



High-throughput computational screening of Covalent–Organic framework membranes for helium purification

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ABSTRACT

Currently, helium purification is carried out by the heat-driven cryogenic distillation process, which is prohibitively energy-intensive and capital-intensive. As an alternative, covalent-organic frameworks (COFs)-based membrane separation technology is considered to be cost-efficient and technically feasible. In this study, a high-throughput computational screening strategy was proposed for the rapid determination of high-performing COF membranes for this particular application. A geometric analysis-based prescreening process was carried out on 688 experimentally synthesized COFs, resulting in 665 COF candidates with pore limited diameter (PLD) no less than 3.8 Å. Subsequently, molecular simulations were performed to estimate the Henry coefficients and self-diffusion coefficients of N₂, H₂, and CH₄ in each COF. Based on the results, the membrane selectivity and permeability of all the COFs were calculated, from which 23 high-performing COF membranes were identified. Additionally, the performances of these 23 COF membranes for a ternary mixture of He/N₂/CH₄ were computationally examined, five of which were highly preferable to permeate He over N₂ or CH₄. The results indicated that a large number of COF membranes exceeded the performance upper limit of polymer membranes owing to their high He permeability. Additionally, the relation between the PLD of COFs and the corresponding separation performances was investigated. Finally, He permeability, as well as He/CH₄ and He/N₂ selectivity of mixed matrix membranes were estimated by using the Maxwell model. The results revealed that the addition of COFs into pure polymers significantly improved the permeability of He up to 11689 Barrer.

1. Introduction

Helium is a non-renewable inert gas, which has a wide range of scientific, medical and industrial applications, such as liquid coolant for superconducting magnets in nuclear magnetic resonance imaging equipment [1], welding shielding gas, coolant in optical cable manufacturing, and working gas in laser and lighting. Helium is also widely used in the laboratory, such as carrier gas for gas chromatography, powder carrier gas of thermal spraying and cold spraying [2]. However, the only commercial source of He is the raw natural gas, and the He concentration is usually below 3% [3]. The current He purification process from sweetened natural gas (CH₄ + N₂ + He) is cryogenic distillation followed by pressure swing adsorption, both of which

require massive energy input.

To address this issue, membranes, especially inorganic membranes, have attracted much attention due to the low energy consumption, small footprint, simple operation, no moving parts and little impact on the environment [2]. Since helium amount in mixture is very low (below 3%), high He selectivity over CH₄ and N₂ is strongly required. Further analysis of the kinetic size and condensability of these gases reveals that high selectivity is more likely achieved by narrow pore size distribution (i.e., diffusion selectivity). Based on these considerations, the nanoporous materials (NPMs), may be a class of promising candidates [4]. NPMs refer to solid materials with high porosity, high internal surface area, and high structural adjustability [5], and two famous ones are metal-organic frameworks (MOFs) and covalent-organic frameworks

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(COFs). The former compose metal ions or clusters and organic connectors [6], while COFs are built only from organic linkers [7].

To the best of the authors' knowledge, in the field of He purification, most of studies focused on MOF membranes, especially using molecular simulation as the screening tool [8]. For example, Kadioglu et al. computationally investigated the separation performances of 139 MOF membranes for He separation from CH₄, and they found that the MOF membranes outperformed the traditional zeolite and polymeric membranes in He permeability [9]. Pezhman et al. carried out a high-throughput computational screening of 500 MOFs as membrane materials for N₂/He separation. Based on the results, ten top-performing MOF membranes were identified, with excellent N₂/He membrane selectivity ranging from 18 to 45 [10]. From a realistic perspective, neat MOF membranes are very brittle and hard to directly operated in real conditions. One approach is blending them with polymers to fabricate mixed matrix membranes (MMMs), which benefit from the remarkable He selectivity over N₂ and CH₄, and the processability of polymer. Due to the partial inorganic nature, the interfacial contact between MOFs and polymers remains unideal [11], leading to lower selectivity than expected. COFs, on the other hand, have much better compatibility with polymers thanks to their organic nature [4,12] and should possess high selectivity of He over CH₄ and N₂ based on their similarity to MOFs. Therefore, aside from the common advantages of MOFs, the miscibility and affinity of COFs to polymers provide more potential to using them as fillers in MMMs. There were few work studying the potential of using COF membranes for He purification. Aydin et al. studied the pure-gas permeability of He, H₂, CH₄ and N₂ in 589 COFs, and then ranked the ideal selectivity of He/CH₄ and He/N₂ respectively¹¹. However, in the screening process, they did not consider separating He from CH₄ and N₂ at the same time, which means that competitive adsorption and collaborative diffusion were not considered.

