compared our data with the existing literature to evaluate the performance of our MMMs with the previously reported MMMs for C_2H_2 and C_2H_4 separation. For instance, a MOF-89/6FDA-ODA MMM having a filler loading of 15.2 wt.% exhibited a C_2H_2 permeability of 36.2 Barrer [13]. In another study, a COF nanosheets/6FDA-ODA MMM showed a C_2H_2 permeability of 10 Barrer [15]. The C_2H_2 permeability of our 15 wt.% MIL-100(Fe)/Pebax MMM (624.1 ± 5.4 Barrer) was measured as approximately 17-times higher than that of MOF-89/6FDA-ODA MMM, and about 62-times higher than the COF nanosheets/6FDA-ODA MMM. Similarly, it is over 11-times higher compared to that of a COF iPAF-1-OH/6FDA-ODA MMM having a filler loading of 15 wt.% (55.6 Barrer) [14]. Additionally, the C_2H_2/C_2H_4 selectivity of the MIL-100(Fe)/Pebax MMM having a filler loading of 17 wt.% (35.6 ± 1.0) is also significantly higher than those of MOF-89/6FDA-ODA MMM (5.6) [14], COF iPAF-1-OH/6FDA-ODA (12.1) [14], and COF nanosheet/6FDA-ODA MMM (6.7) [15]. This comparison illustrates the exceptional performance of MIL-100(Fe)/Pebax MMMs synthesized in this work for acetylene separation.

To check the reproducibility and the long-term stability of the MMMs, we prepared another batch of the MMM with 17 wt.% MIL-100(Fe) loading and tested its separation performance. The comparison of the acetylene separation performance of this new batch with the first one confirmed the perfect reproducibility of the MMM. Subsequently, the long-term stability was assessed over a time-on-stream of 75-hour under identical operating conditions. Data provided in **Figure 8A-2** demonstrated that the MMM exhibited stable C_2H_2 and C_2H_4 permeabilities within an error range of less than $\pm 8\%$, the corresponding average values were determined as 565.8 ± 45 with a standard deviation of 28.7 and 14.2 ± 2 with a standard deviation of 0.9 Barrer, respectively. Similarly, as **Figure 8.6** shows, the C_2H_2/C_2H_4 selectivity remained constant at 39.8 ± 3 (with a standard

deviation of 1.9). Moreover, to assess the integrity of the MMM before and after this long-term measurement, XRD analysis was conducted on the used MMM. The results presented in **Figure 8A-3** showed the lack of any significant changes in the peak positions of the MIL-100(Fe)/Pebax MMM, confirming that the membrane maintained its structural integrity throughout the test, further supporting its robust performance for C_2H_2/C_2H_4 separation. This stability is particularly notable given the challenging nature of the separation of the gas pair.

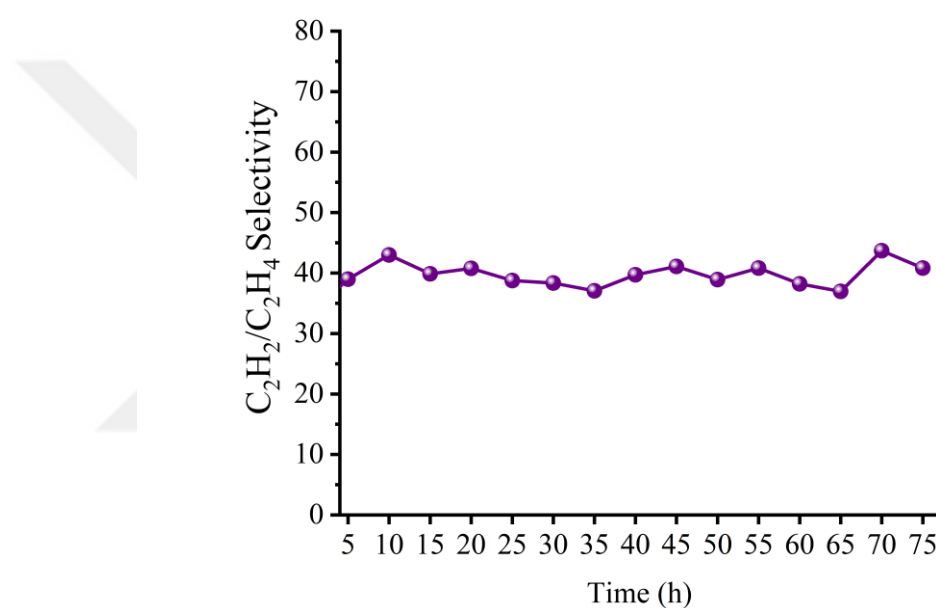


Figure 8.6. Variation of C_2H_2/C_2H_4 selectivity of MIL-100(Fe)/Pebax MMM having a filler loading of 17 wt.% over a time-on-stream of 75 hour at 35 °C and 1 bar.

