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Citation: Yu, Guangli, Li, Yanqin, Wang, Ziyang, Liu, Terence, Zhu, Guangshan and Zou, Xiaoqin (2019) Mixed matrix membranes derived from nanoscale porous organic frameworks for permeable and selective CO₂ separation. Journal of Membrane Science, 591. p. 117343. ISSN 0376-7388

Published by: Elsevier

URL: <https://doi.org/10.1016/j.memsci.2019.117343>
<<https://doi.org/10.1016/j.memsci.2019.117343>>

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Mixed matrix membranes derived from nanoscale porous organic frameworks for permeable and selective CO₂ separation

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Graphical Abstract

Highlights

■ A new porous organic framework of MAPDA was synthesized with particle size in nanoscale.

■ Continuous mixed matrix membranes were successfully fabricated by blending nanosized porous organic frameworks of MAPDA and PIM-1 polymer.

■ Enhanced CO₂ permeability and improved CO₂/N₂ selectivity were realized by selective and rapid transport of CO₂ molecules through pores of the MAPDA filler.

Abstract:

Membrane separation has great potential for carbon dioxide capture. We have been developing porous organic frameworks (POFs) as a new class of nanofillers for mixed matrix membranes fabrication. A triangle monomer of melamine (MA) reacts with another linear monomer of 1, 4-piperazinedicarboxaldehyde (PDA) in a microwave system to form the POF material (designated as MAPDA). As-synthesized MAPDA possesses an open framework featured with high surface area of $548.3 \text{ m}^2 \text{ g}^{-1}$ and a large pore of $\sim 1.0 \text{ nm}$. SEM shows that MAPDA particles are in size of $\sim 42 \text{ nm}$, and adsorption measurement reveals that MAPDA is favorable for adsorbing CO_2 with an uptake of $47.0 \text{ cm}^3 \text{ g}^{-1}$ at 298 K and 101 kPa . Mixed matrix membranes of MAPDA/PIM-1 with different MAPDA loadings (0-20 wt%) are produced by blending nanofillers of MAPDA and soluble matrices of PIM-1. Single gas permeations demonstrate that CO_2 permeability is increased dramatically from 3694.5 to 7861.9 Barrer, meanwhile the CO_2/N_2 selectivity is enhanced from 18.9 to 23.9 for pure PIM-1 and for a representative membrane of MAPDA/PIM-1 with 15 wt% MAPDA. High porosity and molecular affinity make the predominant contribution to the enhancements of CO_2 permeability and CO_2/N_2 selectivity. MAPDA/PIM-1 membranes are also very selective for capturing CO_2 from gas mixtures of $50\text{CO}_2:50\text{N}_2$ and $15\text{CO}_2:85\text{N}_2$ with separation performances exceeding the latest upper bound. The good separation property and the high stability of MAPDA/PIM-1 have shed a light on next-generation membrane for CO_2 separation development.

Keywords

porous organic framework, mixed matrix membrane, CO_2 separation, nanoparticle, permeability and selectivity.

1 **Introduction:**

2 Carbon dioxide (CO₂) as the major component of greenhouse gas has drastically
3 altered global climate. Advanced CO₂ capture and separation technologies are in
4 urgent demand to overcome such serious environmental issue [1]. Several
5 technologies such as cryogenic distillation, chemical looping, solvent absorption,
6 pressure swing adsorption, and membrane process have been developed for CO₂
7 separation [2]. Among these, membrane process is widely recognized as the most
8 promising technology owing to its low energy consumption and high separation
9 efficiency [3]. Generally, membranes can be made in homogeneous and
10 heterogeneous structures. Mixed matrix membranes (MMMs) as a representative of
11 heterogeneously structured membranes have attracted much attention from
12 researchers because MMMs combine individual merits of matrices and fillers [4].
13 Polymers have been widely used as matrices and microporous materials are a class of
14 major fillers for such membrane fabrication. In particular, those microporous
15 materials with ordered porous structures attracted increasing attention in the
16 fabrication of MMMs in recent years [4], because of its porous nature which offers
17 great benefits in tailoring membrane separation property.

18 According to chemical component, ordered microporous materials can be mainly
19 divided into three catalogues as zeolites [5], metal organic frameworks [6-10], and
20 porous organic frameworks (POFs) [11-13]. POFs consist of pure organic components
21 and these components are linked with each other *via* covalent bonds to form open and
22 extended networks [11]. The similarity between polymer and POF in organic
23 chemistry makes POFs an ideal candidate for filler materials. In addition, POFs
24 possess interesting physicochemical properties such as diverse structures, high surface
25 areas, tunable pore sizes, preeminent thermal/chemical stabilities and
26 multi-functionalities [11]. These stated characteristics are expected to contribute
27 largely to gas separation when POFs are reinforced into membranes [3]. Some POFs
28 have been developed in recent five years as the fillers for MMM application [14-36],
29 showing that this research area is in an early stage. Thus, this research needs our
30 further and extensive studies because it has the potential of growth in the membrane

community thanks to the aforementioned unique properties of POFs. This work is to create new MMMs based on POFs from materials perspective and to examine CO₂ separation properties.