In this work, a high throughput computational screening was used to study the performance of pure COF membranes and COF-based MMMs for two target gas pairs (He/CH₄ and He/N₂), and through our collaborative screening strategy, 23 best COFs that can be applied to the separation of these two gas pairs at the same time were selected from 688 experimentally synthesized COFs. Then we simulated the separation of gas mixtures under real working conditions which is more accurate than that under pure-gas conditions, and finally screened out 5 COFs with the best performance. In addition, we explored the structure-performance relationship of COF-based membranes for He purification, which would provide guidance for the synthesis of COFs for He purification in the future.

2. Computational methods

2.1. COFs and polymers

The crystallographic information of COF structures used in this work was obtained from the CURATED (Clean, Uniform, and Refined with Automatic Tracking from Experimental Database) COF database, which currently contains 688 kinds of experimentally synthesized COF structures. All structures have been cleaned from solvent molecules and have no partial occupation or structural disorder [13].

11 various highly permeable polymers, namely Homo AF [2], Teflon AF2400 [14], Teflon AF1600 [14], HFP-TFE [15], Nafion [16], 2-methyl-2-ethyldioxole-1,3 [17], 6FDA/PMDA (10/90)-TAB [18], 6FDA/PMDA (25/75)-TAB [18], 6FDA-TAB [18], PTMSP [19], and PIM-1 [20], have been employed in this work. The combination of high He-selective COF and highly permeable polymer phase may lead to the membrane with superior He separation, even potentially surpassing the 2008 Robeson's upper bound [21]. The experimentally measured gas permeabilities and selectivities of polymers were taken from the literature [2,14,16,18–20] and listed in Table S1.

2.2. Screening strategy

The screening strategy is illustrated in Fig. 1, and consists of 6 steps: ① the structural descriptors of COFs were estimated using Zeo++ code (version 0.3) [22], including pore limited diameter (PLD), largest cavity diameter (LCD), density, and porosity. The pore volume was calculated with a probe radius of 0 Å. After the calculation, in order to enable He, N₂, and CH₄ molecules to transport through the pores, we excluded those COFs with PLD less than 3.80 Å, the largest kinetic diameter of studied gases (3.80 Å for CH₄, 3.64 Å for N₂ and 2.60 Å for He). Finally, we obtained 665 COFs to be further screened. ② Henry coefficient K_i^0 and self-diffusion coefficient D_i^0 at infinite dilution were calculated by grand canonical Monte Carlo (GCMC) simulation and molecular dynamics (MD) simulation respectively. We excluded COFs with gas self-diffusion coefficient below 10^{-8} cm²/s for accuracy concerns. ③ In this step, the permeability P_i^0 and membrane selectivity $S_{mem,i/j}^0$ of COF membranes at infinite dilution were calculated based on the equations shown in Table 1. ④⑤ These two steps screened COFs for He/N₂ and He/CH₄ gas pairs, respectively. Due to the difficulty of simulation of mixture gas, considering the calculation time, only top 30 COFs in selectivities were selected for both gas pairs, respectively. The He permeabilities of all these COFs are greater than 5×10^5 Barrer, and their membrane selectivities are greater than 2.9 for He/N₂ gas pair and 2.1 for He/CH₄ gas pair. The intersection of these two lists contained 23 COFs. ⑥ The adsorption, diffusion, and permeation of a three-component He/N₂/CH₄ mixture (5:4:1 mol ratio) in these 23 selected COFs were evaluated at 298 K and 1.2 bar. The calculation formulas are shown in Table 1. Finally, we identified five best COFs for the membrane separation of He/N₂/CH₄ mixture.

In step ②, an appropriate force field needed to be selected. Although the universal force field (UFF) has achieved good performance in the simulation of MOFs [23–26], we still carried out the experiment of pure-gas adsorption isotherm, as shown in Fig. S1. The results show that for the simulation of COFs, DREIDING force field shows better consistency with the experimental data than UFF. This observation is in line with the conclusion of Yan and Zhong et al. for COF simulation [27]. Therefore, DREIDING force field was used in all simulations in this paper. Henry coefficient at infinite dilution K_i^0 was evaluated by GCMC simulation at 298 K. The GCMC simulations were run for a total of 5.5×10^4 cycles separated into 5×10^3 cycles for initialization and 5×10^4

