Development of ternary-component mixed-matrix membranes for advanced gas separations

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**DEVELOPMENT OF
TERNARY-COMPONENT MIXED-MATRIX MEMBRANES
FOR ADVANCED GAS SEPARATIONS**

S. A. SULASHI CHATHUSHKA SAMARASINGHE
Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute
Singapore Membrane Technology Centre

2019

DEVELOPMENT OF TERNARY-COMPONENT MIXED-MATRIX MEMBRANES FOR ADVANCED GAS SEPARATIONS

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**Interdisciplinary Graduate School
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A thesis submitted to the Nanyang Technological University in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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S. A. Sulashi C Samarasinghe

Supervisor Declaration Statement

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Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journal, where I was the first author and/or co-author.

Chapter 4 is published as S. A. S. C. Samarasinghe, C. Y. Chuah, W. Li, G. S. M. D. P. Sethunga, R. Wang, and T.-H. Bae, Incorporation of CoIII acetylacetonate and SNW-1 nanoparticles to tailor O₂/N₂ separation performance of mixed-matrix membrane, *Separation and Purification Technology*, 223, 133-141, (2019). DOI: 10.1016/j.seppur.2019.04.075.

The contributions of the co-authors are as follows:

- A/Prof Tae-Hyun Bae provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. C.Y. Chuah.
- I co-designed the study with A/Prof Tae-Hyun Bae and performed all the laboratory work at the School of Chemical and Biomedical Engineering.
- I performed the data analysis and interpreted the results with the help of coauthors.
- G.S.M.D.P. Sethunga conducted FESEM measurements at the Singapore Membrane Technology center using the samples prepared by myself.
- W. Li assisted in the preparation of ODPA-TMPDA polymer.
- Dr. C.Y. Chuah assisted gas adsorption tests.
- Prof R. Wang provided feedback for the project direction.

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The contributions of the co-authors are as follows:

- A/Prof Tae-Hyun Bae provided the initial project direction and edited the manuscript drafts.
- I drafted the manuscript and Dr. C.Y. Chuah made the revisions.
- I performed all the experimental work including characterizations.
- I performed data analysis and interpreted the results with the help of other coauthors.
- Dr. Y. Yang provided guidance for the synthesis of ns-CuBDC.
- Dr. C.Y. Chuah helped for gas adsorption tests.

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ABBREVIATIONS

Abbreviation	Description
PSA	Pressure Swing Adsorption
TSA	Temperature Swing Adsorption
MMM	Mixed-matrix membrane
MOFs	Metal Organic Frameworks
COFs	Covalent Organic Frameworks
Low-Mw	Low molecular weight
PEG	Polyethylene glycol
MWCNTs	Multi-walled carbon nanotubes
GO	Graphene oxide
FS	Fumed silica
POSS	Octatrimethylsiloxy polyhedral oligomeric silsesquioxane
ZIF-8	Zeolitic Imidazole Framework-8
PS- <i>b</i> -PHEA	Polystyrene- <i>b</i> -poly(hydroxyl ethyl acrylate)
CoPcMPs	Microneedle-shaped cobalt(II) phthalocyanine particles)
TMPDA	2,4,6-trimethyl- <i>m</i> -phenylenediamine
ODPA	4,4'-oxydiphthalic anhydride
Co(acac) ₃	Cobalt(III) acetylacetonate

Hmim	2-methylimidazole
TEA	Triethylamine
DMSO	Dimethyl sulfoxide
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
THF	Tetrahydrofuron
FESEM	Field Emission Scanning Electron Microscopy
EDS	Energy-dispersive spectroscopy
FTIR	Fourier-transform infrared spectroscopy
XRD	X-ray diffraction
TGA	Thermo-gravimetric analyzer
DSC	Differential thermal analyzer
AFM	Atomic force microscopy
CoPc	Cobalt(II) phthalocyanine
CoTPP	Cobalt(II)tetraphenylporphyrin
PEO	Polypropyleneoxide

SUMMARY

Polymer-based mixed-matrix nanocomposites are increasingly researched as gas separation membranes. In contrast to the conventional single-filler mixed-matrix membranes (MMMs), here in this thesis study, I examined the utility of ternary-component MMMs for gas separation applications. The strategy employed in this thesis was to develop Matrimid-based MMMs using filler and a polymeric compatibilizer. As the filler, I selected a well-known oxygen carrier, cobalt phthalocyanine. As the compatibilizer, I employed a block copolymer, Pluronic F-127. The ternary-component membrane exhibited 64% improvement in O_2 permeability and 40% improvement in O_2/N_2 selectivity. To improve the selectivity, I focused on a high-permeability polymer, ODPA-TMPDA, as the next step. The filler (cobalt (III) acetylacetonate) successfully improved the selectivity but at the cost of permeability. Thus, I examined a porous covalent organic framework, SNW-1, together with cobalt (III) acetylacetonate as the next step. This strategy improved both O_2 permeability and O_2/N_2 selectivity. Due to the success of ODPA-TMPDA-based ternary-component membrane for O_2/N_2 separation, I have used ODPA-TMPDA for the development of another ternary-component membrane for CO_2/CH_4 separation. In this final step of the thesis work, I have incorporated 2D CuBDC nanosheets and 3D ZIF-8 nanoparticles to improve CO_2/CH_4 selectivity and CO_2 permeability, respectively. Overall, this study demonstrates the potential of ternary-component MMMs for developing gas separation membranes that can surmount Robeson's Upper Bound relation for permeability-selectivity trade-off.

1 GENERAL BACKGROUND AND THESIS OVERVIEW

1.1 Gas separation industry

Several gases and gas mixtures, separated from air, collected from natural resources, or obtained from chemical processes, are heavily used in industrial processes. Nitrogen (N_2), oxygen (O_2), argon (Ar), krypton (Kr), neon (Ne), and xenon (Xe) are some of the main gases separated from the air. Acetylene (C_2H_2), nitrous oxide (N_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4) are among the gases obtained from natural resources or chemical routes [1].

Among the industrial gases, O_2 and N_2 are likely to be the most utilized gases for industrial processes. N_2 is used to blanket toxic and dangerous chemicals at a low cost. It can also be used to protect sensitive products (chemicals, certain polymers, and food) from O_2 or moisture [2]. In addition to pure gases, mixed gases are quite vital for many processes, which might be produced as pure components and mixed later on. Or alternatively, they can be obtained as mixtures as in the cases of enriched air products: i) O_2 -enriched air (mainly used for enhancing the thermal efficiency in combustion processes), and N_2 -enriched air (mainly used for blanketing and to inert atmospheres) [2, 3].

As examples of produced gases, natural gas (~60–90% CH_4) or biogas (CH_4/CO_2 mixture) is among the most demanded products, which are used as energy sources. According to a report published by Yeo *et al.*, natural gas consumption in 2003 was 95 trillion cubic feet, which will increase to 182 trillion cubic feet in 2030 [4]. However, the composition, and hence the quality, of both natural gas and biogas varies significantly [4]. Since only methane has a

calorific value, the enrichment of natural gas as well as biogas is of relevance from an economic point of view. On the other hand, unwanted compounds like hydrogen sulphide (H_2S) and carbon dioxide (CO_2) can be removed by separation, which increases the heating value, helps protect the pipelines, and reduces the environmental impact of combustion processes [5]. Hence, natural gas as well as biogas need to be conditioned according to different requirements imposed by the processes and customers [4]. On another aspect, the isolated contaminant gases might sometimes find use on their own. For example, the separated CO_2 stream might serve as an industrial gas [2].

1.2 Gas separation technologies

For the preparation of industrial gases, several processes are available ranging from absorption- and adsorption-based processes to cryogenic and membrane-based methods. Below, those methods are explained briefly.

1.2.1 Absorption-based separation

Absorption is a process where the required gas is separated from a gas mixture using a solvent that has a high affinity to the gas of interest, in which the mechanism of affinity can be chemical absorption or physical absorption [6]. When the binding strength is high, the effectiveness of the separation increases even at low partial pressures for both chemical and physical processes. The physical absorption processes are typically slower and less efficient compared to chemical absorption, but both methods are still used in the industry for different gases. All absorption

processes typically share the same drawbacks, such as high solvent demand, solvent loss during operation, and high capital and maintenance costs [4].

1.2.2 Adsorption-based separation

In the adsorption processes, solid particles with active sites preferentially attract with a specific gas component in the gas mixtures under high temperature or pressure while the non-adsorbed species are collected separately. When the surfaces of adsorbents are saturated with adsorbed gas species, the gas of interest is collected by the regeneration of adsorbents [4]. For regeneration, the equilibrium holding capacity of the adsorbents should be shifted, which is accomplished by either reducing the pressure (known as pressure swing adsorption, PSA) or heating (known as temperature swing adsorption, TSA) [7]. For the case of air separation, the most widely used adsorbents are zeolites as N_2 molecules preferentially adsorb on them effectively. In fact, most of the commercial adsorbents for air separation are also capable of removing water, CO_2 , and hydrocarbons, eliminating the need for sophisticated pre-treatments [7]. On the other hand, the main challenge associated with the adsorption process is the need to increase the bed size with the increase of production capacity. As a result, the capital costs of adsorption processes are quite high [7].

1.2.3 Cryogenic separation

Cryogenic separation is mainly employed for air separation as it can generate high-purity products. In this process pre-cooled air is compressed until liquidification. A distillation column is then employed to separate O₂ and N₂, based on their boiling point differences. Due to its lower boiling point (70 K), N₂ is collected from the top of the column while O₂ (boiling point: 90K) is collected from the bottom of the column with purity greater than 99% [8]. However, the high energy consumption imposes a critical challenge for this separation [9].

1.2.4 Membrane-based gas separation

In membrane processes, a mixture of compounds is passed through a selective barrier (membranes) that shows a preference to certain component(s) in the mixtures. This process commonly takes place in 3 steps. The gas molecules first dissolve in the membrane, then diffuse through, and desorb from the downstream side with pressure acting as the driving force [10]. This transport mechanism is illustrated in **Figure 1-1**.

Figure 1-1: Schematic representation of gas permeation through a membrane. (Thickness of the membrane and gas molecule sizes are for illustration purposes only.)

Membrane-based gas separations attract growing attention as alternatives to other more traditional methods explained above. The simplicity of membrane operations, the involvement of no phase changes, and low/modest maintenance and capital costs are the key reasons behind the increasing demand for the membrane-based gas separation processes. On the other hand, the membrane-based gas separation units/plants often have a small footprint, are energy-efficient, and can be operated continuously for a long time without the necessity for regeneration [4]. Still increasing the production volume is often not favourable compared to the cryogenic processes due to increased cost considerations [7]. Moreover, the membrane-based gas separation processes are favourable only when no harmful substance for the membranes exists in the gas mixture to be separated. Furthermore, to achieve energy efficiency and economical benefit, the pressure and temperature of the feed streams should be similar or close to the operating

conditions of the separation process [8]. For such reasons, membrane-based biogas separation processes are still unattractive compared to the amine-based adsorption process [4]. Also, the necessity for pre-treatment (to remove moisture and sulphur-containing compounds) incurs additional costs and the plasticization of the membranes (by CO₂) consequently degrades the quality of the product stream [11]. Still, for air separation, membrane-based gas separation processes are widely available, e.g., nitrogen products with 95–99.5% purity [2].

1.3 Fundamentals of Membrane-based Gas Separation Technology

1.3.1 Transport mechanisms of gas separation membranes

Gas separation membranes can be categorized according to their pore structure as porous and dense membranes. Porous membranes can further be categorized as macroporous (pore size > 50 nm), mesoporous (50 nm > pore size > 2 nm), and microporous (pore size < 2 nm). This categorization based on the pore structures relates to the gas transport mechanism, as well. Below, the 3 main transport mechanisms are explained and grouped under the mechanisms for porous and dense membranes [8].

1.3.1.1 Gas transport in porous membranes

Knudsen diffusion

Knudsen diffusion, which is the prominent transport mechanism for macroporous and mesoporous membranes, takes place when membrane pores are smaller than the mean free path of gas molecules. As a result, the gas molecules collide with the pore walls more frequently than they do with each other [8]. As such, the dimensionless Knudsen number (K_n) can be defined as follows:

$$K_n = \frac{\lambda}{r} \dots\dots\dots \text{Eq. (1.1)}$$

where the mean free path of a gas molecule is denoted by λ and pore radius is denoted by r .

For Knudsen diffusion to take place effectively, K_n should have a value greater than 1. If K_n results in a value of less than one, viscous flow will take place with no selectivity [8]. The Knudsen gas flow (G_{Kn}) can be expressed as follows:

$$G_{Kn} = \frac{8r(P_1 - P_2)}{3L\sqrt{2\pi MRT}} \dots\dots\dots \text{Eq. (1.2)}$$

where P_1 and P_2 are the upstream and downstream pressures, respectively. L is the pore length, M is the molecular weight, T is temperature, and R is the universal gas constant. Therefore, the Knudsen diffusion of a specific gas component in a gas mixture will be determined by its upstream partial pressure and molecular weight [8]. However, the Knudsen diffusion process is affected by several factors such as the occurrence of back diffusion and concentration polarization that limits the gas molecules in accessing the pore and viscous flow due to the presence of defects [8].

Molecular sieving

When the pore diameter of the membrane is in between the kinetic diameters of gas molecules in a mixture, molecular sieving can take place. Only the gas molecules smaller than the pore radius permeate effectively through the membrane, resulting in high selectivity at the expense of low permeability in general. Typical membranes that can provide this type of transport mechanism are zeolites, carbon molecular sieves, porous glass, and microporous silica [4].

1.3.1.2 Gas transport in dense membranes

Solution-diffusion

Solution-diffusion is a three-step process. The gas molecules first adsorb to the upstream side of the membrane surface. Next, the adsorbed molecules diffuse through the membrane, which is the key step in the overall transport process. Finally, the molecules reach the other side of the membranes and desorb to join the downstream flow. To explain this process, permeability (P) of a gas species is defined, which is governed by the solution-diffusion process that depends on the solubility coefficient (S) and diffusivity coefficient (D) as expressed below [8]:

$$P = DS \dots\dots\dots \text{Eq. (1.3)}$$

The gas flow rate per unit area or flux (J) can be expressed as follows according to Fick's law:

$$J = \frac{D (C_1 - C_2)}{l} \dots\dots\dots \text{Eq. (1.4)}$$

where C_1 and C_2 are the concentrations of the gas species at upstream and downstream sides, respectively, and l is the membrane thickness. When Henry's law is considered,

$$C = Sp \dots\dots\dots \text{Eq. (1.5)}$$

where p is the partial pressure of the species in contact with the system, then the equation (1.4) can be rewritten as;

$$J = \frac{DS(P_1 - P_2)}{l} \dots\dots\dots \text{Eq. (1.6)}$$

Then, the permeability can also be expressed as;

$$P = \frac{Jl}{\Delta p} \dots\dots\dots \text{Eq. (1.7)}$$

As such, it can be understood that the solution-diffusion transport can play a vital role in separating gas molecules which have close kinetic diameters but different solubility in the dense membranes [8].