Efficient membrane CO₂ separation requires fast and selective permeation for CO₂ over other gas species through crack-free mixed matrix membranes. In this regard, an open-structured POF of MAPDA (Scheme 1) is designed and synthesized as the filler. A triangle monomer of melamine (MA) is polymerized with another linear monomer of 1, 4-piperazinedicarboxaldehyde (PDA) through Schiff base reaction. The built network is anticipated to have a pore diameter of around 1.4 nm and nitrogen-rich entities, which are beneficial for both transport and affinity of CO₂ gas. Small particles particularly for nanoscale particles play a prerequisite role in making crack-free membranes. For reducing the particle size, microwave synthesis is adopted and MAPDA nanoparticles are rapidly formed after microwave heating the precursor containing 1, 4-piperazinedicarboxaldehyde and melamine (5 MPa, 2 h). PIM-1 is selected as the polymer matrix upon the consideration of its easy processability, and the relatively high porosity could additionally contribute to gas permeability. The MMM of MAPDA/PIM-1 is facilely prepared by mixing MAPDA nanofillers and PIM-1 matrix.

Scheme 1. Synthesis route and the most likely structure for MAPDA POF using MA and PDA monomers in a microwave system (the pore size is estimated from materials studio and subtracted van der Waals radii of wall-lined atoms).

Experimental:

Chemicals

Melamine ($\text{C}_3\text{H}_6\text{N}_6$, Aladdin, 99%), 1, 4-piperazinedicarboxaldehyde ($\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2$, Alfa Aesar, 98%), 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, Alfa Aesar, 98%), 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN, Alfa Aesar, 98%), anhydrous potassium carbonate (K_2CO_3 , Sigma-Aldrich, 99%) and dimethyl sulfoxide ($\text{C}_2\text{H}_6\text{SO}$, Aladdin, 99.5%) were purchased from corresponding commercial companies. Solvents of methanol (CH_3OH), acetone (CH_3COCH_3), dichloromethane (CH_2Cl_2), chloroform (CHCl_3), *N, N*-dimethylformamide (DMF) and tetrahydrofuran (THF) in analytical grade (AR) were obtained from Beijing Chemical Works and used without further treatment.

Synthesis of MAPDA

MAPDA (also called CIN-1) was synthesized *via* a modified protocol [37]. Specifically, 1, 4-piperazinedicarboxaldehyde (140.8 mg, 1.0 mmol, abbreviated as PDA) and melamine (83.3 mg, 0.7 mmol, abbreviated as MA) were dissolved in 10 mL of dimethyl sulfoxide (DMSO) under stirring for 30 minutes. The resulted precursor was transferred to a Teflon-lined microwave reactor (XT-9900A Intelligent Microwave Digestion System, Xintuo Analytical Instruments Co., LTD, Shanghai, China) and heated at a constant pressure of 5 MPa for 2 h (pressure induced temperature of $\sim 180^\circ\text{C}$). The powder was obtained by filtration, and subsequently washed with THF, acetone and dichloromethane under ambient condition. The product was dried overnight at 100°C under vacuum, and the final POF material was designated as MAPDA.

Synthesis of PIM-1

Prior to PIM-1 synthesis, TTSBI was purified by recrystallization from methanol, while another monomer TFTPN was sublimated under vacuum. PIM-1 was prepared by consulting the literature procedure [38]. Briefly, a mixture with certain amount of anhydrous K_2CO_3 (6.24 g), TTSBI (7.68 g) and TFTPN (4.53 g) was added in 150 mL anhydrous DMF under an inert environment of N_2 . After magnetically stirring at 65°C for 72 h, a bright yellow precipitate was collected by filtration and further purified by Soxhlet extraction in deionized water to remove excess inorganic catalyst. Following this, the precipitate was refined in a three-cycle process by dissolving the

crude polymer in chloroform and re-precipitation in methanol for removing unreacted monomers. The final product was dried in a vacuum oven at 100 °C for 12 h to give PIM-1, and then kept in a capped vial for other analyses. Molecular weight of $M_w=144,271$ Da and PDI=2.0 were confirmed for the purified PIM-1 polymer using gel permeation chromatography (GPC).