8.4 Conclusion

In this study, Pebax/MIL-100(Fe) MMMs with various filler loadings were synthesized and tested for selective separation of C_2H_2 from C_2H_4 . The MIL-100(Fe) exhibited exceptional affinity for acetylene, driven by the strong interactions with the Fe^{3+} and surface OH sites, leading to a favorable separation of C_2H_2 over C_2H_4 . The gas permeation experiments conducted at 1 bar and 35 °C showed that the neat Pebax has permeabilities of 434.8 ± 19.0 and 29.6 ± 0.5 Barrer for C_2H_2 and C_2H_4 , respectively, along with a C_2H_2/C_2H_4 selectivity of 14.7 ± 1.0 . Incorporating MIL-100(Fe) into the Pebax

membrane enhanced its C_2H_2 permeability and C_2H_2/C_2H_4 selectivity. The MMMs containing 15 and 17 wt.% MIL-100(Fe) demonstrated C_2H_2 permeabilities of 624.1 ± 5.4 , and 509.3 ± 7.3 Barrer, respectively, with corresponding C_2H_2/C_2H_4 selectivities of 23.4 ± 2.3 and 35.6 ± 1.0 , respectively. The best performance was achieved with 17 wt.% MIL-100(Fe) loading, setting a new benchmark for C_2H_2/C_2H_4 separation. With only a handful of previous studies in the literature focusing on this separation using MMMs, this work sets a new benchmark in the field by exploiting the distinct properties of MIL-100(Fe) within a new polymer matrix, addressing the challenging task of C_2H_2/C_2H_4 separation.



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APPENDIX 8A

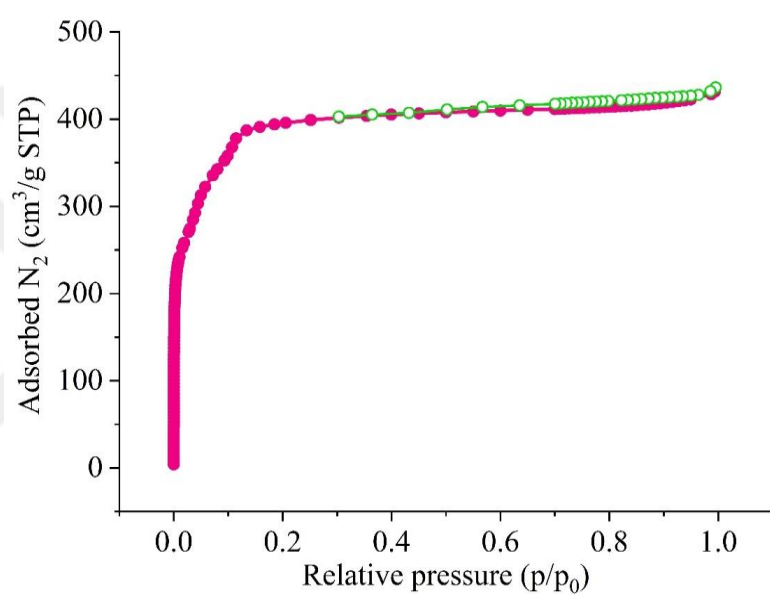


Figure 8A-1. N₂ adsorption-desorption isotherms of pristine MIL-100(Fe).

Table 8A-1. Dual-site Langmuir fit parameter for pristine MIL-100(Fe).

	Dual-site Langmuir Model					
	Gas	q ₁ (cc/g)	k ₁ (1/mbar)	q ₂ (cc/g)	k ₂ (1/mbar)	R ²
MIL-100(Fe)	C ₂ H ₂	2.36	122.61	158.77	0.27	0.99
	C ₂ H ₄	0.92	98.73	158.73	0.22	0.99

Table 8A-2. Comparison of C₂H₂/C₂H₄ adsorption selectivity of MIL-100(Fe) with literature at 1 bar and 298 K.