1.4 Gas separation membrane types

1.4.1 Polymer membranes

Polymeric materials, both rubbery and glassy varieties, dominate the membrane separation industry with their cost-effectiveness, and easy processability (to different shapes and modules) [8]. The rubbery polymers, with glass transition temperatures below room temperature, move more freely and can accommodate the motion of gas molecules without restricting the diffusion process [8, 12]. Hence, the selectivity of a membrane to a certain gas pair is essentially governed by the solubility coefficients, which is a function of gas molecules' condensability and its interaction with the polymer at a specific operating temperature and pressure. As such, when penetrant-polymer interactions are not dominant, the ability of a penetrant to condense into the

polymer matrix becomes the governing factor. Generally, gas molecule condensability depends on its critical temperature, normal boiling point and Lennard-Jones force constant, with larger molecules exhibiting better condensability [13].

Glassy polymers, on the other hand, with their glass transition temperatures way above room temperature, exhibit a rigid behaviour and restrict the diffusion of gas molecules [8, 14]. It is worth emphasizing that most glassy polymers demonstrate an enhanced selectivity compared to rubbery polymers due to their low and narrow-distribution of free volume [8]. Besides, in glassy polymers, the gas permeation can be a rather complex process due to the dual mode sorption behaviour. This phenomenon is attributed to the different solubility characteristics occurring in two distinct regions of the polymers, which are densified regions occupied by polymer chains (that obey Henry's law) and "hole" regions (gaps between stiff chains) described by Langmuir expression [15]. In this respect, the concentration of molecules in the polymer matrix (C) can be given as follows:

$$C = C_D + C_H \dots\dots\dots \text{Eq. (1.8)}$$

with C_D and C_H denoting the concentrations of gas molecules in densified and hole regions, respectively [15]. When operating temperature for the membrane is close to its glass transition temperature non-equilibrium free volume of glassy states reduces approaching to zero ($C = C_D$) [16].

The main drawback of the polymer-based membrane is their trade-off between permeability and selectivity. Polymers having an attractive permeability but low selectivity fails for processes that require high-purity products [17]. Below,

Table 1-1 and **Table 1-2** illustrate CO₂/CH₄ separation and O₂/N₂ separation performance of some widely used commercial polymers, respectively.

Table 1-1: CO₂/CH₄ separation performance of some widely used commercial polymers

Membrane	Pressure (bar)	Temperature (°C)	CO ₂ Permeability (Barrer)	CO ₂ /CH ₄	Ref.
Pebax 1657	3	25	110.67	11.09	[18]
PDMS	4	25	3000 [†]	3 [†]	[19]
Polysulfone	–	–	5 [†]	24 [†]	[20]
Matrimid	2	35	8.34	36.3	[21]
Polycarbonate	10	35	6.3	24	[22]

[†] Approximate values obtained from the graphs by digitalization

Table 1-2: O₂/N₂ separation performance of some widely used commercial polymers

Membrane	Pressure (bar)	Temperature (°C)	O ₂ Permeability (Barrer)	O ₂ /N ₂	Ref.
Pebax 1657	3	30	3 [†]	2.8 [†]	[23]
PDMS	0.9	25	350 [†]	2.17	[24]
Polysulfone	1	35	2.01	4.23	[25]
Matrimid	1	35	2.72	5.97	[25]
Polycarbonate	1	35	1.07	4.65	[26]
Polyurethane	4	25	2.8	4.0	[9]

[†] Approximate values obtained from the graphs by digitalization

1.4.2 Inorganic membranes

Similar to polymeric membranes, inorganic membranes can be broadly categorized as dense and porous. Dense inorganic membranes are highly specific to gas separations and work according to solution-diffusion or solid-state ionic conduction transport mechanisms. However, these membranes are still under extensive research mainly to limit the use of precious metals and to develop commercially viable synthesis and operating conditions. In contrast, porous inorganic membranes are inexpensive since they can be synthesized from simple ceramics like alumina, titania, glass, and silica or metals such as stainless steel and silver. Due to their high porosity, these membranes exhibit higher permeability but lower selectivity compared to the dense inorganic [8]. Compared to the polymeric membranes, inorganic membranes exhibit high thermal and chemical stability as key advantages. They are suitable for gases that induce plasticization (mainly CO₂) due to their stability in a high-pressure environment. In addition, the use of highly crystalline materials provides better control over pore size, which is attractive for applications that demand precise selectivity. Nonetheless, the handling of inorganic membranes is sometimes problematic for commercial applications due to their brittleness. Also, fabricating these membranes into modules with a high aspect ratio without introducing cracks is a challenge [4].

1.4.3 Mixed-matrix membranes

Despite huge efforts, it is still a challenge to overcome Robeson's Upper Bound relation with polymeric materials, and the inorganic membranes have their own issues as explained above [8]. At this point, the idea of mixing polymeric materials with inorganic materials, yielding mixed-matrix membranes (MMMs), offers a way to achieve high-performance yet easy-to-handle

materials at an affordable cost [8, 27]. In a typical MMM (a.k.a. composite membrane), the polymeric material serves as the matrix and homogeneously dispersed inorganic particles are considered as filler materials. In general, these fillers can increase the overall selectivity of the resulting membrane by either acting as a molecular sieve or a barrier for the gas diffusion or can increase the permeability via micro cavities by interrupting the polymer chain arrangements [8].

1.5 Fillers for mixed-matrix membranes

1.5.1 Nonporous particles

Nonporous fillers (such as regular metal oxides and silica particles) do not possess porosity, thus cannot impart molecular sieving effect or improve gas diffusion intrinsically. Still, the surface properties of these fillers can exhibit affinity to the desired solute. Also, nonporous fillers can influence the packing density of the membranes by altering the arrangement of polymer chains. As a result, the free volume of the polymer matrices can be altered, leading to variations in tortuosity, gas diffusivity, and selectivity [28, 29].

1.5.2 Porous particles

Porous fillers are commonly the particles that have a porosity level between 0.20-0.95 %. The pores can be closed or open, depending on the interconnectedness of pores. For gas separation applications, open (interconnected) pores are preferred, in general, as it enhances gas diffusion. The morphology of the pores can vary such as cylindrical, spherical, or slit type [30]. The most widely utilized porous materials in the gas separation field in MMM design are zeolites, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs) [28]. A brief description

of MOFs and COFs will be followed as these have been employed as fillers for MMM described in precedent chapters. (For a broad discussion about the porous fillers, please refer to the book “Nanocomposite Membrane Technology Fundamentals and Applications” by Tewari [29].)

1.5.2.1 Metal-organic frameworks

The building blocks of MOFs are metal ions and organic linkers [31, 32]. They are mainly characterized by high porosity and surface area that favours high capacity for adsorbent sorption, and enhanced mixing with a polymer matrix due to organic linkers. MOFs are able to separate gases by interacting with them physically or chemically. MOFs can broadly be categorized as rigid or dynamic. Rigid MOFs do not exhibit any framework flexibility, whereas dynamic MOFs display expanding framework structures at high operating conditions [33]. However, each MOF has its own advantages and disadvantages when it comes to separating a certain gas mixture. Therefore, choosing a MOF to prepare a MMM should be done wisely and consideration should be given to the compatibility with the polymer matrix, desired specifications of the end product and the stability with the operating conditions. **Table 1-3** lists pros and cons of some widely used MOFs for O₂/N₂ separation and **Table 1-4** lists separation capabilities of some selected MOFs for CO₂/CH₄ separation.

Table 1-3: Pros and Cons of some popular MOFs for O₂/N₂ separation

MOF	Pros	Cons
MIL 101	High water stability, feasible in improving O ₂ permeability [34]	Cannot improve O ₂ /N ₂ selectivity [34]
HKUST-1	Capable of improving O ₂ permeability [25]	Intermediate moisture stability [34] Negligible O ₂ /N ₂ sorption selectivity [25]
MOF-177 ¹	Has pure O ₂ /N ₂ adsorption selectivity around 1.8 at 1 atm and 298 K [35]	Low stability in the ambient atmosphere [35]
Cu-BPY-HFS ²	Moisture stable, Can improve O ₂ permeability [36]	Cannot improve O ₂ /N ₂ selectivity [36]
Cr ₃ BTC ₂	Pure gas adsorption selectivity around 22 at 298 K [37]	Performance deteriorates with repeated cycles [37]
Fe ₂ DOBDC ³	Pure gas adsorption at 298K is around 7.5[38]	Room temperature O ₂ adsorption is irreversible [38]

¹MOF-177 –(ZnH₃BTB) and H₃BTB- 1,3,5-Tris(4-carboxyphenyl)benzene

²Cu–4,4'-bipyridine–hexafluorosilicate

³dobdc⁴⁻ -2,5-dioxido-1,4-benzenedicarboxylate

Table 1-4: CO₂/CH₄ separation properties of some popular MOFs

MOF	Operating conditions	[†] CO ₂ adsorption (mmol/g)	CO ₂ /CH ₄	Reference
MIL-53 (Al)	1bar, 30°C, 50/50 mixture	1.3	7	[39]
MIL-53 (Cr)	10 bar, 30°C, 50/50	3.4	4	[40]
CuBTC	6 bar, 30°C, 50/50	2.0	10	[41]
ZIF-8	1 bar, 25°C, pure	0.8	3	[42]
MOF-177	800 torr, 25°C, pure	4 wt%	8	[43]
MOF-5	800 torr, 25°C, pure	7 wt%	20	

[†]Approximate values obtained from the graphs by digitalization

1.5.2.2 Covalent organic frameworks

COFs are composed of covalently bonded organic moieties. Due to their fully organic composition, they have been extensively researched as fillers in MMMs anticipating improved filler-polymer interactions. On the other hand, they exhibit inherent permanent porosity, well-defined pore architecture, and superior thermal stability [44]. However, to the best of my knowledge COFs have not been tested for O₂/N₂ separation. CO₂/CH₄ separation performances of some well-known COFs are given in **Table 1-5**.

Table 1-5: CO₂/CH₄ separation properties of some popular COFs

COF	Operating conditions	[†] CO ₂ adsorption (mg/g)	[†] CO ₂ /CH ₄	Reference
ACOF-1	1bar, 25°C, pure	80	11	[45]
HEX ¹ COF-1	1bar, 25°C, pure	55 cm ³ /g	4	[46]
SNW-1	1bar, 25°C, pure	48 cm ³ /g	6	[44]
COF-1	35 bar, 25°C, pure	190	5	[47]
COF-5		770	9	
COF-6		300	5	
COF-8		590	7	
COF-10		790	10	
COF-102		1180	6	
COF-103		1170	7	

¹hexphenylbenzene[†]Approximate values obtained from the graphs by digitalization

1.5.3 Facilitated carriers

Facilitated carriers are a type of filler that can selectively transport a gas component from a gas mixture. The carrier can be physically or chemically bound to the polymer matrix. Here the facilitated carrier makes a reversible complex with the solute that has an affinity with it at the upstream side of the membrane. The solute then will diffuse through the membrane by hopping to the next available carrier by reversing the solute-carrier complex formation and will de-couple from the downstream side of the membrane. Thus, a gas component that has an affinity with the carrier will diffuse through the membrane more easily and rapidly. In general, some of the

Cobalt based complexes like cobalt cosalen, cobalt porphyrin and cobalt phthalocyanine are recognized as good candidates for facilitated oxygen transport, and secondary amines like ethanolamine are preferred as carriers for CO₂ [48, 49]. O₂/N₂ separation performances of carrier-based MMMs from selected literature are summarized in **Table 1-6**.

Table 1-6: Performance of some fixed site carrier membranes for O₂/N₂ separation

Polymer	Operating conditions	Facilitated carrier	Loading (wt%)	O ₂ permeability	O ₂ /N ₂	Ref.
Pebax	2 Kgcm ⁻² , 30 °C, pure gas	-	-	0.06 GPU	2.9	[49]
		CoPc	1	1.12 GPU	8.5	
ESBS ¹	360 mmHg, 30°C, pure gas	-	-	[†] 17.90 Barrer	[†] 2.9	[50]
		(CoS2) ²	-	17.70	3.6	
		(CoS3) ³	-	16.90	3.5	
		(CoS4) ⁴	-	15.00	3.4	
polycarbonate	35°C	-	-	[†] 1.00 Barrer	[†] 5.0	[51]
		Co(SalPr) ⁵	3	2.50	7.0	
polycarbonate	5°C	-	-	[†] 0.36	[†] 9.0	[52]
		CoSalen ⁶	3	0.34	15.0	

¹ epoxidized styrene-butadiene-styrene triblock copolymer

²N,N-ethylenebis(3,7-dimethyls alicylideneiminato)cobalt(II)

³N,N-ethylenebis(3-methyl-7-phenylsalicylideneiminato)cobalt(II)

⁴N,N-phenylenebis(3-methyl-7-phenylsalicylideneiminato)cobalt(II)

⁵Cobalt di-(salicylal)-3,Y-diimino-di-N-propylamine

⁶N,N-dialicylidene ethylene diamine) cobalt(II) (CoSalen)

[†]Approximate values obtained from the graphs by digitalization

1.6 Additives used for MMMs

1.6.1 Low-molecular weight additives

Low molecular weight (low-Mw) additives are a type of fillers that can be added in to the polymer matrix to serve various purposes, such as overcoming plasticization, enhancing gas separation performance or improving compatibility between another type of filler and the polymer matrix in a simple and cost-effective method. In general, naphthalene-based additives such as phenyl naphthyl-amine and 1,1-bi(2-naphthol) can prevent the plasticization of polysulfone membranes, whereas low-Mw polyethylene glycol (PEG) is the preferred additive for CO₂/CH₄ separation due to its high affinity to CO₂. Also, the molecules like p-nitroaniline and 2,4,6-triaminopyrimidine can be incorporated into MMMs with zeolites as they can interact with both zeolite and polymer chains to achieve a defect-free MMMs. This is considered as an easy, cost-effective, and rapid method [53-57].

1.6.2 Block co-polymeric additives

Block co-polymers have been used widely as a compatibilizer in membrane preparation. Due to their amphiphilic nature, these molecules can interact with both polar and non-polar materials. Thus, block co-polymers are popular in compatibilizing immiscible polymers, and yielding well-mixed blends. Recently, the block co-polymers gained attention for preparing MMMs for a similar reason. Many research groups have proved that the addition of block co-polymers can improve the particle-polymer compatibility and reduce the particle aggregation in MMMs [58]. However, it is worth to note that the compatibilization ability of the block co-polymers mainly depends on the interactions between the polymers and particles.