Fabrication of MAPDA/PIM-1 mixed matrix membranes

All membranes were fabricated by the solution-casting technique. A solution with 6.25 wt% PIM-1 was prepared beforehand by dissolving 0.8 g PIM-1 polymer in 8.0 mL chloroform (CHCl_3). Pristine PIM-1 membrane was casted from a dilute solution (2.0 wt% PIM-1) using CHCl_3 as the diluent. For MAPDA/PIM-1 membranes, an extra step was needed in which pre-calculated amount of MAPDA powder was homogeneously dispersed in 5.0 mL of CHCl_3 via ultrasonication. PIM-1 and MAPDA were blended through dropping MAPDA suspension into PIM-1 solution. The total concentration of MAPDA and PIM-1 in CHCl_3 was maintained at 2.0 wt% in all cases. The resultant precursor was kept under magnetically stirring overnight and sonicated for another 1 h to remove any remaining air bubbles. The homogeneous precursor was then poured onto a clean petri dish. After slow evaporation of the solvent for 12 h under ambient atmosphere and room temperature, the membrane was peeled off successively from the petri dish. MAPDA loadings were varied from 0 wt% to 20 wt% based on the total weights of MAPDA and PIM-1 (i.e. MAPDA/PIM-1-15 membrane consists of 15 wt% MAPDA particles and 85 wt% PIM-1 polymer.).

Characterizations of MAPDA and membranes

FTIR spectra (KBr) were garnered from a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer. Solid-state NMR spectra were measured on a Bruker Avance III model 400 MHz solid-state nuclear magnetic resonance (NMR) spectrometer at a magic angle spinning (MAS) rate of 5 kHz. Thermogravimetric analysis (TGA) was performed in N_2 flow from 303 K to 1073 K at a heating rate of 10 °C min^{-1} (Mettler Toledo, TGA/DSC 3⁺). Morphologies and sizes of both MAPDA particles and membranes were observed with field emission scanning electron microscopy (FE-SEM, SU-8000, Hitachi). For the porosity analysis, nitrogen

adsorption-desorption experiments were executed at 77 K on an Autosorb iQ2 adsorptometer, Quantachrome Instrument. CO₂ and N₂ adsorption isotherms at 273 K and 298 K were also carried out on the same instrument. High-pressure adsorption isotherms of CO₂ and N₂ were collected on iSorb HP1, Quantachrome Instrument. UHP-grade (>99.999%) N₂ and CO₂ gases were applied for all adsorption measurements. Before the tests, the samples were degassed at 373 K overnight (~10 h) under vacuum (<2.7 Pa). Mechanical properties of membranes were operated at room temperature (~25 °C) using an electronic stretching apparatus (MARK-10, Series 5) at a strain rate of 2.0 mm min⁻¹. The mean value was reported for each membrane from three tests.

Gas separation measurements

All membranes were fixed in a home-made membrane chamber and sealed with xylene-resistant fluorocarbon O-rings and the chamber was then connected to a gas flow system. Single (CO₂: 100 mL min⁻¹ or N₂: 100 mL min⁻¹) or binary gases (CO₂: 50 mL min⁻¹ and N₂: 50 mL min⁻¹) were introduced into the membrane module from the feed side, and the permeate gas was carried by helium (120 mL min⁻¹) sweep gas. The gas concentrations of feed and permeate were monitored by on-line gas chromatography (GC-456, SCION). For all measurements, gas permeation performances were analyzed after reaching the steady state (permeate concentrations changed smoothly with test error ≤10% for three consecutive runs). Each membrane was repeated for five times at each condition to guarantee the result reproducibility. The gas permeability was calculated using Equation (1):

$$P_i = \frac{J_i}{\Delta p_i} \times l \quad (1)$$

P_i is the permeability of component i in Barrer (1.0 Barrer = 1.0×10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹), l (m) is the membrane thickness, J_i is the flux of permeate component i (mol m⁻² s⁻¹), Δp_i is the pressure drop of component i between feed and permeate sides of membrane (Pa).

The membrane selectivity for gas permeation was calculated according to Equation (2):

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j} \quad (2)$$

P_i , P_j , S_i , S_j , D_i and D_j are the permeability, solubility and diffusivity of components i and j , respectively. S_i and S_j can be calculated from measured gas uptakes at high pressures (CO_2 and N_2 uptakes of 54.08 and 4.48 $\text{cm}^3 \text{g}^{-1}$ for PIM-1, and 67.28 and 4.94 $\text{cm}^3 \text{g}^{-1}$ for MAPDA/PIM-1 with 15 wt% MAPDA respectively at 298 K and 3.0 bars. PIM-1 and MAPDA/PIM-1 are assumed to have the same density of 0.92 g cm^{-3} according to their similar element compositions and surface areas) [38]. D_i and D_j can be mathematically derived from Equation (3):

$$P = S \times D \quad (3)$$

The theoretical gas permeability was calculated employing the Maxwell model and its equation is described below:

$$P_{i,MMM} = P_{i,p} \left[\frac{P_{i,f} + 2P_{i,p} - 2\Phi_f(P_{i,p} - P_{i,f})}{P_{i,f} + 2P_{i,p} + \Phi_f(P_{i,p} - P_{i,f})} \right] \quad (4)$$

$P_{i,MMM}$ is the permeability of gas i through the MMM, $P_{i,p}$ and $P_{i,f}$ are the permeabilities of gas i in the polymer (p) and the filler (f) respectively. Φ_f is the volume fraction of the filler in membrane.