MOF	C ₂ H ₂ uptake (cm ³ /g)	C ₂ H ₂ /C ₂ H ₄ Adsorption Selectivity	Reference
NCU-100a	102.4	14.2	[1]
UTSA-200a	81.8	5.79	[2]
M'MOF-3a	42.5	4.7	[3]
NbOFFIVE-2-Ni-i	67.2	3.7	[4]
SIFSIX-2-Cu	120.5	2.6	[5]
UTSA-100a	95.7	2.5	[6]
ZUL-200	105.1	2.3	[7]
ZUL-100	119.0	1.9	[7]
SIFSIX-2-Ni	73.9	1.8	[5]
UTSA-67a	114.9	1.8	[8]
NbU-1	81.5	1.7	[9]
SIFSIX-2-Zn	82	1.6	[5]
UTSA-60a	70.1	1.5	[10]
NOTT-300	142.1	1.4	[11]
NUM-11a	50.4	1.4	[12]
UTSA-220	76.2	1.3	[13]

NKMOF-1-Ni	60.9	1.2	[14]
Cu(BDC-Br)	34.3	-	[15]
DICRO-4-Ni-i	43	-	[15]
FeMOF-74	152	1.11	[16]
MIL-100(Fe)	36	1.2	This Study

Table 8A-3. C₂H₂ and C₂H₄ permeabilities and C₂H₂/C₂H₄ selectivity of the MMMs having different filler loadings at 35 °C and 1 bar.

Membrane	Filler Loading (wt.%)	Permeability (Barrer)		Selectivity
		C ₂ H ₂	C ₂ H ₄	C ₂ H ₂ /C ₂ H ₄
Pure Pebax	0	434.8±19	29.6±0.5	14.7±1.0
MIL-	10	528.0±26.0	30.5±4.5	17.3±1.7
100(Fe)/Pebax	15	624.1±5.4	26.7±3.0	23.4±2.3
MMMs	17	509.3±7.3	14.3±1.2	35.6±1.0

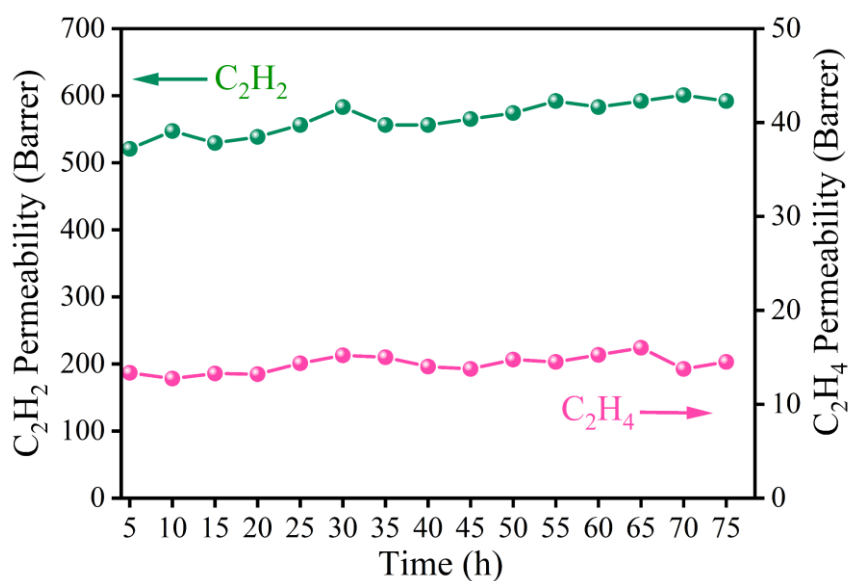


Figure 8A-2. Long-term permeability measurements of MIL-100(Fe)/Pebax MMM having a filler loading of 17 wt.%. Data were collected over a period of 75 hours at 35 °C and 1 bar.