1.7 Challenges in fabricating defect free MMM

In an ideal MMM, morphology should be such that it allows preferential gas transport through incorporated fillers. This morphology permits fillers to dominate the gas transport pathway. However, this scenario is not realistic due to the phenomenon called ‘percolation threshold’. This implies that the filler loading in the polymer matrix cannot exceed a certain value as it will give rise to the undesired particle aggregation and increased membrane thickness [59]. On the other hand, filler-polymer compatibility is critical to develop a membrane without any non-ideal morphology. These non-ideal morphologies can be [60];

- 1) Matrix rigidification which arises due to the restricted motion of polymer chains at the polymer-filler interface during membrane formation. This gives rise to a ‘sealed’ morphology at the interface and lowers the gas permeability. The occurrence of this defect can generally be validated via TGA/DSC analysis.
- 2) Sieve-in-a-cage morphology which occurs due to the poor polymer-filler compatibility and can be observed through FESEM. Due to the defective-void that has been created at the polymer-filler interface, selectivity will be compromised.
- 3) Plugged sieves that can take place due to the presence of solvent or rigidified polymer. This results in a drastic decrease of permeability in the membrane. In general, this phenomenon can clearly be identified by measuring the gas adsorption of the membrane.

1.8 Multi-component MMMs

Multi-component MMMs are often formed by three components, yielding ternary-component MMMs. The reasons for using three components together are to overcome the non-ideal morphologies explained above and to improve physical properties (mechanical strength, plasticization resistant), and selectivity/permeability of membranes [60, 61].

Loloei *et al.* have prepared a ternary MMM composed of Matrimid (as the polymer matrix), zeolite ZSM-5 (as the filler), and PEG 200 (low-MW additive). The purpose of ZSM-5 was to improve the CO₂/CH₄ separation performance, while the addition of PEG 200 enhances the CO₂-philicity of the membrane. As a result, the developed membranes exhibited improved CO₂ permeability and CO₂/CH₄ selectivity compared to the neat membrane [55]. Polysulfone membrane with layered Silicate-1 and HKUST-1 was developed by Zornoza and co-workers that showed improved CO₂ permeability. The authors claim that synergistic incorporation of the two different fillers increases the free volume of the membrane [62]. In another work, Li and co-workers have developed membranes with high CO₂ permeability and CO₂/CH₄ selectivity based on Matrimid, multi-walled carbon nano tubes (MWCNTs), and Graphene Oxide (GO) nanosheets. MWCNTs improved the CO₂ permeability through its pore and GO improved selectivity by acting as a barrier [63]. Another ternary membrane was prepared by Rezakazemi *et al.* by incorporating fumed silica (FS) into the PDMS and octatrimethylsiloxy polyhedral oligomeric silsesquioxane (POSS) nanoparticles. They achieved an improved CO₂ permeability and CO₂/CH₄ selectivity [64]. Li and co-workers developed a membrane with improved CO₂/CH₄ separation and mechanical properties by the combined use of Zeolitic Imidazole Framework-8 (ZIF-8) and GO stacks in ODPA-TMPDA polymer matrix. The 3D MOF enhances

the CO₂ permeability while GO stacks help to improve the CO₂/CH₄ selectivity [61]. The results of these discussed works are summarized in **Table 1-7**.

The dual-layer hollow fiber membrane, developed by Jiang and co-workers with polysulfone and zeolite beta, showed poor compatibility and O₂/N₂ selectivity. However, after treating this dual membrane with the P-xylenediamine a ternary membrane was created where they assumed that –NH₂ of the diamine molecule forms simultaneous hydrogen bonds with –OH of the zeolite surface and sulfonyl oxygen or aryether groups in the polysulfone. This phenomenon helps to compatibilize zeolite beta with the polymer matrix, which consequently improves the gas separation performances [65]. In a similar work, Patel *et al.* employed polystyrene-b-poly(hydroxyl ethyl acrylate) (PS-b-PHEA) block copolymer to compatibilize Matrimid and Zeolite 5A. The group claims that improved compatibility is due to the hydrogen bonding between –OH groups in block copolymer with Matrimid and zeolites [66]. This discussed work is summarized in **Table 1-8**.

Table 1-7: Performance of some ternary MMM for CO₂/CH₄ separation

Matrix	Filler 1	Loading (wt%)	Filler 2	Loading (wt%)	Additive	Loading (wt%)	Temp. (°C)	Pres. (bar)	CO ₂ Permeability (Barrer)	CO ₂ /CH ₄	Ref.
Matrimid	-	-	-	-	-	-	35	10	7.68	35	[55]
	ZSM-5	5	-	-	-	-			8.63	54	
	-	-	-	-	PEG 200	5			9.62	40	
	ZSM-5	5	-	-	PEG 200	5			11.53	60	
Polysulfone	-	-	-	-	-	-	35	2.75	[†] 4.50	[†] 24	[62]
	Silicate-1	8	-	-	-	-			[†] 9.50	[†] 20	
	-	-	HKUST-1	8	-	-			[†] 8.80	[†] 15	
	Silicate-1	8	HKUST-1	8	-	-			[†] 9.00	[†] 23	
Matrimid	-	-	-	-	-	-	30	2	8.84	34	[63]
	GO	10	-	-	-	-			6.46	70	
	-	-	CNT	10	-	-			10.29	28	
	G	5	CNT	5	-	-			38.07	85	
PDMS	-	-	-	-	-	-	35	2			[64]
	POSS	2	-	-	-	-			[†] 4500.00	[†] 3	
	-	-	FS		-	-					
	POSS	2	FS	15	-	-			[†] 4900.00	[†] 3	
ODPA-TMPDA	-	-	-		-	-	25	1	30.70	32	[61]
	ZIF-8	10	-	-	-	-			49.50	31	
	-	-	GO	5	-	-			33.00	41	
	ZIF-8	10	GO	5	-	-			49.10	41	

[†] Approximate values obtained from the graphs by digitalization

Table 1-8: Performance of ternary MMM for O₂/N₂ separation

Matrix	Filler 1	Loading(wt%)	Additive	Loading(wt%)	Temp.(°C)	Pres.(bar)	O ₂ Permeability	O ₂ /N ₂	Ref.
Polysulfone	-	-	-	-	35	5	[†] 0.6 GPU	[†] 6	[65]
	Zeolite beta	30%	-	-			[†] 31.0 GPU	[†] 1	
	Zeolite beta	30%	P-xylenediamine	-			[†] 1.8 GPU	[†] 3	
Matrimid	-	-	-	-	35	[†] 4	1.5	6	[66]
	Zeolite 5A	10	-	-			1.0	15	
	-	-	PS-b-PHEA	5			2.8	5	
	Zeolite 5A	10	PS-b-PHEA	5			0.8	20	

[†] Approximate values obtained from the graphs by digitalization

1.9 Research Objectives and Thesis Overview

1.9.1 Research Objective

After more than two decades of research, the MMM concept is still not commercialized. To make the MMM practically useful, two main strategies can be followed:

- 1) Reducing the cost of high-performance polymers using cost-reducing fillers without sacrificing the performance considerably and
- 2) Improving the performance of common (and affordable) polymers with high-performance filler materials.

The primary objective of this thesis is to test the applicability of both these strategies, for air separation and to gain a comprehensive insight into preparation and characterization of polymers, fillers and membranes. Unexplored polymer-filler combinations have been prepared and tested. As application of these strategies is again challenged by the problems associated with the conventional dual component membranes, the second objective of this study is to address this issue by developing ternary component membranes while gaining an in-depth understanding of gas transport phenomenon in membranes. The novelty of the research is maintained by incorporating ternary components beyond the state-of the art. The third objective is to extend this idea to develop a ternary component for CO₂/CH₄ separation that can overcome trade-off relationship in a facile manner. The membrane was developed by employing metal-organic frameworks of two different dimensions - a concept that has not yet been tested by the research community so far. As such, these three objectives provide insights into the ways in which one

can wisely choose and engineer the materials beyond the state-of-the-art to develop practical and cost-effective gas separation membranes. Below is the brief of each of the three experimental chapters of the thesis that have been designed to achieve these objectives.

1.9.2 Thesis overview

The first experimental section (**Chapter 3**) of the thesis is focused on improving the O₂/N₂ separation performance for Matrimid polymer. Matrimid can be considered as the best commercially available polymer candidate for air separation. The pristine membrane has a superior O₂/N₂ selectivity of around 5. However, its O₂ permeability is around 1.5 Barrer, which is quite low. Hence, the aim of the first experimental chapter was to improve the performance of Matrimid in a technically feasible way for the industrial applications. As such, commercially available cobalt phthalocyanine was chosen as a fixed site carrier to improve the O₂ permeability of the membrane. However, it was observed that dual mixed-matrix membrane developed with only Cobalt phthalocyanine microparticles as the filler and Matrimid as the polymer matrix is not capable of improving the gas separation performance as desired. This was attributed to the poor compatibility and aggregation of the filler which hinders the optimal use of filler. To overcome this challenge, there are two options. The first option was to modify the polymer or cobalt phthalocyanine to improve the compatibility with each other and to improve the homogeneous dispersion of the filler. This option is time-consuming, expensive and may not be industrially viable. Thus another option was to add a third component that can aid in compatibilization and dispersion which is more cost-effective and practical. Pluronic F-127, a commercially available block copolymer, was chosen. The developed ternary MMM exhibited improved compatibility

and homogenous dispersion of cobalt phthalocyanine which resulted in a 64% improvement in O₂ permeability and 40% improvement in O₂/N₂ selectivity.

In the family of polyimides ODPA-TMPDA is an outstanding polymer for gas separation. However, this polymer is not yet commercialized and has not been a popular material for academic research. Pristine ODPA-TMPDA exhibits O₂ permeability of around 16 Barrer and O₂/N₂ selectivity of around 4.6. The synthesis of this polymer is simple compared to other highly popular 6FDA-based polyimides as it does not require extensive monomer purification or careful polymerization protocol. Therefore, the aim of the second experimental chapter (**Chapter 4**) is to use ODPA-TMPDA for O₂/N₂ separation for obtaining an outstanding gas separation performance. As ODPA-TMPDA is considered as a high-permeability polymer, the main aim of this chapter is to improve its selectivity without sacrificing the permeability. To this end, commercially available cobalt (III) acetylacetonate was employed to improve the O₂ solubility primarily. However, the resulting MMM developed from this combination reduced the O₂ permeability. Hence, to retrieve the O₂ permeability the SNW-1 COF was used. The fully organic framework of SNW-1 aided in compatibilizing with the polymer matrix and its 5Å pore aperture helped to increase the O₂ permeability. Thus, ternary MMM results in a synergistic improvement in both O₂ permeability and O₂/N₂ selectivity.

The third study (**Chapter 5**) deals with the applicability of the ODPA-TMPDA polymer matrix for CO₂/CH₄ separation. The pristine polymer has a CO₂ permeability of around 112 Barrer and CO₂/CH₄ selectivity of around 36. Although the pure ODPA-TMPDA membrane is better than most of the commercially available polymers for CO₂/CH₄ separation, the matrix still needs to be improved to beat the Robeson upper bound. The strategy employed here was to develop a ternary MMM by employing two MOFs with different dimensionalities. As such the

2D MOF, CuBDC nanosheets (ns-CuBDC) were used to improve the selectivity of the membrane. Ns-CuBDC, due to its high aspect ratio provides a tortuosity path for larger CH₄ molecule but smaller CO₂ molecule can pass through its pore opening. On the other hand, 3D MOF ZIF-8 nanoparticles contain high micro pore volume which can aid in high gas adsorption resulting in high gas permeability. Thus, the combined use of 2D ns-CuBDC and 3D ZIF-8 nanoparticles provides a novel strategy to employ MOFs in gas separation membranes.

2 MATERIALS AND CHARACTERIZATIONS

2.1 Materials and chemicals

Microneedle-shaped cobalt(II) phthalocyanine particles (CoPcMPs), Pluronic® F-127(Pluronic), 2,4,6-trimethyl-*m*-phenylenediamine (TMPDA), 4,4'-oxydiphthalic anhydride (ODPA), acetic anhydride (Ac₂O), cobalt (III) acetylacetonate (Co(acac)₃), melamine (C₃H₆N₆), terephthalaldehyde (C₆H₄(CHO)₂), Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), 1,4-benzenedicarboxylic acid (H₂BDC), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 2-methylimidazole (Hmim), and triethylamine (TEA) were purchased from Sigma Aldrich. Absolute ethanol (C₂H₅OH), chloroform (CHCl₃), dimethyl sulfoxide (DMSO), methanol (CH₃OH), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), acetonitrile (CH₃CN) and tetrahydrofuran (THF) were purchased from VWR. Matrimid® 5218 (Matrimid) was purchased from Huntsman Corp. (in powder form). All chemicals were used as received without further purification. The chemical structures of CoPcMPs and commercial polymers are illustrated in **Figure 2-1** below.

Figure 2-1: Chemical structures of (a) Pluronic (Pluronic® F-127); (b) CoPcMPs, and (c) Matrimid (Matrimid® 5218)

2.2 Characterizations

2.2.1 Field Emission Scanning Electron Microscopy (FESEM)

The morphology of fillers (CoPcMPs, SNW-1 COF, ns-CUBDC, and ZIF-8 nanoparticles) and membrane cross-sections were observed by field-emission scanning electron microscopy (FESEM, JSM-7600F) equipped with energy-dispersive spectroscopy (EDS) mapping. Microscopy specimens were prepared as follows. The CoPcMPs were dispersed in ethanol, and several drops of CoPcMPs dispersion were deposited on a freshly cleaned silicon wafer substrate. As for SNW-1, several drops of SNW-1 suspension in CHCl_3 were placed on a silicon wafer and dried overnight. Similarly, ns-CuBDC was suspended in DCM while ZIF-8 was suspended in methanol. For the observation of the cross-sectional views of the membrane samples, permeation-test-ready samples (annealed membranes) were fractured by using liquid nitrogen, followed by air drying at room temperature and platinum sputtering.

2.2.2 Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopes (FTIR) of fillers and membranes were determined using an IRPrestige-21 spectrophotometer (Shimadzu Corp.) at a range of 400 to 4000 cm^{-1} .

2.2.3 X-ray diffraction (XRD)

The crystalline structures of the fillers and membranes were investigated using powder X-ray diffraction (PXRD, Bruker D2 phaser) equipped with $\text{Cu K}\alpha$ radiation. The samples were scanned with a step size of 0.02° for the range of 2θ from 5° to 40° at ambient conditions using a zero-background single-crystal silicon sample holder. For CoPcMP several drops from a

suspension in ethanol were used while for the ns-CUBDC suspension was synthesized using CHCl_3 . All the other fillers were used in powder form.