Results and discussion

As we know, nanomaterials are superior in the fabrication of MMMs. Thus, MAPDA nanoparticles were synthesized *via* the microwave-assisted approach (Scheme 1). Fig. 1a shows the infrared (IR) spectra of melamine (MA), 1, 4-piperazinedicarboxaldehyde (PDA) and MAPDA. Stretching vibrations associated with the aldehydes at 1653 cm^{-1} (C=O) and 2877 cm^{-1} (C-H) disappear in the final product of MAPDA. The IR bands at 3470 and 3420 cm^{-1} corresponding to $-\text{NH}_2$ are significantly reduced. Accompanying the absences of amino and aldehyde fragments, an IR band at 1198 cm^{-1} evolves, indicating the formation of C=N groups. Meanwhile, IR bands from triazine rings (1550 cm^{-1} and 1480 cm^{-1}) are still detected in the prepared material. IR spectra indicate that MAPDA is successfully synthesized through efficient Schiff base reaction of melamine and 1,

1 4-piperazinedicarboxaldehyde. Fig. 1b shows the ^{13}C solid state nuclear magnetic
 2 resonance (NMR) spectrum of MAPDA. Two chemical shifts of 166.07 ppm and
 3 53.53 ppm are observed, namely aromatic carbons of triazine and imine (166.07 ppm)
 4 and aliphatic carbons of piperazine (53.53 ppm). The NMR data validates the
 5 successful formation of MAPDA network. The thermogravimetric curve is shown in
 6 Fig. 1c. MAPDA experiences a first weight loss at 65 °C ascribed to solvent escape
 7 (THF or acetone) and a second loss at 350 °C attributed to framework collapse. The
 8 TG analysis indicates that MAPDA is stable up to 350 °C. The morphology of
 9 MAPDA was visualized by using scanning electron microscopy (SEM) and the image
 10 is shown in Fig. 1d. The particles are quite uniform in size and spheroidal shape is
 11 observed from Fig. 1d. Statistically from counting ≥ 100 particles, the average size of
 12 MAPDA is estimated to be 42 nm (the inserted histogram in Fig. 1d).

13
 14 **Fig. 1.** IR spectra of MA and PDA monomers and MAPDA POE (a), ^{13}C solid-state
 15 NMR spectrum (b), TG in black and DTG curves in red (c), and SEM image of
 16 MAPDA and the particle size distribution is shown in an inserted histogram (d).

17

18 The open structure of MAPDA was characterized using physical nitrogen sorption.
 19 Fig. 2a presents the N₂ adsorption and desorption isotherms at 77 K. A rapid
 20 adsorption occurs in the low pressures, characteristic for microporous structure. Due

1 to the voids between small particles of MAPDA in the powder form, additional
 2 adsorption is observed at $P/P_0 \geq 0.8$, commonly found in other types of porous
 3 nanosolids [39-40]. The adsorption and desorption branches overlap together,
 4 suggesting that the pores are connected for reversible gas adsorption. Based on the
 5 isotherm, a Brunauer-Emmett-Teller (BET) surface area of $548.3 \text{ m}^2 \text{ g}^{-1}$ is calculated
 6 and a pore volume of $0.53 \text{ cm}^3 \text{ g}^{-1}$ is determined as well. As shown in the histogram
 7 (inset in Fig. 2a), the pore diameter is dominant at 1.0 nm, which is close to the
 8 theoretical value of 1.4 nm (Scheme 1). The membrane porosity of MAPDA/PIM-1
 9 was studied and N_2 adsorption-desorption isotherms are plotted in Fig. 2b. BET
 10 surface area of $771.4 \text{ m}^2 \text{ g}^{-1}$ is calculated for the MAPDA/PIM-1 membrane with 15
 11 wt% MAPDA and this surface area is a bit larger than the weight-average one of
 12 $732.4 \text{ m}^2 \text{ g}^{-1}$ (S_{BET} of $764.9 \text{ m}^2 \text{ g}^{-1}$ for PIM-1). However, the S_{BET} value of
 13 MAPDA/PIM-1 containing 20 wt% MAPDA is decreased to $614.2 \text{ m}^2 \text{ g}^{-1}$ compared
 14 to the one normalized by their corresponding weights ($S_{\text{BET}}=721.6 \text{ m}^2 \text{ g}^{-1}$). This
 15 finding suggests that incorporating MAPDA into PIM-1 can increase the membrane
 16 porosity, while an excess amount of MAPDA will reduce the free volume of the
 17 mixed matrix membrane.