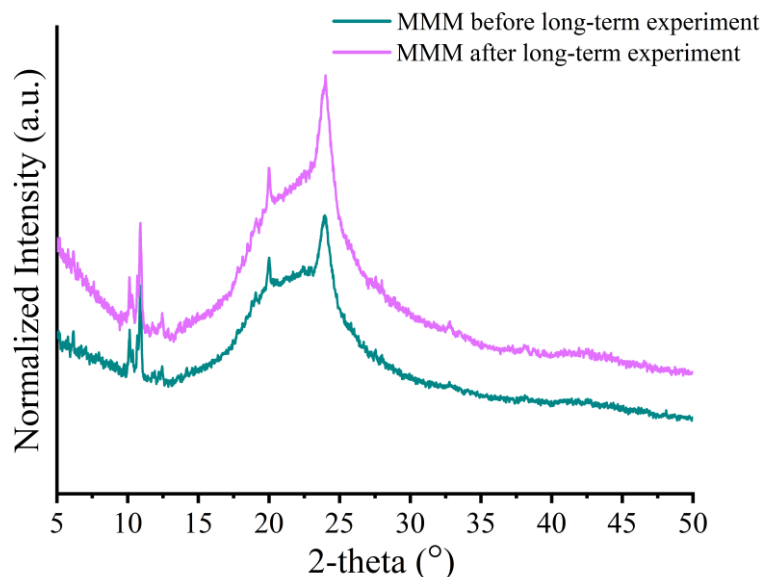


Figure 8A-3. Comparison of XRD spectra of the MIL-100(Fe)/Pebax MMM with a filler loading of 17 wt.%, before and after long-term stability measurements.

References for APPENDIX 8A

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Chapter 9

Conclusions and Outlook

In this thesis, the state-of-the-art IL/MOF/polymer MMMs were synthesized and characterized for advanced gas separation applications, with a particular focus on CO₂ and C₂H₂ separation. The study comprehensively addressed the challenges associated with the development of high-performance IL/MOF/polymer MMMs, overcoming the trade-off between permeability and selectivity of traditional polymer membranes. A diverse range of ILs and MOFs were explored, expanding beyond conventional materials to introduce novel composites that demonstrate exceptional gas separation properties.

The results highlighted the significant impact of IL/MOF composite incorporation into polymer matrices, particularly in the context of CO₂/N₂, CO₂/CH₄, and C₂H₂/C₂H₄ separations. The introduction of pyrrolidinium-based ILs into MIL-101(Cr) and MOF-177 demonstrated remarkable improvements in selectivity and permeability, with the IL/MOF/polymer MMMs developed in these study exceeding Robeson's upper bound for CO₂/N₂ and CO₂/CH₄ separation. These membranes achieved new benchmark values in CO₂/N₂ selectivity of IL/MOF/polymer MMMs. Additionally, the challenges associated with ensuring the structural integrity of the composites and their uniform dispersion within the polymer matrix were successfully addressed, leading to the development of MMMs with enhanced gas separation performance. Moreover, a critical issue of IL leaching was encountered, which was carefully mitigated through optimizing the composite design and synthesis, ensuring the stability of IL/MOF composite in IL/MOF/polymer MMMs.

This dissertation also contributed to the growing field of industrially relevant separations, particularly the challenging separation of C₂H₂ and C₂H₄, by developing MIL-100(Fe)-based MMMs that exhibited excellent performance in C₂H₂/C₂H₄ separations. The membranes showed substantial permeability and selectivity

improvements, indicating their potential for real-world applications in gas separation technologies. Furthermore, the long-term stability tests demonstrated the durability and robustness of these MMMs, suggesting their potential for industrial applications.

In summary, this research has made a significant contribution to the development of advanced IL/MOF/polymer MMMs various gas separations, providing insights into novel material combinations, optimizing membrane synthesis, and overcoming performance barriers. The findings not only offer new pathways for improving gas separation technologies but also provide a foundation for future research aimed at further enhancing the efficiency and applicability of IL/MOF-based membranes in environmental and industrial processes. The future of IL/MOF/polymer MMMs lies in addressing critical challenges to fully unlock their potential. In this chapter, we outline key areas of focus that can drive the advancement of these materials.