2.2.4 Thermogravimetric/differential thermal analyzer (TGA/DSC)

The thermal behaviors of fillers and all membranes were determined using thermogravimetric/differential thermal analyzer (TG/DTA, SDT Q600, TA Instruments) between 40 to 800°C with a heating rate of 10 °Cmin⁻¹ under nitrogen purging at a flow rate of 100 mL min⁻¹.

2.2.5 Electrokinetic analyzer

The surface streaming potential measurements of the membranes were performed on an electrokinetic analyzer (SurPASS™ 3, Anton Paar) using 10 mM sodium chloride solution as the supporting electrolyte without pH adjustment (pH ~6).

2.2.6 Elemental analyzer

The purity of the polymer was verified using an elemental analyzer (PerkinElmer, CHNS/O 2400).

2.2.7 Analytical ultra microbalance

The densities of the membranes were determined using an analytical ultra microbalance (ME204, Mettler-Toledo) equipped with a density measurement setup (Density Kit ME-DNY-43, Mettler-

Toledo). Using ethanol as the auxiliary liquid, the density calculations were made according to Archimedes' principle as described by the manufacturer.

2.2.8 Atomic force microscopy (AFM)

The height profile of ns-CuBDC was measured using atomic force microscopy (AFM, Veeco Multimode Nanoscope 3A microscope) in the tapping mode. Prior to the measurement, the ns-CuBDC samples were first prepared by subjecting several drops of suspension of nanosheets in DCM onto the silicon wafer and then dried overnight.

2.2.9 Surface area analysis

The accessible surface area and the pore volume of SNW-1 were quantified by measuring N₂ physisorption at 77K, which was measured using a volumetric gas sorption analyzer (Autosorb AS-1, Quantachrome). Prior to measurement, SNW-1 was activated at 160°C for 8 hours under a high vacuum to remove any residual solvents that could be present in the sample.

2.2.10 Young's modulus analysis

To analyze the Young's modulus of the neat and composite membranes, samples were prepared by cutting into rectangles of 5 mm width and 30 mm length. Then the samples were loaded to the Instron 5543 tensile meter equipped with 100 N grip, at room temperature.

2.3 Gas adsorption analysis

Pure O₂, N₂, CO₂, and CH₄ adsorption isotherms of the membranes were measured using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome Instruments). All the samples were activated at 160 °C for 8 hours under high vacuum prior to the analysis to remove any residual solvents. For O₂ and N₂ adsorption, the temperature was kept constant at 35°C under the pressure range of 0–5 bar due to low adsorption of both O₂ and N₂ at the point of interest (0.21 bar for O₂ and 0.79 bar for N₂). However, for ODPA-TMPDA based membranes 0-1 bar pressure range was sufficient to achieve desired adsorption data. On the other hand, CO₂ and CH₄ adsorption were measured at 25 °C under the pressure range of 0-1 bar. The amount of gas adsorbed (q) was determined from the extrapolation of the isotherm for each membrane according to linear isotherm. The solubility of the gas in the membrane, S (e.g., O₂ and N₂) can be calculated based on the following relationship:

$$S = \frac{q\rho}{p} \dots\dots\dots \text{Eq. (1)}$$

where q is the amount of gas adsorbed per mass of membrane, p is the pressure (0.21 bar for O₂, 0.79 bar for N₂ and 0.50 bar for CO₂ and CH₄, respectively), and ρ is the density of the membrane. Gas diffusivity in the membrane (D) could then be calculated by dividing the permeability by the solubility.

2.4 Gas permeation test

The gas permeation test was carried out using the constant pressure-variable volume system developed by GTR Tec Corp. Helium (He), compressed air (O_2/N_2 :21/79), and CO_2/CH_4 (50/50) mixtures were purchased from Air Liquide. The membrane was first mounted onto the permeation cell with the desired temperature set ($35^\circ C$ for O_2/N_2 and $25^\circ C$ for CO_2/CH_4) and operated with the feed pressure of 1 bar. Here it is important to note that diffusion of O_2 and N_2 increases with temperature [67]. Therefore, to obtain enhanced values (recordable) O_2/N_2 separation was performed at $35^\circ C$ rather than at ambient temperature ($25^\circ C$). Still, as explained in future plan, an operating temperature that is suitable for practical operation should carefully be chosen with more experiments. Throughout the analysis, the test gas mixture and He were continuously flown upstream and downstream, respectively, by controlling the flow rates with mass flow controllers until the concentrations of test gases do not fluctuate. The downstream gas permeating through the membrane was swept by He periodically. The concentrations of permeated test gases were determined using gas chromatography attached to gas permeation setup. To ensure the reproducibility of gas permeation results, the measurements were repeated for at least three times with different samples for each membrane.

3 ENHANCED AIR SEPARATION OF MATRIMID-BASED MIXED-MATRIX MEMBRANES FILLED WITH PLURONIC-COMPATIBILIZED COBALT PHTHALOCYANINE MICRONEEDLES

3.1 Introduction

The separation of O₂ and N₂ from the air is highly challenging due to their close kinetic diameters (3.46 Å and 3.64 Å for O₂ and N₂, respectively) [68]. Small kinetic diameter difference of O₂ and N₂ brings a great challenge for employing molecular sieving (by porous fillers such as zeolites or reticular frameworks) for separation as the sole principle of separation [69, 70]. As a matter of fact, certain metal-organic frameworks (MOFs), such as chromium (II) carboxylate MOF (Cr₃BTC₂) and MOF-5, possess high O₂/N₂ selectivity. However, their structure instability with operation cycles limits the prospects of practical use [35, 37]. At this point, the facilitated carriers (as molecules and solid particles) offer new opportunities for designing composite membranes for O₂/N₂ separation.

Facilitated carriers typically favor the permeation of one of the gas species in a gas mixture, by hopping mechanism. For the case of O₂/N₂ gas pair (air), the hopping mechanism takes place by the selective and reversible complexation of O₂ by jumping from one carrier to another through transport event [49]. (Note that N₂ is inert.) Among the carrier alternatives for facilitating the transport of O₂, cobalt-based complexes, namely cobalt (II) phthalocyanine (CoPc), and cobalt (II) tetraphenylporphyrin (CoTPP), stand out with their O₂ selectivity. Considering its wide availability and low cost, the effect of CoPc on O₂/N₂ separation performance of polyimide-based membranes was decided to be tested. Aimed at achieving a high-performance MMM design, Matrimid® 5218 as the polyimide matrix was selected, which provides an intrinsic O₂/N₂ selectivity close to 6 [25]. The permeability of Matrimid® 5218

needs improvement for fabricating a high-performance MMM out of it. As observed by Md and co-workers using the polysulfone-CoPc system, non-selective voids forming between the polymer matrix and carriers might enhance the permeability [71]. However, non-selective voids might lead to the formation of more substantial defects, causing dramatic reductions in selectivity performance, as well [60]. Therefore, it is imperative to compatibilize CoPc particles with the polymer matrices, in a well-tuned manner. To this end, the surface modification of CoPc particles with tert-butyl groups, for example, is a viable strategy but requires a step of additional chemical modification [72, 73]. Alternatively, as reported by several groups, block co-polymers might serve as efficient compatibilizers between fillers and polymer matrices [66, 74]. As such, this research introduces the innovative idea to compatibilize fixed carries in polymer matrixes using suitable block co-polymers. The approach to accomplish this task is described in detail in the experimental section.

Here I report a high-performance MMM for O₂/N₂ separation based on Matrimid® 5218 (in short, Matrimid) as a polymer matrix, CoPc microparticles (CoPcMPs) as fixed-site carriers, and Pluronic® F-127 (in short, Pluronic) as a block co-polymer compatibilizer. Based on the gas permeation analysis, the incorporation of 5 wt% CoPcMP and 10 wt% Pluronic improves the O₂ permeability and O₂/N₂ selectivity of Matrimid by 68% and 33%, respectively. By performing a solubility/diffusivity analysis, it was found that the Pluronic-compatible Matrimid-CoPcMP system exhibits improvement in both O₂/N₂ solubility and diffusivity selectivity compared to neat polymer (Matrimid). Given each component of the Matrimid-Pluronic-CoPcMP system is commercially available and fairly affordable; it is justifiable to believe that the demonstrated MMM design is promising for industrial O₂/N₂ separation applications.

3.2 Experimental

3.2.1 Membrane fabrication

Pure Matrimid® 5218 membrane was fabricated by dissolving 0.5 g of polymer in 2.3 g of DMF. The dope solutions containing CoPcMPs were prepared by mixing the required amount of Matrimid, CoPcMPs, and/or Pluronic inside glass vials by adding DMF on top. For instance, the composite membrane containing 80% Matrimid, 10wt% CoPcMPs, and 10wt% Pluronic was prepared by adding 0.4 g of Matrimid 0.05 g of CoPcMPs, and 0.05 g of Pluronic into 2.3 g of DMF solution. The dope solution was agitated overnight using a magnetic stirrer. Once the mixtures become well-mixed to the naked eye, the membranes were prepared by casting on a Teflon-made Petri dish. After allowing at room temperature for around 1 hour, the Petri dishes were placed at a vacuum oven at 60 °C overnight to ensure the resulting membranes were pre-dried. Lastly, the pre-dried membranes were further dried and annealed in a vacuum oven at ~76 cmHg and 160°C for 24 hours prior to the gas permeation tests.

3.3 Results and Discussion

3.3.1 Characterization of Carrier and Compatibilizer

The structural properties of CoPcMP and Pluronic were first verified using FTIR (**Figure 3-1(a)**). The characteristic peaks of C–H aliphatic stretching, O–H in-plane bending and C–O stretching of Pluronic can be observed at the frequency of 2800, 1300, and 1100 cm^{-1} , respectively. On the other hand, Co–N bond vibration, C–H plane bending, C–N stretching, and C=C ring deformation of CoPcMPs can be identified on the frequencies of 750, 1100, 1500, and 1600 cm^{-1} , respectively. The FTIR spectra of CoPcMPs and Pluronic used in this work were

comparable to the results reported in the literature [75, 76]. Besides, the characteristic peaks of CoPcMP and Pluronic were identified based on the XRD pattern (**Figure 3-1(b)**), in which the peak position coincides with the results reported in previous works [76, 77]. Thermal stabilities of CoPcMP and Pluronic were determined using TGA analysis (**Figure 3-1(c)**), which both materials demonstrate the thermal decomposition temperature of 620 °C and 380 °C respectively, indicating that the annealing temperature of 160 °C will not compromise the overall crystallinity of CoPcMP and stability of Pluronic when these fillers were incorporated in Matrimid matrix. Besides, the DTA analyses reveal another sharp feature in the heat flows at 55 °C (**Figure 3-1(d)**), which corresponds to the melting temperature of Pluronic [78].

Figure 3-1: Characterization of filler (CoPcMP) and compatibilizer (Pluronic) by (a) FTIR, (b) powder XRD, (c) TGA, and (d) DTA.

3.3.2 Characterization of neat, blended, and composite membranes

FTIR measurements were performed on all membranes prepared and tested in this study (**Figure 3-2**). The spectrum clearly exhibited symmetric and asymmetric C=O stretching (1720 and 1770 cm^{-1}) as well as C–N stretching, which are characteristic imide features.

Figure 3-2: FTIR spectrum of (a) CoPc-based membrane; (b) Pluronic F-127-based membrane; (c) CoPc and Pluronic F-127-based membrane (after annealing).

And, importantly, the superimposition of the peaks for Pluronic and CoPcMP with the Matrimid peaks was observed, without noticeable shifts in their spectra. Based on the XRD measurements, it was verified that the CoPcMPs remain in crystalline form in MMMs (**Figure 3-3**). Pluronic, on the other hand, does not remain in crystalline form upon being blended with Matrimid (**Figure 3-3(b)**). And notably, the comparison of the TG/DTA profiles of neat/blended

and composite membranes indicates that the CoPcMPs do not alter the thermal stability of Matrimid or Pluronic (**Figure 3-5** and **Figure 3-6**).

Figure 3-3: XRD diagrams of (a) CoPc-based membrane; (b) Pluronic F-127-based membrane; (c) CoPc and Pluronic F-127-based membrane (after annealing)

The interfacial morphologies of the composite membranes provide valuable insights regarding the compatibility of matrices and fillers. Therefore, the cross-sectional views of neat (Matrimid) and blended (Matrimid-Pluronic) membranes were compared with composite membranes (Matrimid-CoPcMP and Matrimid-Pluronic-CoPcMP) under FESEM (**Figure 3-6**). The cross-sectional image of the neat Matrimid membrane was considerably smooth with features attributable to the fracture lines, which appear inevitably.

Figure 3-4: Comparison of MMMs that contain 10 wt% Pluronic F-127 before and after the thermal annealing process using (a) FTIR; (b) TGA, and (c) DTA.

CoPcMPs into Matrimid even at 5 wt% (**Figure 3-6(a)**), on the other hand, caused the formation of a non-ideal interfacial morphology, which was in agreement with previous works [71]. Further increase of CoPcMPs to 10 wt% (**Figure 3-6(b)**) seemingly triggered the aggregation of particles, which can be considered as “defects” in a practical sense. However, the Matrimid-Pluronic blended membrane does not look rich in defects. As visual evidence on the promise of the Pluronic-based compatibilization approach, the Matrimid-Pluronic-CoPcMP indicates a much smoother cross-sectional morphology (**Figure 3-6(c)**) compared to the Pluronic-free composite membranes.

Figure 3-5: TGA and TDA of (a) CoPc-based membrane; (b) Pluronic F-127-based membrane; (c) CoPc and Pluronic F-127-based membrane (after annealing)

This observation indicates that Pluronic served its desired functionality (as a compatibilizer) in the Matrimid-Pluronic-CoPcMP system by suppressing the adverse effect of the interfacial incompatibility of Matrimid and CoPcMPs.

Figure 3-6: Cross-sectional FESEM images of **(a)** Matrimid-CoPcMP (with 5 wt% CoPcMP), **(b)** Matrimid-CoPcMP (with 10 wt% CoPcMP), **(c)** Matrimid-Pluronic (with 10 wt% Pluronic), and **(d)** Matrimid-CoPcMP-Pluronic (with 5 wt% CoPc and 10 wt% Pluronic) membranes. (Note that the inset of **Figure 3-6 (d)** shows the morphology of CoPcMPs deposited on a silicon wafer substrate.)