18 **Fig. 2.** N_2 adsorption-desorption isotherms for the MAPDA material (a), inset is the
 19 pore size distribution histogram; and PIM-1, MAPDA/PIM-1 membranes with 15 wt%
 20 and 20 wt% MAPDA (b) measured at 77 K.

The gas adsorption particularities of MAPDA were examined by adsorptions of CO₂ and N₂ at different temperatures (Fig. 3a). The isotherm for CO₂ experiences a quick uptake at the beginning and a steady increase in uptake with increasing pressure. An uptake of 47.0 cm³ g⁻¹ for CO₂ is measured at 101 kPa and 298 K. In contrast, a very small amount of N₂ can be adsorbed into MAPDA, and this is evidenced by 6.1 cm³ g⁻¹ for N₂ at 101 kPa and 298 K. Eight-fold CO₂ uptake sheds light on the adsorption affinity for CO₂ over N₂. Further, the isosteric heats of adsorption (Q_{st}) for CO₂ and N₂ were calculated from the temperature-dependent isotherms. Fig. 3b plots the variations of Q_{st} for CO₂ and N₂ in function of uptake. At small uptakes (0.012 mmol g⁻¹), the Q_{st} values for CO₂ and N₂ are 34.9 kJ mol⁻¹ and 15.7 kJ mol⁻¹, respectively. This huge difference is derived from abundant basic nitrogen which can strongly interact with acidic CO₂ molecules. Ideal absorbed solution theory (IAST) was used to predict the thermodynamic selectivity for CO₂ over N₂. A CO₂/N₂ adsorption selectivity of 50.3 is calculated at the total pressure of 101 kPa for the equimolar gas mixture (Fig. 3c).

Fig. 3. CO₂ and N₂ adsorption-desorption isotherms at 273 K and 298 K (a), isosteric heats of adsorption for CO₂ and N₂ (b), and IAST predicted selectivity for CO₂ over N₂ adsorption on MAPDA at 273 K (c).

PIM-1 with macromolecular nature (Mw=144,271 Da) and porous structure (764.9 m² g⁻¹, pore size of 0.59 nm) was prepared according to our previous report [38]. The

1 prepared MAPDA nanoparticles were subsequently blended with PIM-1 to produce
 2 mixed matrix membranes (MMMs, denoted as MAPDA/PIM-1). The detailed
 3 morphologies of MMMs with different MAPDA loadings were further inspected with
 4 SEM (Fig. 4). In contrast to single phase of pure PIM-1 (Fig. 4b), two phases of
 5 MAPDA and PIM-1 are observed in MMMs with MAPDA contents of 5-20 wt% (Fig.
 6 4c-l). As seen from SEM images of MMMs, MAPDA nanoparticles are embedded in
 7 PIM-1. From magnified images (inset pictures), no visible cracks can be observed
 8 between MAPDA and PIM-1, indicating good filler-matrix compatibility. This close
 9 phase contact is probably originated from the interaction of MAPDA particles
 10 surfaces and PIM-1 chains at microscale level owing to their similar organic nature.
 11 When the loading reaches 20 wt%, some MAPDA aggregates can be observed (shown
 12 by circle in inset of Fig. 4l), and PIM-1 in the membrane is changed to a fibrils-like
 13 morphology (shown by arrows in inset of Fig. 4l).

14
 15 **Fig. 4.** SEM side views of MAPDA/PIM-1 membranes with MAPDA contents of 0 wt%

(a, b), 5 wt% (c, d), 8 wt% (e, f), 12 wt% (g, h), 15 wt% (i, j) and 20 wt% (k, l).

The mechanical property of the prepared membrane was examined (Fig. 5) and the important data is summarized in Table 1. As can be seen, Young's modulus increases and the strain becomes smaller when MAPDA is loaded into PIM-1. The higher stiffness of MAPDA/PIM-1 in comparison to that of PIM-1 is assumed to be stemmed from mutual interaction between MAPDA nanoparticles and PIM-1 chains. The drastic drop in Young's modulus after further increasing the MAPDA amount to 20 wt% can be ascribed to the looser attachment of MAPDA to PIM-1 [26, 32], which is in agreement with SEM result (Fig. 4l).

Fig. 5. Stress-strain curves of MAPDA/PIM-1 MMMs with MAPDA contents from 0 wt% to 20 wt%.