- ***Addressing practical and industrial challenges:*** Although efforts have been made to explore IL/MOF composites for gas separation under mixed gas conditions, most studies still predominantly focus on high-purity gas separations, which do not fully capture the complexities of real-world industrial applications. To bridge this gap, future research should prioritize the investigation of mixed gas environments containing impurities typically present in industrial processes. Moisture sensitivity of MOFs, for instance, can significantly impact the integrity of IL/MOF composites and MMMs by altering their structural properties, reducing selectivity, or leading to pore blockage. Therefore, developing strategies to mitigate these issues, such as using advanced functionalized fillers, modifying polymer chemistry by using crosslinking techniques, will be helpful in advancing gas separation technologies for industrial applications.
- ***Unexplored and challenging gas separation pairs:*** While substantial progress has been made in gas separations such as CO₂/CH₄ and CO₂/N₂, several industrially significant and challenging gas pairs remain underexplored, providing opportunities to develop new IL/MOF composites to address these gaps. For instance, acetylene/ethylene (C₂H₂/C₂H₄), ethylene/ethane (C₂H₄/C₂H₆), and propylene/propane (C₃H₆/C₃H₈) separations are critical for petrochemical industries, yet their close molecular sizes and physical properties make them difficult to efficiently separate using conventional methods. Similarly, the

separation of H_2/CH_4 is essential for refining and hydrogen purification, O_2/N_2 separation is crucial for producing oxygen-enriched air for medical and industrial applications, NH_3/H_2 separation also presents a significant opportunity as ammonia gains traction as a hydrogen carrier, requiring materials that selectively adsorb ammonia or facilitate hydrogen permeation. Another underexplored pair, CO/N_2 , is vital for refining syngas and chemical production. In this thesis, we synthesized MOF/polymer MMMs C_2H_2/C_2H_4 separation, next focus should be on developing novel IL/MOF composites and IL/MOF/polymer MMMs to address these complex gas pairs for significant advancements in the gas separation field.

- ***Transforming MMMs into Thin-Film Composite MMMs:*** While the current dissertation highlights the promising performance of IL/MOF/polymer MMMs, further advancements can be made by transforming these MMMs into thin-film composite membranes. Thin-film composite membranes have shown great potential for improving gas separation efficiency due to their thin active layers, which can reduce diffusion resistance and enhance selectivity. The integration of IL/MOF composites into a thin-film structure could further optimize the performance of the membranes, allowing for more efficient and cost-effective separation processes. This transformation can open new avenues for industrial applications, offering a balance between high selectivity, permeability, and stability.
- ***Revisiting Performance Benchmarks:*** The new MMMs have demonstrated performance that exceeds the updated Robeson's upper bound for a range of gas separations, pushing the established boundaries of membrane technology. This underscores the necessity of revisiting the Robeson upper bound, as the ongoing innovations in IL/MOF/polymer MMMs suggest that the traditional trade-off between permeability and selectivity may no longer apply, making it necessary to revise the performance benchmark to keep up with the rapid advancements in the field.
- ***Integrating Simulation and Experimental Approaches:*** In the field of adsorption, integrating simulation techniques is advancing research by providing more accurate predictions of adsorption behaviors and enhancing the rational design of new materials. These simulations provide a detailed understanding of

how adsorbents interact with gas molecules at the atomic level, enabling the prediction of adsorption isotherms and the optimization of adsorbent structures before extensive experimental work is undertaken. However, in the case of MMMs, advanced simulation techniques are needed that can predict the optimal combination of ILs, MOFs, and polymers for the rational design of MMMs. Such simulations can also help fine-tuning the amounts of ILs and fillers to achieve precise membrane structures and tunable separation performance without excess material use. However, simulations alone cannot capture all the complexities of real-world membrane systems, such as defects, impurities, and processing conditions. This is where experimental validation becomes essential. Experimental studies, including gas permeability tests, structural characterizations (such as SEM or XRD), and thermal stability analysis (TGA), allow researchers to validate the simulation results. Additionally, techniques like EXAFS (Extended X-ray Absorption Fine Structure) should be utilized for characterizing IL/MOF composites and IL/MOF/polymer MMMs at the atomic level. EXAFS enables the investigation of the local coordination environment of metal nodes within the MOF, providing valuable information on the interaction between metal sites and functional groups of the IL or polymer matrix. Overall, experimental methods, combined with computational strategies, could accelerate the screening of IL/MOF composites and IL/MOF/polymer MMMs, making it possible to evaluate hundreds of materials.