3.3.3 Gas Permeation Analysis

The overall O_2/N_2 separation performances of all membranes were studied using constant-volume-variable-pressure gas permeability analysis. At 3 wt% CoPcMP loading, the O_2/N_2 selectivity increased by 14.5% at the expense of over 40.7% decrease in O_2 permeability. When the CoPcMP loading increases from 3 wt% to 5 wt%, the O_2/N_2 selectivity further increases from

14.5% to 31.6%. And importantly, the permeability drop also becomes lower for 3 wt%. On the other hand, a drastic change of O₂/N₂ separation performance was observed when loading was 10 wt%, indicating the escalation of non-ideal interfacial morphologies. This type of phenomenon was also observed by Md *et al.* as CoPcMPs was incorporated into a polysulfone matrix [72]. And, the Matrimid-Pluronic blended membrane, exhibited an improved O₂/N₂ selectivity (at the expense of limited permeability). The Pluronic-compatible MMM (80 wt% Matrimid, 10 wt% Pluronic, and 10 wt% CoPcMP), on the other hand, improved O₂ permeability by 101.2% and O₂/N₂ selectivity by 24.5%. These results indicated that the presence of Pluronic was helpful for improving the interfacial morphology between the matrix (Matrimid) and the filler (CoPcMP), which provided performance-based support to the conclusion we reached based on the FESEM imaging (**Figure 3-6(d)**).

Facilitated carriers, such as CoPcMP, generally promote gas separation performance by selectively diffusing one of the gas species (for this case, O₂) through the hopping mechanism. When carriers are free to move (as observed in a liquid medium), the transport event is rather straightforward, commonly involving the carrying of the solutes as a “cargo” [49]. However, when the carrier is immobilized in a solid matrix (like polymer-based separation membranes), it is of importance to have a homogeneous dispersion of the carriers within the solid matrix for “hopping” events to occur effectively. The prevention of aggregation is thus essential. The Pluronic-family polymers are commercially available amphiphilic tri-block co-polymers of hydrophobic polypropyleneoxide (PEO) units (as side-blocks) and hydrophilic polyethylene oxide (PEO) units (as mid-blocks) [79]. This amphiphilic nature of Pluronic helps to bridge Matrimid and CoPcMP, thereby enhancing the compatibility of the resulting composite. As a result, the hopping of the O₂ molecules took place in a more homogeneously dispersed web of

carrier sites, which consequently leads to the increase of O₂ diffusion through the membrane. However, it should be emphasized that the mixing ratio is critical to achieving the desired performance improvement with the Pluronic-based compatibilization approach. For a process where improved selectivity is the criteria of interest, 5 wt% Pluronic might be preferred over 10 wt% Pluronic case for the composite membranes. Note that the O₂/N₂ selectivity at 10% Pluronic content is lower than that of 5 wt% Pluronic for the composite membrane design, albeit it provides the benefit of higher permeability.

Table 3-1: O₂/N₂ gas permeation behavior of neat (Matrimid), blended (Matrimid-Pluronic), and composite (Matrimid-CoPcMP and Matrimid-Pluronic-CoPcMP) membranes at 35 °C under 1 bar O₂/N₂ feed pressure.

Membrane Composition [†]	O ₂ permeability (barrer)	% change (wrt. Matrimid)	O ₂ /N ₂ selectivity (unitless)	% change (wrt. Matrimid)
Matrimid (neat)	1.72 ± 0.29	—	5.79 ± 0.12	—
3wt% CoPcMP	1.02 ± 0.22	−40.7	6.63 ± 0.08	14.5
5wt% CoPcMP	1.32 ± 0.32	−23.3	7.62 ± 0.54	31.6
10wt% CoPcMP	3.37 ± 0.40	96.0	4.20 ± 0.16	−9.5
5wt% Pluronic	0.93 ± 0.32	−45.9	7.09 ± 1.09	22.5
10wt% Pluronic	0.77 ± 0.07	−55.2	6.19 ± 0.64	6.9
5wt% CoPcMP, 5wt% Pluronic	1.66 ± 0.15	−3.4	3.82 ± 0.18	−34.0
5wt% CoPc, 10wt% Pluronic	2.82 ± 0.24	64.0	7.75 ± 1.44	33.9
10wt% CoPc, 10wt% Pluronic	3.46 ± 0.44	101.2	7.21 ± 0.60	24.5

[†] Note that for all blended and composite membranes, Matrimid serves as the main element of the mixture.

To better explain the nature of performance improvement in Pluronic compatibilized composite membranes (Matrimid-Pluronic-CoPcMP), the solubility-diffusivity analyses were

performed. By measuring the pure-component O₂ and N₂ adsorption isotherms at 35 °C, the adsorption properties of neat (Matrimid), blended (Matrimid-Pluronic), and composite (Matrimid-CoPcMP and Matrimid-Pluronic-CoPcMP) membranes were first characterized (**Figure 3-7**). By doing so and accounting the density of each membrane, a solubility-diffusivity analysis was performed later, as summarized in (**Table 3-2**). This evaluation, overall, shows that the incorporation of Pluronic and/or CoPcMP (yielding blended or composite membranes) suppresses the solubility of both O₂ and N₂ as compared to the neat Matrimid membrane. Nevertheless, the incorporation of CoPcMPs (at 5 wt%) improves the solubility selectivity substantially (53.7%). In contrast, the reduced gas diffusion (of O₂ and N₂) further supports the existence of the “barrier effect” caused by the aggregation of CoPcMPs. For the Pluronic-free composite membrane with 10wt% CoPcMP, the diffusion of both gas molecules increased, which further verified the presence of “non-selective voids” originated from the incompatibility of Matrimid and CoPcMPs. On the other hand, the blended membrane (with 10wt% Pluronic) suffered from a notable decrease in diffusivity selectivity as compared to the neat Matrimid membrane. However, when all three components were incorporated to form a single membrane, a harmony between the components took place. This helped to overcome the predicaments caused by the dual component membrane.

Figure 3-7: O_2 and N_2 adsorption isotherms of neat, blended, and composite membranes as measured at 35 °C at different pressures.

Based on the XRD and DSC characterizations (**Figure 3-3** and **Figure 3-5**), it can be observed that Pluronic loses its crystallinity when blended with Matrimid. This suggests that the Pluronic chains do not separate into two phases but form a well-mixed polymer network, presumably as driven by the interactions between the hydrophobic blocks of Pluronic (PPO side chains) and Matrimid. For such a scenario, three types of gas diffusion domains can be portrayed: (1) Matrimid-rich domains; (2) intermixed Matrimid-PPO regions; and (3) PEO-rich interfacial domains (on CoPcMPs). The Matrimid-rich domains should normally behave like neat Matrimid with lower permeability and mediocre selectivity. The Matrimid-PPO regions should supposedly provide a lower selectivity but higher permeability. The behavior of PEO-rich interfacial domains, on the other hand, is expectedly rather complex due to the involvement of the hopping events taking place nearby.

It is also worthy of taking note that although the solubility of both gases was lower for the blended membranes (compared to that of the pure Matrimid membrane), solubility selectivity was considerably higher, too. Therefore, the Pluronic-compatible composite membrane with 10 wt% Pluronic and 5wt%CoPcMP exhibited an apparent enhancement in solubility selectivity. Besides, when the dispersion of the CoPcMPs throughout the matrix is improved, the diffusion of O₂ molecules seemingly increased. However, interestingly, in the the composite membrane with 10 wt% Pluronic and 10 wt% CoPcMP, the solubility O₂ molecules has decreased by around 13%. Nevertheless, the diffusivity selectivity was superior due to the increased carrier loading without aggregation. Thus, it is of importance of incorporating CoPcMP and Pluronic at optimized levels according to the desired outcome.

Table 3-2: Solubility and diffusivity data for neat (Matrimid), blended (Matrimid-Pluronic), and composite (Matrimid-CoPcMP and Matrimid-Pluronic-CoPcMP) membranes.

Property	Solubility($\text{molm}^{-3}\text{bar}^{-1}$)		Diffusivity $\times 10^{-12}$ (m^2s^{-1})		Density (gcm^{-3})
Membrane [†] / Gas	O ₂	N ₂	O ₂	N ₂	
Matrimid (neat)	31.3	24.3	1.87	0.415	1.24
5 wt% CoPcMP	27.9	19.4	1.60	0.302	1.25
10 wt% CoPcMP	24.8	17.7	4.61	1.23	1.27
10 wt% Pluronic	12.4	7.0	2.11	0.603	1.13
5 wt% CoPcMP, 10 wt% Pluronic	20.6	7.1	4.65	1.74	1.17
10 wt% CoPcMP, 10 wt% Pluronic	18.2	11.1	6.43	1.47	1.24

[†] Note that for all blended and composite membranes, Matrimid serves as the main element of the mixture.

Uniaxial tensile tests were performed to determine the mechanical strength of membranes (**Figure 3-8**). Accordingly, it was observed that incorporation of either CoPCMP or Pluronic reduces the stiffness of the membrane compared to the neat membrane. Stiffness of the ternary component membrane is reduced compared to dual component membranes. However, membrane with 10wt% CoPcMP and 10wt% Pluronic exhibits increased stiffness compared to 5wt% CoPCMP and 5wt% Pluronic membrane. This again proves the increased compatibility and homogeneous mixing of CoPCMP with the addition of necessary amount of Pluronic.

Figure 3-8: Young's modulus of neat and composite membrane

3.4 Conclusion

Using two commercially available materials, Pluronic (Pluronic® F-127) and CoPcMPs (needle-shaped cobalt phthalocyanine microparticles), the O₂/N₂ separation performance of Matrimid (Matrimid® 5218) was enhanced. The CoPcMPs served as a facilitated carrier but failed at performance enhancement without the use of Pluronic, which was the compatibilizer. It was found that 5 wt% CoPcMPs improved both O₂ permeability (by 64%) and O₂/N₂ selectivity (by 34%) when 10 wt% Pluronic is used for compatibilization. The analysis of solubility and diffusivity contributions to selectivity indicated that both solubility and diffusivity enhances for Pluronic-compatible composite membranes (Matrimid-Pluronic-CoPcMP). Thus, this study exemplifies that no sophisticated strategy is needed to modify carrier particles for achieving performance improvement in O₂/N₂ separation. Due to its practicality, the proposed strategy is promising for designing membranes potentially useful for actual applications.

4 INCORPORATION OF CO^{III} ACETYLACETONATE AND SNW-1 NANOPARTICLES TO TAILOR O₂/N₂ SEPARATION PERFORMANCE OF MIXED-MATRIX MEMBRANE

4.1 Introduction

The successful application of facilitated carriers like cobalt phthalocyanine has been limited by the poor compatibility with common organic solvents (e.g., chloroform and dichloromethane) which causes a non-uniform distribution of carriers in the membrane resulting in limited separation performance. It has also been reported that for carriers like cobalt (II) porphyrin extreme conditions (e.g., low partial pressures) are necessary to ensure that the carriers can actively participate in selective O₂ transport [80, 81].

Therefore, in this work, cobalt (III) acetylacetonate (Co(acac)₃) was used as it is not only well-dispersed in common organic solvents but also readily available. With the appropriate choice of a polymer matrix, the interaction of metal ions with the carbonyl groups in the polymer matrix can facilitate the selective transport of oxygen molecules, thus increasing O₂/N₂ selectivity [82], which can be achieved even with a small loading of Co(acac)₃. Hence, ODPA-TMPDA (ODPA=4,4'-oxydiphthalic anhydride; TMPDA=2,4,6-trimethyl-*m*-phenylenediamine) polyimide was selected as the polymer matrix in this study. This polymer is also much more permeable than conventional commercial glassy polymers (e.g., Matrimid[®], polysulfone, Ultem[®]) and can be readily scaled up without the monomer purifications necessary for 6FDA-based polymers to increase the final molecular weight [83, 84]. Additionally, to minimize the effect of reduced O₂ permeability when Co(acac)₃ was incorporated into the polymer matrix, SNW-1 was also added into the polymer matrix, as it possesses reasonably large micropores (5 Å) [85, 86] for rapid O₂ transport. On the other hand, organic moieties in SNW-1 can provide a

favorable interaction with the polymer matrix, thus restricting the formation of non-ideal interfacial morphology which gives a negative impact on the overall O₂/N₂ separation performance. It should be noted that such a strategy (the use of multiple fillers) has been widely utilized in the mixed-matrix membrane for CO₂ separation [87-89]. However, the application of such a strategy in O₂/N₂ separation is still rare. On the other hand, a severe problem that may arise when trying to incorporate a ternary component to MOF incorporated MMM is the plugged sieves non-ideal defect. This arises mainly due to the interaction of the metal in MOF with the ternary component. As a solution to this problem, the concept to employ a covalent organic framework instead of a MOF is also demonstrated through this research. After studying the gas permeation properties, the roles of the filler and the complex were then verified by analyzing the solubility and diffusivity of O₂ and N₂ in the mixed-matrix membrane.

4.2 Experimental

4.2.1 Synthesis of ODPA-TMPDA polymer

Figure 4-1: Reaction scheme for the synthesis of ODPA-TMPDA polymer.

The synthesis of ODPA-TMPDA was conducted based on the procedures described in previous work (**Figure 4-1**) [89-91]. First, 1.63 g of TMPDA was added to a round-bottom flask, followed by the addition of 20.0 g of DMAc. The resulting mixture was stirred vigorously prior to adding 3.36 g of ODPA. The mixture was then agitated for 24 hours to obtain a viscous solution that contained 20wt% of polyamic acid. Next, an imidization process was conducted by incorporating 4.44 g of Ac₂O and 4.39 g of TEA. The mixture was stirred for an additional 24 hours before being poured into a beaker containing 300 ml of absolute ethanol. The precipitated ODPA-TMPDA polymer was washed with copious amounts of fresh ethanol before being dried in a vacuum oven at 160°C overnight.

4.2.2 Synthesis of SNW-1

Figure 4-2: Reaction scheme for the synthesis of SNW-1

SNW-1 was synthesized based on the method used in previous work (**Figure 4-2**) [92], with the reaction conducted under continuous N₂ purging. In a typical synthesis, 0.313 g of melamine and 0.500 g of terephthalaldehyde were added to 15.5 ml of DMSO. The mixture was heated at 180°C for 72 hours. After the resulting mixture was cooled to room temperature, the precipitate obtained was washed thoroughly with both DMF and THF. Subsequently, the sample was dried in a vacuum oven at 120°C overnight.

4.2.3 Membrane fabrication

All of the membrane fabrication in this work was conducted using the solution-casting method. The pure ODPA-TMPDA membrane was fabricated using a dope solution made by dissolving 0.5 g of polymer into 4 g of CHCl₃. Note that chloroform (CHCl₃) can effectively dissolve both the polymer and the cobalt complex. Its low boiling point (61 °C) is also beneficial in the synthesis of the dense membrane which requires solvent evaporation. A series of mixed-matrix membranes that contain SNW-1 and Co(acac)₃ were synthesized as summarized in **Table 4-1**. As a representative, a dope solution which contained 10 wt% SNW-1 and 2 wt% Co(acac)₃, was prepared as follows. First, 10 wt% SNW-1 was dispersed into 4 g of CHCl₃ with the aid of sonication. Next, the polymer was added to the resulting suspensions, which were then gently shaken with laboratory shaker for three to four hours under ambient conditions. Subsequently, 2 wt% of Co(acac)₃ was added to the resulting suspension, which was shaken for 24 hours. Thereafter, the dope solution was cast on the glass plate using a casting knife in a glove bag filled with CHCl₃ vapor. The nascent membranes were left undisturbed at room temperature for 24 hours. The resulting membrane was annealed in a vacuum oven at 160°C for 24 hours prior to gas permeation testing.