Table 1. Specific mechanical properties of PIM-1 and MAPDA/PIM-1 MMMs with different MAPDA loadings measured at 298 K.

Membrane	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
PIM-1	37.29	14.3	0.95
MAPDA/PIM-1-5	37.08	8.9	0.97
MAPDA/PIM-1-8	35.52	7.2	0.99
MAPDA/PIM-1-12	34.98	6.6	1.04
MAPDA/PIM-1-15	31.76	4.7	1.16
MAPDA/PIM-1-20	22.99	3.9	0.79

Above analysis has revealed the success of MAPDA/PIM-1 membrane synthesis, thereafter, gas separation test was carried out by the permeation of CO₂ and N₂ single gases. Table 2 summarizes the permeation results for MAPDA/PIM-1 membranes with varied filler loadings (0-20 wt%). When the loading amount of MAPDA is increased from 0 wt% to 15 wt%, the measured permeabilities for both CO₂ and N₂ are increased. This increase in gas permeability can be interpreted by two reasons: although MAPDA has a bit less surface area than PIM-1, it owns a more open framework which favors building straight gas transport pathways within the MAPDA/PIM-1 membrane (Scheme 1). Extra pores generated in MAPDA/PIM-1 (Fig. 2b) also allow more number of gas molecules penetrating across the membrane per unit time. The selectivity for CO₂ over N₂ is increased as well, showing that the filler of MAPDA plays a dominant role in improving the membrane selectivity. The specific contributions of MAPDA and PIM-1 were quantitatively determined using the Maxwell model [41], and the result is also compiled in Table 2. The theoretical permeability of CO₂ is reached at 208,481 Barrer, which is comparable to most POFs from simulations [42, 43]. This further proves the significant contribution of MAPDA to gas permeability of MAPDA/PIM-1. When the loading content is reached at 15 wt%, the measured gas permeability is larger than the theoretical one, exemplified by CO₂ permeability ratio of 0.7 for experimental value over theoretical number. This discrepancy sheds light on the creation of alternative path for gas permeation in the membrane. When an excess amount of MAPDA is loaded (20 wt%), the membrane performance is degraded. The decrease in CO₂ permeability possibly comes from free volume loss of the PIM-1 matrix [36, 44], and the decline in CO₂/N₂ selectivity might be resulted from the blockage of MAPDA pores by the nearby PIM-1 chains [45, 46]. This preliminary conclusion is in line with data from SEM (Fig. 4l), mechanical test (Table 1) and N₂ adsorption (Fig. 2b).

Table 2. Permeability and ideal selectivity of CO₂ and N₂ obtained from single gas permeations for MAPDA/PIM-1 membranes with different MAPDA loadings at 298 K and upon 0.3 MPa feed pressure.

Membrane ^[a]	CO ₂ permeability (Barrer) ^[b]		Ratio ^[d]	N ₂ permeability (Barrer) ^[b]		Ratio ^[d]	CO ₂ /N ₂ selectivity ^[c]	
	Experimental	Theoretical		Experimental	Theoretical		Experimental	Theoretical
PIM-1	3694.5(±19.7)	-	-	195.4(±3.0)	-	-	18.9(±0.4)	-
MAPDA/PIM-1-5	4227.5(±18.9)	-	1.0	219.0(±7.0)	-	1.0	19.3(±0.7)	-
MAPDA/PIM-1-8	4993.9(±15.9)	4572.6(±31.1)	0.92	245.9(±3.1)	234.2(±12.3)	0.95	20.3(±0.3)	19.5(±1.2)
MAPDA/PIM-1-12	6232.1(±11.3)	5066.1(±52.2)	0.81	289.2(±8.1)	255.5(±18.7)	0.88	21.5(±0.7)	19.8(±1.8)
MAPDA/PIM-1-15	7861.9(±24.5)	5463.7(±69.6)	0.70	329.0(±6.4)	272.5(±14.4)	0.83	23.9(±0.5)	20.1(±1.3)
MAPDA/PIM-1-20	3048.2(±58.5)	6185.9(±103.9)	NA	157.3(±13.0)	303.0(±35.2)	NA	19.4(±2.1)	20.4(±3.1)

[a] MAPDA/PIM-1 membranes with 5 wt%, 8 wt%, 12 wt%, 15 wt% and 20 wt% are designated as MAPDA/PIM-1-5 to MAPDA/PIM-1-20.

[b] Experimental permeability is measured by single gas permeation and theoretical permeability is calculated from the Maxwell equation (the permeability in MAPDA filler is based on MAPDA/PIM-1-5 with an assumption of its perfect MMM structure).

[c] CO₂/N₂ selectivity is calculated from the corresponding experimental and theoretical permeability.