Table 4-1: Membranes synthesized in this work

Legend ¹	Membrane
0	ODPA-TMPDA
1	2 wt% Co(acac) ₃
2	4 wt% Co(acac) ₃
3	10 wt% SNW-1
4	15 wt% SNW-1
5	10 wt% SNW-1 + 2 wt% Co(acac) ₃
6	15 wt% SNW-1 + 2 wt% Co(acac) ₃

¹ It corresponds to the label in **Figure 4-9**

4.3 Results and Discussion

4.3.1 Characterization of SNW-1 and Co(acac)₃

The successful synthesis of SNW-1 was confirmed using FTIR analysis. By comparing the FTIR of the raw materials (**Figure 4-3(a)**) [93], the characteristic peak assigned to terephthalaldehyde (1700 cm^{-1} , C=O stretching vibration, 2700 and 2800 cm^{-1} , C–H stretching vibration) and melamine (3420 and 3470 cm^{-1} , -NH₂ stretching vibration) was not observed. Instead, a broad peak at 3400 cm^{-1} corresponding with the -NH- stretching vibration was detected, indicating that melamine had been successfully converted. However, the peak at 800 cm^{-1} corresponds to the para-substitution of the benzene ring, whereas the presence of the triazine ring in SNW-1 was further verified at the 1300 cm^{-1} , 1400 cm^{-1} , and 1550 cm^{-1} spectrum bands, suggesting that a successful reaction between terephthalaldehyde and melamine had taken place [85, 94]. The structure of Co(acac)₃ was further verified from the FTIR measurement (**Figure 4-3 (b)**), with the structure comparable to the results reported in the literature [82]. Further, based on the TGA

analysis (**Figure 4-3(c)**), both SNW-1 and $\text{Co}(\text{acac})_3$ have been observed to be thermally stable up to 450 °C and 230°C, respectively, indicating that the C–N bond formed between terephthalaldehyde and melamine in the formation of SNW-1, and the ionic bonding between Co^{3+} and acac^{3-} , are strong enough to withstand the fabrication of mixed-matrix membrane with an annealing process at 160 °C. The morphology and size of SNW-1 nanoparticles were observed through FESEM (**Figure 4-3(d)**). The result showed that the synthesized samples were mostly irregular, with a particle size of less than 100 nm. For the case of $\text{Co}(\text{acac})_3$, the observation with SEM was not possible due to its magnetic nature as reported in previous work [95].

Figure 4-3: (a) FTIR of SNW-1, with the monomers (terephthalaldehyde and melamine), were included as the reference; (b) FTIR of $\text{Co}(\text{acac})_3$; (c) TGA of SNW-1 and $\text{Co}(\text{acac})_3$; (d) FESEM of SNW-1

The porosity properties of SNW-1 nanoparticles were measured using N₂ physisorption at 77 K. In general, the SNW-1 sample demonstrates a property typical of microporous materials with type 1 isotherms, where high N₂ sorption was observed in a low-pressure region (**Figure 4-4(a)**). The computed surface areas and pore volumes are summarized in **Table 4-2**. O₂ and N₂ adsorption isotherms of SNW-1 were measured at 35°C (**Figure 4-4(b)**). Linear O₂ and N₂ isotherms were observed over the pressure range tested. Such a result indicates the absence of strong binding sites allowing favorable O₂ and N₂ adsorption in SNW-1. Nevertheless, owing to its large micropore volume (0.209 cm³/g) in SNW-1, the rapid diffusion was observed in the adsorption kinetics study for both O₂ and N₂. On the other hand, O₂ and N₂ adsorptions on Co(acac)₃ were observed to be negligible over the selected pressure range. This result implies that an appropriate medium (e.g. polymer matrix) is required to allow the selective transport of O₂ (against N₂) in the membrane [82].

Figure 4-4: (a) N₂ physisorption of SNW-1 at 77 K; (b) O₂ and N₂ adsorption of SNW-1 and Co(acac)₃ at 35 °C.

Table 4-2: Surface areas and pore volumes of SNW-1

Sample	S_{BET} (m^2/g) ^[a]	S_{LANG} (m^2/g) ^[a]	S_{micro} (m^2/g) ^[b]	V_{micro} (cm^3/g) ^[b]
SNW-1	653	893	442	0.209

[a] BET (S_{BET}) and Langmuir (S_{LANG}) surface area are obtained at $P/P_0 = 0.05$ -0.3.

[b] Micropore surface area (S_{micro}) and volume (V_{micro}) are determined using t -plot method under the pressure range of $P/P_0 = 0.4$ -0.6.

4.3.2 Fabrication of mixed-matrix membrane

Figure 4-5: (a) FTIR spectrum of ODPA-TMPDA; FESEM of (b) 2 wt% $\text{Co}(\text{acac})_3$; (c) 10 wt% SNW-1 and (d) 10 wt% SNW-1 + 2 wt% $\text{Co}(\text{acac})_3$ in ODPA-TMPDA

The synthesis of the ODPA-TMPDA polymer was first verified with the FTIR spectrum (**Figure 4-5 (a)**). The imide peaks' characteristics, which correspond to symmetric and asymmetric C=O stretching (1720 and 1770 cm^{-1}) in addition to C–N stretching (1360 cm^{-1}), clearly indicated the successful synthesis of the polymer. In general, the synthesis of ODPA-TMPDA is conducted by a two-step reaction; monomer condensation for the formation of polyamic acid followed by the chemical imidization process. Thus, the absence of a peak at 3500 cm^{-1} strongly indicated the absence of polyamic acid. The synthesized polymer is capable of dissolving in organic solvents (e.g., chloroform, dichloromethane, and dimethylformamide) and is thus easily processed into thin-dense membranes. Therefore, the mixed-matrix membrane containing $\text{Co}(\text{acac})_3$, SNW-1, and both fillers were fabricated using ODPA-TMPDA as the polymer matrix.

Figure 4-6: FT-IR spectrum of respective mixed-matrix membranes

The incorporation of fillers in MMMs, in general, does not alter the overall properties and thermal stabilities of the polymer matrix, as depicted in **Figure 4-6** and **Figure 4-7**. According to the FTIR analysis, the shift of peak to a lower wave number (C–N peak, from 3584 cm^{-1} to 3389 cm^{-1}) possibly indicates the presence of hydrogen bonding between SNW-1 (–NH group) and ODPDA-TMPDA (C=N group), although the interaction between cobalt complex and membrane is weak [85].

Figure 4-7: TGA curve of respective mixed-matrix membranes

Moreover, the respective membranes' morphologies were observed using FESEM (**Figure 4-5(b, c, d)**) and the presence of Co(acac)₃ was verified using EDS mapping (**Figure**

4-8). In general, the poor compatibility between filler and polymer typically observed for inorganic fillers such as zeolite was not observed in this study. This can be attributed to the presence of organic moieties in $\text{Co}(\text{acac})_3$ and SNW-1 that are fully organic in nature and allow better interaction with the polymer chains. In view of their high filler/polymer contact area, nano-sized particles are generally an effective method of enhancing filler-polymer compatibility when the nanoparticles are distributed homogenously [89, 96].

Figure 4-8: EDS Mapping of (a) 2 wt% Co(acac)₃; (b) 4 wt% Co(acac)₃ and (c) 10 wt% Co(acac)₃ in ODPA-TMPDA membrane (Note: 10 wt% Co(acac)₃ in ODPA-TMPDA membrane was characterized to verify the requirement of higher loading of Co(acac)₃ in ODPA-TMPDA so as to ensure that cobalt(Co) element can be detected.

4.3.3 Gas permeation analysis

Table 4-3: O₂ and N₂ permeability and O₂/N₂ selectivity of pure and MMMs measured at 1 bar upstream pressure at 35°C.

Legend	Membrane	O ₂ permeability (Barrer)	% O ₂ permeability enhancement	O ₂ /N ₂ selectivity	% O ₂ /N ₂ selectivity enhancement
0	ODPA-TMPDA	17.5 ± 1.7	-	4.62 ± 0.1	-
1	2 wt% Co(acac) ₃	14.7 ± 0.6	-15.9	5.00 ± 0.1	8.2
2	4 wt% Co(acac) ₃	12.3 ± 0.8	-29.7	5.09 ± 0.1	10.2
3	10 wt% SNW-1	20.3 ± 0.8	14.7	4.84 ± 0.4	4.9
4	15 wt% SNW-1	23.5 ± 0.5	34.2	4.38 ± 0.1	-5.2
5	10 wt% SNW-1 + 2 wt% Co(acac) ₃	23.6 ± 2.6	33.3	5.44 ± 1.1	18.0
6	15 wt% SNW-1 + 2 wt% Co(acac) ₃	25.2 ± 1.4	43.9	4.29 ± 0.1	-7.1

The overall transport properties of the O₂/N₂ binary mixture in the pure and MMMs prepared in this work were evaluated at 35 °C and total feed pressure (with a binary mixture; O₂/N₂= 21/79) of 1 bar. Based on the gas permeation data, the incorporation of SNW-1 alone made a feasible improvement to the overall O₂ permeability, with no significant change in O₂/N₂ selectivity. As shown in **Figure 4-4(b)**, there is no noticeable difference in adsorptions of O₂ and N₂ onto SNW-1, such that the incorporation of SNW-1 alone may be insufficient to improve the O₂/N₂ selectivity of the ODPA-TMPDA polymer. When the loading of SNW-1 increased from 10 to 15 wt%, the overall O₂/N₂ selectivity decreased at the expense of increased O₂ permeability (34%). This can presumably be attributed to an increased tendency of non-ideal defects, namely the defects that may be present on the interface between the filler and polymer, in addition to an agglomeration of SNW-1 nanoparticles in the polymer matrix. In contrast, Co(acac)₃ alone made

a feasible improvement to O_2/N_2 selectivity despite its low loading. This trend was consistent even as the amount of $Co(acac)_3$ present in the membrane increased (2 to 4 wt%). Nonetheless, a substantial decrease in O_2 permeability was observed (30%) at the expense of increasing O_2/N_2 selectivity (10%), consistent with results reported elsewhere. Thus, given the expected enhanced performance of MMMs when different fillers are used, the combined use of fillers may be feasible to tune such enhancements in a favorable direction.

This idea was validated by fabricating MMMs using a combination of two different fillers to further test O_2/N_2 separation. As demonstrated in **Table 4-3**, the combination of two fillers (10 wt% SNW-1 and 2 wt% $Co(acac)_3$) provided feasible improvements to O_2 permeability and O_2/N_2 selectivity, of 33% and 18%, respectively. Nonetheless, no further enhancement was observed when the loading of SNW-1 nanoparticles was increased. Thus, based on the gas permeation data, when the loading of SNW-1 and $Co(acac)_3$ is optimal, combined fillers feasibly improve the performance of mixed-matrix membrane in a favorable direction compared with a single filler. As depicted in **Figure 4-9**, the overall performance of the membrane moved toward the upper bound as both fillers were incorporated into the membrane. The comparison with literature data also revealed that this membrane showed better performance than mixed-matrix membranes reported thus far (**Table 4-4**). Furthermore, the fabrication of mixed-matrix membrane using a combination of two fillers can be conducted easily, without major hurdles.

Figure 4-9: Performance of membranes with respect to the Robeson upper bound for O_2/N_2 separation that was constructed in 2008 [95]. (a) Membranes developed in this work; (b) comparison with the literature data. The detailed O_2/N_2 separation properties are summarized in Table 4-4.

Table 4-4: Comparison of O₂/N₂ separation performance with results reported in the literature

Polymer	Fillers	Filler loading (wt%)	O ₂ permeability (Barrer)	O ₂ /N ₂ selectivity	Ref.
Polysulfone	-		1.6	4.5	[62]
	ZIF-8/Silicalite-1	8% ZIF-8; 8% silicalite-1	1.8	7	
	HKUST-1/Silicalite-1	8% HKUST-1; 8% silicalite-1	1.75	8	
Polysulfone	-		2.01	4.23	[25]
	HKUST-1	20	9.62	4.71	
Matrimid	-		2.72	5.97	
	HKUST-1	20	5.59	6.18	
Matrimid	-		1.28	5.56	[97]
	amino-grafted nano-silica particles	20	1.15	6.08	
Polyurethane	-		2.8	4.0	[9]
	UiO-66 (Zr)	28	6.1	5.5	
	MIL-101 (Cr)	28	9.7	4.2	
Polycarbonate	-		1.80	6.70	[98]
	Zeolite 4A	30	1.60	8.90	
PDMS-41 ¹	-		32.24	2.69	[99]
	CNT	10	39.81	2.23	
Polysulfone	-		1.5	5.9	[34]
	MIL-101 (Cr)	24	5.8	5.8	
Pu-PTH ²	-		8	2.5	[100]
	TiO ₂	20	10	2.5	
	SiO ₂	20	10	2.5	
ODPA-TMPDA	-		17.5	4.62	This work
	SNW-1/Co(acac) ₃	10% SNW-1; 2% Co(acac) ₃	25.8	5.56	

¹6FDA-6FpDA-PDMS copolymer²PMG-HDMI-MOCA (1:3:2): (polytetramethyleneglycol)-(Hexamethylenediisocyanate)-(4,4',-methylenebis(2-chloroaniline))

Subsequently, to comprehend why the O₂/N₂ separation performance was enhanced, the solubilities and diffusivities of O₂ and N₂ in the MMMs were calculated based on the permeabilities and gas sorption measurements. The O₂ and N₂ adsorption properties of the pure

polymer and mixed-matrix membrane were measured at 35°C, and the results were plotted (Figure 4-10). The solubility and the diffusivity of O₂ and N₂ are summarized in Table 4-5.

In general, incorporating Co(acac)₃ is a feasible means of improving the solubility of oxygen (4%), as compared with SNW-1 (-11%), in MMMs, without increasing N₂ solubility. This can be attributed to a favorable interaction between the Co^{III}-complex and O₂ (as compared with N₂) during the adsorption process, which leads to an increase in O₂/N₂ solubility selectivity (4%) [85]. However, SNW-1, freely accessible to O₂ and N₂ molecules, also led to an increase in overall diffusion selectivity (61%). Nonetheless, with Co(acac)₃ incorporated in the mixed-matrix membrane, both O₂ and N₂ diffusivity decreased drastically (-19% and -22%), indicating that the membranes containing Co(acac)₃ were densified with a reduction of the polymer's free volume for effective gas diffusion. This phenomenon arises from the interaction between the polymer and the Co^{III}, leading to a reduction of the inter-nodule distance in the polymer matrix as reported previously [101]. Apart from this, the presence of acetylacetonate (acac) ligand tends to create an additional obstacle for the gas diffusion as it fills the free volume of the polymer matrix. Combining the Co(acac)₃ and the SNW-1 yielded a synergistic effect with faster permeation and an improved sieving effect, giving rise to increases in both permeability and selectivity. Meanwhile, the mixed-matrix membrane containing both SNW-1 and Co(acac)₃ effectively enhanced both O₂ permeability and selectivity. Overall, owing to the synergistic effects mentioned above, the performance of the mixed-matrix membrane was improved in a desirable direction on the selectivity-permeability map.

Figure 4-10: O₂ and N₂ adsorption of ODPa-TMPDA polymer and mixed-matrix membrane

Table 4-5: Solubility and diffusivity data for ODPa-TMPDA and mixed-matrix membranes

Membrane	Density (g/cm ³) ¹	O ₂ solubility(mo l/m ³ .bar)	O ₂ diffusivity, x 10 ⁻¹¹ (m ² /s)	N ₂ solubility (mol/m ³ .bar)	N ₂ diffusivity, x 10 ⁻¹¹ (m ² /s)
ODPA-TMPDA	1.285	22.7	2.62	27.8	0.464
2 wt% Co(acac) ₃	1.292	23.7	2.11	27.8	0.360
10 wt% SNW-1	1.252	20.3	3.39	38.1	0.374
10 wt% SNW-1 + 2 wt% Co(acac) ₃	1.280	18.9	4.23	26.4	0.558

¹ The density of each membrane was measured using analytical balance, using ethanol as the auxiliary liquid.

4.4 Conclusion

The incorporation of both $\text{Co}(\text{acac})_3$ and SNW-1 into ODPA-TMPDA membranes is a feasible means of improving both O_2 permeability (48%) and O_2/N_2 selectivity (20%). The resulting performance is generally attractive compared with the addition of a single filler ($\text{Co}(\text{acac})_3$ or SNW-1) to ODPA-TMPDA, which is only capable of improving either O_2 permeability or O_2/N_2 selectivity. Based on the analysis of solubility and diffusivity, the overall O_2/N_2 diffusivity-selectivity improved substantially without significant sacrifices in O_2/N_2 solubility-selectivity. Thus, these results indicate that the combination of two fillers in MMMs can be considered a feasible approach to tuning the membrane performance in a favorable direction and thus an effective way to conduct O_2/N_2 separation in an energy-efficient manner.

5 TAILORING CO₂/CH₄ SEPARATION PROPERTIES OF MIXED-MATRIX MEMBRANES VIA COMBINED USE OF TWO- AND THREE-DIMENSIONAL METAL-ORGANIC FRAMEWORKS

5.1 Introduction

Polyimides account for the largest share in membrane-based natural gas sweetening and biogas upgrading due to its strong size sieving ability and exceptional chemical and mechanical stability [102]. Among the various members of this family, the versatile ODPa-TMPDA has been less exploited. To the best of my knowledge, Duan and co-workers were the first to report a gas separation membrane with ODPa-TMPDA as the polymer matrix. Here they employed CuBTC filler to improve the performance of membrane in CO₂/CH₄ separation and compared to Matrimid based membrane ODPa-TMPDA exhibited exceptional gas separation performance [103].

On the other hand, recently, the potential utility of ZIF-8 and nanosheets of CuBDC (ns-CuBDC; copper-1,4-benzene dicarboxylate) as a filler of mixed-matrix membranes has been reported. For instance, ZIF-8 nanocrystals possessing three-dimensional (3D) geometry were proved to be an effective filler to significantly enhance CO₂ permeability due to the presence of large pore cavities (ca. 11.6 Å) that allows the rapid transport of CO₂ [104, 105]. The presence of the narrow 6-membered ring window (ca. 3.40 Å) that connects to the large cavities allows an efficient molecular separation. It is noteworthy that the effective window size can be extended up to 4.12 Å due to the flexibility of the framework [106, 107]. In contrast, two-dimensional (2D) ns-CuBDC, which possess a high aspect ratio and a pore aperture (ca. 5.2 Å) that can preferentially transport CO₂ over CH₄, are of great interest because CH₄ is forced to adopt a tortuous path that results in a dramatic increase in its diffusion path in the membrane, which

leads to improved CO₂/CH₄ selectivity [84, 108]. More importantly, such a 2D filler enhances CO₂/CH₄ selectivity even with a small filler loading (e.g., 2 wt%), whereas the incorporation of a 3D MOF typically requires a high filler loading (e.g., 10 wt% or above) to attain a clear enhancement in performance. However, studies conducted to date have tended to investigate the properties of mixed-matrix membranes containing only one type of MOF (2D or 3D), which can mostly improve either CO₂ permeability or CO₂/CH₄ selectivity. In such cases, it may be difficult to tailor the direction of performance enhancement in a specific desired direction on the selectivity-permeability map. For example, the enhancement in CO₂/CH₄ selectivity by incorporating 2D filler is typically accompanied by a sacrifice in the permeability [33, 34]. In contrast, highly porous 3D fillers that can effectively improve gas permeability often show the limited effect on CO₂/CH₄ selectivity [10, 14, 27].

Therefore, in this work, the tailored enhancement of CO₂/CH₄ separation performance of a mixed-matrix membrane via the combined use of 2D and 3D MOF fillers is demonstrated. ODPA-TMPDA (ODPA=4,4'-oxydiphthalic anhydride; TMPDA=2,4,6-trimethyl-*m*-phenylenediamine) polyimide was selected as the polymer matrix in this study as it is generally more permeable than conventional commercial glassy polymers (e.g., Matrimid[®], polysulfone, Ultem[®]), and it can be readily synthesized with no further purification of monomers, which is highly desirable for potential large-scale production [84, 91, 109]. Although, the incorporation of two different fillers in a single polymer matrix is not new, the idea of incorporating metal organic frameworks with two different dimensions bring a new opportunity for membrane design as it has not been employed widely before. This research introduces a stepwise procedure for fabricating a MMM design with fragile 2D MOFs with robust 3D MOFs. In addition, the effects

of 2D and 3D fillers on the solubility and diffusivity of gases in the mixed-matrix membrane are also studied to understand the mechanism behind the enhancement in performance.

5.2 Experimental

5.2.1 Synthesis of CuBDC nanosheets (ns-CuBDC)

ns-CuBDC were synthesized using the three-layer method as described elsewhere using a glass tube with an inner diameter of 13 mm [84, 108]. The bottom layer (3 g of H₂BDC dissolved in 2 ml DMF and 1 ml CH₃CN, middle layer (2 ml, mixture of DMF and CH₃CN in a 1:1 ratio), and top layer (3 g of Cu(NO₃)₂·3H₂O dissolved in 1 ml of DMF and 2 ml of CH₃CN) were cautiously poured to the tube to avoid premature mixing. The tube was then placed in a convection oven at 40 °C for 24 hr under a static condition. The blue precipitate was collected by repetitive centrifugation-redispersion cycles with DMF (3 times) and CHCl₃ (3 times). The resulting material was left suspended in DCM for the subsequent characterizations and composite membrane fabrication.

5.2.2 Synthesis of ZIF-8

ZIF-8 nanocrystals were synthesized according to the method reported in previous work [110]. In two separate storage flasks, 1.47 g of Zn(NO₃)₂·6H₂O and 3.24 g of Hmim were dissolved in 100 ml methanol. Once the solutions were completely dissolved, the solution containing Zn(NO₃)₂·6H₂O was rapidly added to the solution containing Hmim under strong agitation. The resulting solution was left for 1 hour before separating the ZIF-8 nanoparticles from the mother liquid and performing repetitive centrifugation-redispersion cycles with fresh methanol. The

ZIF-8 nanocrystals were eventually dried in a vacuum oven at 60 °C for subsequent characterizations and composite membrane fabrication.

5.2.3 Membrane fabrication

All membranes were fabricated using the solution casting method. The pure ODPA-TMPDA membrane was fabricated from a dope solution made by dissolving 0.5 g of polymer into 4 g of CHCl_3 . However, to make the dope solutions for the composite membranes, a specified amount of the (ZIF-8 [10 wt%] and/or ns-CuBDC [2 wt%]) was dispersed into 4 g of CHCl_3 with the aid of sonication. Next, 0.25 g of polymer was added to the resulting suspensions, which were then gently shaken with a laboratory shaker at room temperature for about 3–4 hours. Subsequently, 0.25 g polymer was again added, and the resulting suspension was shaken continuously for 1 day. Thereafter, the dope solution was cast on a glass plate with a casting knife in a glove bag that was filled with CHCl_3 vapor, and the nascent membranes were left undisturbed at room temperature for 1 day. The resulting membranes were annealed in a vacuum oven at 160°C for 1 day prior to gas permeation testing.

5.3 Results and Discussion

5.3.1 Synthesis of ns-CuBDC and ZIF-8

The successful synthesis of ns-CuBDC and ZIF-8 was verified by identification with PXRD as shown in **Figure 5-1(a)**. The patterns obtained from the samples matched well with the reference pattern reported in the literature. In particular, a peak broadening was observed for the ZIF-8 nanocrystals, indicating the formation of smaller crystallites, and was further verified by visual

observation. As shown in the FESEM image (**Figure 5-2(a)**), the average particle size was estimated to be about 50 nm. However, the ns-CuBDC possess only two characteristic peaks at 17° and 34° that correspond to the $(\bar{2}01)$ and $(\bar{4}02)$ planes, respectively. Through the analysis of both the FESEM (**Figure 5-2(b)**) and AFM images (**Figure 5-2(c)**), the lateral dimension and thickness were measured to be around 1–7 μm and 20 nm, respectively, which translates into a high aspect ratio of 50–350. Besides, the investigation of thermal stability using TGA analysis (**Figure 5-1(a)**) indicated that both ZIF-8 and CuBDC demonstrate reasonable stability up to 300 $^\circ\text{C}$ and 600 $^\circ\text{C}$, respectively.

Figure 5-1: (a) Powder XRD pattern and (b) TGA of ZIF-8 and ns-CuBDC

Figure 5-2: Morphological analysis of MOFs used. (a) and (b) FESEM images of ZIF-8 and ns-CuBDC, respectively; (c) AFM image of ns-CuBDC (red line indicates 1 μm); (d) Height profile for ns-CuBDC

Besides, N_2 physisorption at 77 K was conducted for ZIF-8 and ns-CuBDC to identify the porosity properties of these MOFs. In general, the sorption properties were comparable with the results reported in the literature. As indicated in **Figure 5-3(a)**, both ZIF-8 and ns-CuBDC show typical behavior of a Type I isotherm due to their high N_2 sorption at low partial pressure. The surface areas and pore volumes determined based on the analysis of N_2 physisorption data are summarized in **Table 5-1**. Following this, the CO_2 and CH_4 adsorption isotherms of ZIF-8 and ns-CuBDC were measured at 25 $^\circ\text{C}$ (**Figure 5-3(b)**). As reported elsewhere, the CO_2 adsorption of ns-CuBDC was measured to be higher than that of ZIF-8 despite the higher micropore volume and surface area of ZIF-8 versus ns-CuBDC. However, both MOFs showed a linear CO_2

isotherm in the pressure range tested, indicating that there are no strong binding sites that can slow down the diffusion of CO₂. As expected, CH₄ uptakes were measured to be far lower than those of CO₂ for both MOFs. However, CO₂/CH₄ sorption selectivity is not that impressive as compared to top-notch MOFs developed for CO₂ capture such as the MOF-74 series and amine-appended MOFs [111-114].

Figure 5-3: (a) N₂ adsorption isotherms (adsorption and desorption points are indicated by filled and open symbols, respectively) at 77K and (b) pure CO₂ and CH₄ adsorption isotherms at 25 °C for ns-CuBDC and ZIF-8.

Table 5-1: Surface areas and pore volumes of ZIF-8 and ns-CuBDC calculated from the N₂physisorption isotherm at 77 K

Sample	$S_{\text{BET}}^{[a]}$ (m ² /g)	$S_{\text{micro}}^{[b]}$ (m ² /g)	$V_{\text{micro}}^{[b]}$ (m ³ /g)
ZIF-8	1147	1131	0.608
ns-CuBDC	126	49.3	0.0250

Note: [a] BET (S_{BET}) is calculated based on the pressure range of $P/P^0 = 0.05-0.3$; [b] Micropore area (S_{micro}) and volume (V_{micro}) are obtained using the t -plot method at a pressure range of $P/P^0 = 0.4-0.6$.

5.3.2 Fabrication of mixed-matrix membrane

The successful synthesis of the ODPA-TMPDA polymer (as explained in **Chapter 4**) was first confirmed via the FTIR spectrum as shown in **Figure 5-4**. The characteristic imide peaks (1719 cm^{-1} and 1774 cm^{-1}), which correspond to the symmetric and asymmetric C=O stretching, were visible together with the peak associated with C–N stretching at 1358 cm^{-1} . The successful imidization was verified by the disappearance of a peak at 3500 cm^{-1} , which is associated with unreacted polyamic acids. Note that the synthesis of the ODPA-TMPDA polymer comprises two steps, namely, 1) condensation reaction of the monomers to form polyamic acid and 2) chemical imidization of the polyamic acid. Besides, the elemental composition of the ODPA-TMPDA polymer as measured by an elemental analysis matched the theoretical calculation well as shown in **Table 5-2**. The resulting polymer dissolved well in the various organic solvents including DCM, chloroform, and DMF and thus could be easily processed into a film form.

Figure 5-4: FTIR spectra of the ODPA-TMPDA polymer

Table 5-2: Elemental analysis of ODPA-TMPDA polymer

Element	Experimental	Theoretical ^[a]
% C	67.37	66.65
% H	3.78	3.87
% N	6.60	6.79

Note: [a] Based on the ratio of elements in the repeating unit of the polymer

With the successful synthesis of the ODPA-TMPDA polymer, mixed-matrix membranes containing ZIF-8, ns-CuBDC and both fillers were fabricated, and the resulting morphologies were observed by FESEM (**Figure 5-5**). The presence of filler materials was also verified using EDS mapping data (**Figure 5-6**). In general, *sieve-in-a-cage* morphology, which is typically observed when the compatibility between the filler and the polymer is poor, was not observed in this study. This is attributed to the presence of organic moieties in ZIF-8 and ns-CuBDC that allow preferential interaction with the polymer chains in ODPA-TMPDA. It was already shown that downsizing MOF crystals to nanocrystals or nanosheets to increase the polymer/filler contact area is an effective method of fabricating high-quality mixed-matrix membranes in which the fillers are uniformly distributed without forming defects [10, 28].