[d] Theoretical permeability dividing experimental one gives the ratio. NA means not applicable for this system.

Additionally, the in-depth study was conducted on the representative MAPDA/PIM-1 membrane with 15 wt% MAPDA. The membrane exhibits a CO₂ permeability of 7861.9 Barrer, two times more than that of pure PIM-1 (Table 2). The ideal selectivity of 23.9 for CO₂ over N₂ is obtained from the permeation of single gases. The greater selectivity for MAPDA/PIM-1 (23.9) than that for PIM-1 (18.9) suggests preferential gas permeation through MAPDA pores, presumably caused by molecular affinity and diffusion freedom toward CO₂ rather than N₂. To prove this synergistic effect, the permeability (P) was deconvoluted into solubility (S) and diffusivity (D), and the calculated result is shown in Table 3. The CO₂ solubility coefficient (herein also called sorption capability measured by high-pressure adsorptometer) for MAPDA/PIM-1 is higher than that for PIM-1 despite its smaller surface area (S_{BET} of 764.9 m² g⁻¹ and 548.3 m² g⁻¹ for PIM-1 and MAPDA), indicating that CO₂ molecules are preferentially adsorbed and closely packed within MAPDA pores. Consequently, higher solubility selectivity ($S_{\text{CO}_2}/S_{\text{N}_2}$) is resulted for

MAPDA/PIM-1. In parallel, CO₂ and N₂ diffusivity coefficients are also calculated in Table 3. Both CO₂ and N₂ molecules diffuse faster in MAPDA/PIM-1. The CO₂ diffusivity coefficient is increased more dramatically than N₂, leading to larger CO₂/N₂ diffusivity selectivity (D_{CO_2}/D_{N_2}) than the corresponding one in pure PIM-1 (Table 3).

Table 3. CO₂ and N₂ solubility (S) and diffusivity (D) coefficients and their corresponding selectivity for PIM-1 and MAPDA/PIM-1 membranes derived from the single gas adsorption and permeation data.

Membrane	Solubility coefficient/ $10^{-3} \text{ cm}^3 \text{ cm}^{-3} \text{ cmHg}^{-1}$		S_{CO_2}/S_{N_2}	Diffusivity coefficient/ $10^{-7} \text{ cm}^2 \text{ s}^{-1}$		D_{CO_2}/D_{N_2}
	CO ₂	N ₂		CO ₂	N ₂	
PIM-1	218(±10)	18(±1.0)	12.1(±1.2)	16.72(±0.8)	10.71(±0.7)	1.56(±0.18)
MAPDA/PIM-1-15	271(±15)	20(±1.2)	13.6(±1.6)	28.62(±2.3)	16.23(±1.1)	1.76(±0.26)

Besides the single-gas permeation, CO₂/N₂ gas mixture separation was also performed on the representative membrane (MAPDA/PIM-1 with 15 wt% MAPDA). CO₂ and N₂ permeabilities of 6533.8 (±35.5) and 192.5 (±3.2) Barrer are measured at a feed pressure of 0.3 MPa and 298 K. The corresponding selectivity for CO₂ over N₂ is estimated to be 33.9(±0.8). To be noted, CO₂/N₂ selectivity for mixture gases is enhanced in comparison to that for single gases (23.9), probably because a competition in gas adsorption and diffusion occurs between CO₂ and N₂ when a mixture gas is fed. To better understand CO₂/N₂ separation by MAPDA/PIM-1 membrane, the description is schematically illustrated in Scheme 2. Three possible permeation pathways could be described in the following: Path 1 built by pure PIM-1, Path 2 constructed by MAPDA and PIM-1, and Path 3 created in the interfacial area. Path 2 is more favorable for gas permeation than Path 1. From structure perspective, abundant and large pores are contained in Path 2, consequently leading to small diffusion resistance for gases. From mass transport view, gas permeation rate is much faster through Path 2, evidenced by larger permeability for CO₂ or N₂ in MAPDA/PIM-1 than PIM-1. Structure-permeability relationship (Table 3) shows that gases are transported selectively in Path 2. Herein, CO₂ is preferentially permeated than N₂. Adsorption affinity of MAPDA is a primary force for driving CO₂ molecules

into this path (zoomed picture). The smaller kinetic diameter of CO₂ (3.3 Å) than N₂ (3.64 Å) also allows the free diffusion of CO₂ gas. Competitive adsorption between CO₂ and N₂ leads to an outcome that CO₂ penetrates within the pores whilst blocking N₂ to some extent. Path 3 coexists with Path 2 at the condition that a large number of MAPDA fillers (8-15 wt%) are introduced in the membrane. Interestingly, we have found that the size of interfacial void in Path 3 is at molecular level, shown by the similar increasing trend of theoretical and experimental CO₂/N₂ selectivity (Column 8 and 9, Table 2).