Figure 5-5: FESEM images of mixed-matrix membranes containing (a) 10 wt% ZIF-8 (b) 2 wt% ns-CuBDC, and (c) 10 wt% ZIF-8 + 2 wt% ns-CuBDC

(a)

Cu Lα1_2

Zn Lα1_2

(b)

Zn Lα1_2

Cu Lα1_2

Figure 5-6: EDS mapping of mixed-matrix membranes containing (a) 2wt% ns-CuBDC, (b) 10wt% ZIF-8, and (c) 2wt% ns-CuBDC+ 10wt% ZIF-8.

5.3.3 Gas permeation results

The transport properties of an equimolar mixture of CO₂/CH₄ in the pure and mixed-matrix membranes prepared in this work were evaluated at 25 °C and 1 bar of total upstream pressure (**Table 5-3**). It was observed that the incorporation of ZIF-8 alone can increase CO₂ permeability by about 30% as compared with that of pure polymer with no significant change in selectivity. Such a result is consistent with the data reported in the literature in which the utilization of ZIF-8 is only capable of increasing the CO₂ permeability and not CO₂/CH₄ selectivity [115-117], mainly because the CO₂/CH₄ selectivity of ZIF-8 is not sufficiently high to increase the selectivity of ODPA-TMPDA which is already as high as 36. Besides, as the loading increased, the CO₂ permeability gradually increased. However, the decrease in CO₂/CH₄ selectivity was observed when the loading was greater than 20 wt%, presumably due to more prominent non-

ideal effects such as defects at filler/polymer interface caused by the increase in filler/polymer interface area and/or the agglomeration of fillers. On the other hand, the utilization of ns-CuBDC alone could increase CO₂/CH₄ selectivity (by about 20%) as compared to pure polymeric membrane although the filler loading was only 2 wt%. However, such enhancement derived from ns-CuBDC filler also caused an undesirable result. A decrease in CO₂ permeability (c.a. 10 %) was observed, which is consistent with results reported elsewhere [108, 118]. The CO₂ permeability further decreased when the loading of ns-CuBDC increased to 4 and 6 wt%. Nevertheless, as two fillers can improve the performance of the membrane in totally different ways, the combined use of these fillers may allow us to tweak the direction of performance enhancement in a desirable direction.

Table 5-3: Gas permeability and CO₂/CH₄ selectivity of pure and mixed-matrix membranes measured at 1 bar upstream pressure and 25 °C

Legend	Membrane	CO ₂ Permeability (Barrer)	% CO ₂ permeability enhancement	CO ₂ /CH ₄ selectivity	% CO ₂ /CH ₄ selectivity enhancement
0	Pure ODPA-TMPDA	112 ± 3	-	36 ± 1	-
1	2 wt% ns-CuBDC	99 ± 7	-11.6	43 ± 4	19.4
2	4 wt% ns-CuBDC	95 ± 3	-15.2	40 ± 2	11.1
3	6 wt% ns-CuBDC	91 ± 1	-18.8	39 ± 2	8.3
4	10 wt% ZIF-8	144 ± 9	28.6	37 ± 4	2.8
5	20 wt% ZIF-8	246 ± 21	119.6	27 ± 3	-25.0
6	30 wt% ZIF-8	316 ± 9	182.1	33 ± 7	-8.3
7	10 wt% ZIF-8 + 2 wt% ns-CuBDC	131 ± 6	16.6	47 ± 3	30.5
8	20 wt% ZIF-8 + 2 wt% ns-CuBDC	172 ± 22	31.3	42 ± 5	16.7
9	10 wt% ZIF-8 + 4 wt% ns-CuBDC	115 ± 2	2.7	41 ± 2	13.9

To validate this idea, we fabricated mixed-matrix membranes containing both fillers and measured the CO₂/CH₄ permeation property. As depicted in **Table 5-3**, the combined use of these two fillers together (10 wt% ZIF-8 and 2 wt% ns-CuBDC) could increase both CO₂ permeability and CO₂/CH₄ selectivity by 17% and 31%, respectively. The higher permeability was also successfully realized when the loading of ZIF-8 increased from 10 wt% to 20 wt% with the fixed loading of ns-CuBDC at 2 wt%. However, no positive enhancement was observed when the loading of ns-CuBDC increased to 4 wt%. I also tested membranes comprising two different 3D fillers (ZIF-8 and HKUST-1) and 2D fillers (graphene oxide and ns-CuBDC) as well (**Table 5-4**).

Table 5-4: Gas permeability and CO₂/CH₄ selectivity of the polymeric membrane and mixed-matrix membranes at 1 bar upstream pressure and 25°C with the equimolar CO₂/CH₄ mixture. Graphene oxide (GO) was purchased from Sigma-Aldrich. CuBTC nanocrystal was synthesized using the method in our previous work [119].

Membrane	CO ₂ permeability (Barrer)	% CO ₂ permeability enhancement	CO ₂ /CH ₄ selectivity	% CO ₂ /CH ₄ selectivity enhancement
Pure ODPA-TMPDA	112	-	36	-
10 wt% ZIF-8	144	29	37	3
10 wt % CuBTC	133	19	39	8
10 wt% ZIF-8 + 10 wt% CuBTC	136	21	40	11
2 wt% ns-CuBDC	99	-12	43	19
2 wt% GO	85	-24	52	44
2 wt% ns-CuBDC + 2 wt% GO	91	-19	71	97
10 wt% ZIF-8 + 2 wt% ns-CuBDC	131	17	47	31

It turned out that the separation performance of membranes comprising both ZIF-8 and ns-CuBDC are more desirable and more attractive than performance realized by incorporating single filler alone or two fillers possessing a similar geometry in membranes. As shown in **Figure 5-7**, the performance of the membrane moves toward the upper bound limit when both fillers are incorporated together. Furthermore, it is noteworthy that this approach is readily applicable to typical mixed-matrix membrane fabrication procedures without any resistance.

Figure 5-7: Performance of pure polymeric membrane and mixed-matrix membrane with respect to the Robeson upper bound established in 2008. The labels indicated in the figure correspond to the membranes in **Table 5-3**.

5.3.4 Gas adsorption properties in mixed-matrix membrane

Figure 5-8: (a) CO₂ and (b) CH₄ gas adsorption isotherms for ODPA-TMPDA and mixed-matrix membrane measured at 25 °C

Subsequently, to understand the mechanism behind the improved CO₂/CH₄ separation performance, the diffusivity and solubility of CO₂ and CH₄ in the mixed-matrix membrane were quantified. To do this, the CO₂ and CH₄ adsorption properties of the pure ODPA-TMPDA and mixed-matrix membrane were measured at 25 °C, and the results are shown in **Figure 5-8**. The solubility and the diffusivity of CO₂ and CH₄ that were computed are also shown in **Table 5-5**. In general, both fillers could improve the solubility selectivity as the MOFs used in this work can selectively take up CO₂ over CH₄ as depicted in **Figure 5-3(b)**. Thus, the major difference between the two fillers can be found in how they changed the diffusivity of CO₂ and CH₄ in the mixed-matrix membrane. The effective diffusivity of CO₂ in the ns-CuBDC mixed-matrix membrane decreased substantially compared to that in the neat polymeric membrane, indicating that the 2D filler significantly inhibited the CO₂ within the membrane resulting in a decrease in CO₂ permeability of the ns-CuBDC mixed-matrix membranes. However, the CH₄ diffusivity decreased even more than that of the CO₂, which resulted in an increase in the CO₂/CH₄ diffusion

selectivity. In contrast, an increase in CO₂ diffusivity was clearly observed upon the incorporation of ZIF-8 in the membrane, which reveals that ZIF-8 can improve CO₂ permeability by improving the diffusivity. Besides, the incorporation of both ZIF-8 and ns-CuBDC does not significantly sacrifice CO₂ solubility as compared to the mixed-matrix membrane containing ZIF-8 alone. Hence, by incorporating the two fillers together, the drawback of the 2D filler, the sacrifice of CO₂ diffusivity, can be easily overcome as ZIF-8 can increase CO₂ diffusivity to a greater extent. Indeed, as shown in **Table 5-5**, the mixed-matrix membrane containing both fillers exhibited a higher CO₂ diffusivity than that of the pure polymer membrane. Meanwhile, the mixed-matrix membrane containing the two fillers together incorporated the benefit of the 2D filler, which is the effective enhancement of CO₂/CH₄ selectivity. Overall, owing to such synergistic effects of the 2D and 3D fillers mentioned above, the performance of the mixed-matrix membrane was improved in a desirable direction on the selectivity-permeability map (**Figure 5-7**).

Table 5-5: Solubility and diffusivity data for ODPA-TMPDA and mixed-matrix membranes

Membrane	Density (g/cm ³)	CO ₂ adsorption (mmol/g) ^[a]	CO ₂ solubility (mol/m ³ - bar)	CO ₂ diffusivity, ×10 ⁻¹² (m ² /s)	CH ₄ adsorption (mmol/g) ^[a]	CH ₄ solubility (mol/m ³ - bar)	CH ₄ diffusivity, ×10 ⁻¹³ (m ² /s)	Solubility selectivity	Diffusivity selectivity
Pure ODPA- TMPDA	1.35	0.671	1340	1.29	0.0712	273	1.77	4.9	7.3
2 wt% ns-CuBDC	1.47	0.595	1337	1.15	0.0562	248	1.45	5.4	7.9
10 wt% ZIF-8	1.25	0.610	1131	1.98	0.05473	202	3.00	5.6	6.6
10 wt% ZIF-8 + 2 wt% ns-CuBDC	1.23	0.586	1099	1.84	0.0436	171	2.52	6.4	7.3

Note: [a] CO₂ and CH₄ adsorption is obtained based on the pressure at 0.5 bar

5.4 Conclusions

In conclusion, both CO₂ permeability and CO₂/CH₄ selectivity in mixed-matrix membranes can be improved by adding both ns-CuBDC and ZIF-8 into ODPA-TMPDA membranes, such that the resulting membrane becomes more attractive for practical applications. The addition of both fillers enhances the overall performance in a more favorable direction as compared to the incorporation of only one type of filler (ns-CuBDC or ZIF-8), which are only capable of improving either CO₂/CH₄ selectivity or CO₂ permeability. Detailed analysis of the diffusivity and solubility revealed that the drawback of individual filler could be overcome by the positive effect of its counterpart. These results suggest that the combined use of 2D and 3D fillers is a facile approach to enhance the performance of mixed-matrix membranes.

6 GENERAL CONCLUSIONS AND FUTURE PROSPECTS

6.1 General Conclusions

I have demonstrated new MMM designs having three components which are prepared by incorporating a filler and a compatibilizer or two different fillers into a polymeric matrix (polyimide) homogeneously. To interpret the role of using three components, I benchmarked ternary-component designs with dual-component membranes prepared by using a filler or compatibilizer with the same matrix, for their potential application in air separation or biogas separation. Based on the key findings of the thesis, the following conclusions can be made:

- 1) Air separation performance of commercially available Matrimid polyimide is economically and technically feasible with the use of CoPc complex and Pluronic F-127 block copolymer. The CoPc-Matrimid membrane exhibited poor compatibility whereas the Pluronic F127-Matrimid membrane exhibited restricted gas diffusion paths. Thus, the mutual combination of the three components aids in overcoming the deficiencies of dual-component membranes.
- 2) Less exploited (and non-commercialized) ODPA-TMPDA exhibits better O_2/N_2 separation performance than the Matrimid as a membrane material. And, ODPA-TMPDA-based membranes can further be optimized by incorporating cobalt (III) acetylacetonate and SNW-1 covalent organic framework very effectively. Thus, I

believe, ODPA-TMPDA might find practical use in the future as long as its industrial-scale production is realized.

- 3) ODPA-TMPDA also demonstrated an application potential for biogas separation. Due to the difference in the behavior of gas mixture in the membrane different optimization has to be considered for CO₂/CH₄ separation. Incorporation of 3D metal-organic frameworks improved CO₂ permeability, whereas the incorporation of 2D MOFs improved membrane selectivity. Thus, the synergistic incorporation of 3D and 2D MOFs into the ODPA-TMPDA polymer matrix resulted in a membrane that could overcome the trade-off relationship.
- 4) The problems associated with the commonly used mono-filler polymer MMM design can be overcome by carefully choosing the third component. The successful formation of these discrete ternary membranes emphasizes an easy and effective way to develop gas separation membranes without sophisticated material development or alteration.

6.2 Future Prospects

The current thesis work has verified the promise of using more than one filler in MMMs. Partially based on our preliminary studies and ongoing works, the following experimental and theoretical research topics might be of great relevance as a continuation of the existing thesis and can make a considerable impact in the field.

1) Optimization of the operating conditions for developed membranes.

As all the experiments have been tested at 1 bar with 35 °C and 25°C for O₂/N₂ and CO₂/CH₄ separation respectively, it is recommended to check for the optimal operating conditions for each membrane developed by giving special attention to the conditions in a potential practical application.

For example, high pressure favors high gas permeability through membranes. However, it may arouse plasticization especially in CO₂/CH₄ separation membrane [120]. On the other hand, in O₂/N₂ separation most of the oxygen carriers exhibits high O₂ solubility at low temperatures [121]. Therefore, these matters should be addressed carefully in future operations.

2) Development of a simulation database to identify potential ternary components that can help to overcome some of the common challenges associated with dual MMM.

Some of the common challenges associated with dual MMM are; compatibility/interaction between fillers when in a polymer matrix, difficulty in identifying a polymer matrix that is suitable to both fillers and identifying solvents suitable for the polymer and fillers. Therefore, a comprehensive simulation database is needed to minimize the research time and optimize the membrane performance. On the other hand, another comprehensive database can be developed to identify problems associated with single filler membranes. Then, simulations can be performed to identify a suitable ternary component that can solve the identified problems and enhance the membrane performance.

For example, although zeolite-based MMMs are being studied for decades as fillers for MMMs, their incompatibility with the polymer matrix poses the main challenge. Thus, simulations can be done to identify some of the potential ternary components that can help to enhance the compatibility with some popular polymer matrixes.

3) Identify some already developed dual-component MMM design to further improve by incorporating a suitable third component.

Many interesting work reported, commercially appealing membrane designs recently. For example, Jeazet and co-workers developed a dual-component MMM with moisture stable MIL 101(Cr) in the polysulfone matrix. Their membrane exhibited around a 4-fold increase in O₂ permeability but selectivity was not improved [34]. As such, if that work is extended by the inclusion of a suitable ternary component that enhances the selectivity too, we believe superior results can be obtained. (Our laboratory is currently planning to conduct such a work in near future). On the other hand, an already developed membrane can be altered by incorporating a suitable third component to suit another completely different application. This kind of strategy might be interesting from an industrial perspective (with its technical simplicity and economic viability). I hope academic researchers will invest more time and energy to further explore this exciting field of research.

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