Scheme 2. Possible gas permeation paths (P_m , P_f and P_v represent permeability in matrix, filler and void; $P_f > P_v$ at low loadings and $P_v > P_f$ at high loadings.), and CO₂ and N₂ transport modes through MAPDA filler in the MAPDA/PIM-1 membrane.

The CO₂ permeability was plotted against CO₂/N₂ selectivity in Fig. 6. After surveying all pertinent materials [25-36], we have found that MAPDA/PIM-1 outperforms most of them and the data point lies far above the 2008 upper bound. To mimic the separation of flue gas, permeation measurements were conducted on gas mixture of 15CO₂:85N₂ in volume. The CO₂ permeability of 5332.2(±21.6) Barrer is obtained, which approaches to that from 50CO₂:50N₂ mixture. Noticeably, the product of permeability and selectivity is also surpassing the upper bound (Fig. 6), demonstrating the superior separation property of the MAPDA/PIM-1 membrane.

Fig. 6. The relationships of CO_2/N_2 selectivity *versus* CO_2 permeability for all relevant membranes (circle, square and triangle symbols respectively show the data from single gas, $50\text{CO}_2:50\text{N}_2$ and $15\text{CO}_2:85\text{N}_2$ mixture gases; the reported membranes in Ref. 25-36 are shown by empty symbols and our membranes are presented by filled symbols, the dash line is 2008 Robeson's upper bound.).

The influence of pressure was also investigated. Fig. 7 plots the changes of gas permeability and selectivity *versus* pressure. As can be seen, both CO_2 and N_2 permeabilities are increasing slightly with an increase of feed pressure, which is likely caused by either or both effects of chain swelling in PIM-1 and interfacial void expansion between MAPDA and PIM-1 under pressure [47]. The CO_2/N_2 selectivity is maintained at high values (27.4-21.8 and 40.0-30.3 for single and mixture gases) in the pressure range of 0.2-0.4 MPa. A minor decrease in CO_2/N_2 selectivity upon increasing the pressure is due to a larger N_2 permeability gained at a high pressure.

Fig. 7. Pressure-dependent permeability and selectivity of CO_2 and N_2 for single (a) and mixture gases (b) through the MAPDA/PIM-1 membrane (15 wt% MAPDA) at

298 K.

The membrane stability during the test was also examined. Fig. 8 plots the variations in gas permeability and selectivity as a function of time. CO₂ permeability remains around 6511.4 Barrer after an execution for 70 hours. No big fluctuation in CO₂/N₂ selectivity (30.1-36.3) shows the high robustness of the MAPDA/PIM-1 membrane.

Fig. 8. The variations of CO₂ and N₂ permeability and CO₂/N₂ selectivity in mixed gas separation (50CO₂:50N₂) for the MAPDA/PIM-1 membrane containing 15 wt% MAPDA in function of test time under 0.3 MPa feed pressure and 298 K.

Conclusions:

In this study, MAPDA POF particles in size of 42 nm have been first synthesized *via* a microwave-assisted approach. The nanofillers of MAPDA have been subsequently mixed with PIM-1 to produce MAPDA/PIM-1 mixed matrix membranes (MMMs). Permeation measurements on single gases have revealed enhanced CO₂ permeability and increased CO₂/N₂ selectivity for the prepared MAPDA/PIM-1 membranes in comparison to PIM-1. The permeations of CO₂ and N₂ gas mixtures have demonstrated limit-beyond CO₂ separation performances. Based on the structure and separation evidences, we have concluded the major contributions made by an introduction of MAPDA into the MMM: (1) Small particle sizes of MAPDA are

1 superior for fabricating continuous membranes with minimized defects. (2) High
2 porosity in terms of high surface area and large pore is advantageous for building
3 alternative and free pathway to facilitate the gas transport. (3) Pore functionality
4 allows preferential adsorption toward CO₂ and consequently leads to high membrane
5 selectivity for CO₂ over N₂. To sum up, MAPDA/PIM-1 has exhibited outstanding
6 membrane properties by virtue of excellent gas separation and high reproducibility,
7 making them of great promise in practical CO₂ separation.

10 **Acknowledgements:**

11 We would like to thank the following funds and agencies for the financial supports:
12 National Natural Science Foundation of China (NSFC grant no. 21531003, 21501024),
13 Jilin Scientific and Technological Development Program (20170101198JC,
14 20190103017JH), Jilin Education Office (JJKH20180015KJ), “111” Program, Jilin
15 Association of Science and Technology (2017-2018), and the Engineering and
16 Physical Sciences Research Council (EPSRC) (EP/S032886/1).

19 **Conflict of Interest:**

20 The authors declare no conflict of interest.

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