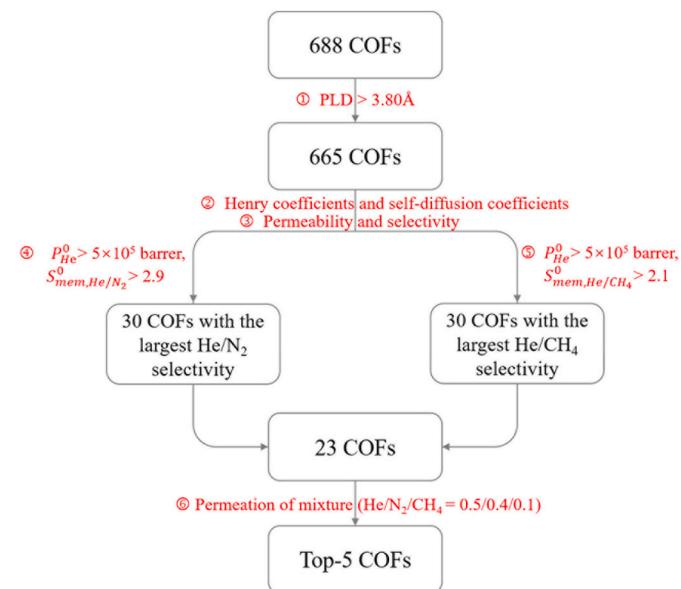


Fig. 1. The high-throughput computational screening strategy for He purification used in this work.

Table 1
Calculated properties of COF-based membranes.

Condition	Property	Formula
Infinite dilution condition	Permeability (Barrer)	$P_i^0 = K_i^0 \times D_i^0$
	Adsorption selectivity	$S_{ads,i/j}^0 = K_i^0 / K_j^0$
	Diffusion selectivity	$S_{diff,i/j}^0 = D_i^0 / D_j^0$
	Membrane selectivity	$S_{mem,i/j}^0 = P_i^0 / P_j^0$
Mixture condition	Permeability (Barrer)	$P_i^{MIX} = N_i^{MIX} \times D_i^{MIX} / f_i$
	Adsorption selectivity	$S_{ads,i/j}^{MIX} = (N_i^{MIX} / N_j^{MIX}) / (y_i^{MIX} / y_j^{MIX})$
	Diffusion selectivity	$S_{diff,i/j}^{MIX} = D_i^{MIX} / D_j^{MIX}$
	Membrane selectivity	$S_{mem,i/j}^{MIX} = P_i^{MIX} / P_j^{MIX}$
MMM condition	Permeability (Barrer)	$P^{MMM} = P^P \times \left[\frac{2 \times (1 - \varphi) + (1 + 2\varphi) \times (P^{COF} / P^P)}{(2 + \varphi) + (1 - \varphi) \times (P^{COF} / P^P)} \right]$

i: gas species (He, CH₄ or N₂); K_i^0 : Henry's constant at infinite dilution (mol/kg/Pa); D_i^0 : self-diffusivity at infinite dilution (cm²/s); f : partial pressure of gas in the mixture (Pa); N : gas uptake at mixture condition (mol/kg); y : molar fraction of gas species in the mixture; P^{MMM} : gas permeability of COF/polymer MMM (Barrer); P^P : gas permeability of polymer (Barrer); P^{COF} : gas permeability of COF membranes (Barrer); η : volume fraction of COF filler in MMM; 1 Barrer = 3.348 × 10⁻¹⁶ mol m/(m² s Pa).

cycles for taking ensemble averages. Self-diffusion coefficients at infinite dilution condition (D_i^0) were calculated by MD simulation. MD simulation was performed at 298 K in steps of 1 fs for a total of 10⁶ cycles, and a total of 30 gas molecules were randomly inserted into the pores of COFs. Due to the infinite dilution condition, the interactions between adsorbates and adsorbates were not considered.

In step ⑥, the adsorption and diffusion of the He/N₂/CH₄ mixture in the 23 prescreened COFs were simulated. In order to represent crude He in industrial production, the composition of He/N₂/CH₄ mixture is set as 5/4/1 (molar ratio), the temperature is 298 K, and the pressure is 1.2 bar [1]. The details of GCMC simulation are consistent with those at infinite dilution condition. In order to obtain the more accurate self-diffusion coefficient in mixture, the initial state of MD simulation was the final state of GCMC simulation. MD simulations were run for a total of 5 × 10⁶ cycles with the first 10³ cycles for initialization and 10⁴ cycles for the equilibration. The step size is still 1 fs, and the mean square displacement (MSD) of 1–5 ns is used to calculate the self-diffusion coefficient of the gas.

All these simulations were carried out at NVT ensemble using RASPA2 software package [28]. Daglar et al. reported that considering structural flexibility has little effect on the final calculation results. Therefore, all of the simulations in this work assumed that the COF structures are rigid [24].

Lennard-Jones 12–6 (LJ) potential and Coulomb potential were used to describe the COF-gas and gas-gas interactions, including repulsion-dispersion force and electrostatic interaction, respectively. The cross interaction between gas molecules and COF atoms was estimated by using Lorentz-Berthelot mixing rule. The charge equilibration method (Qeq [29]) in RASPA2 software was used to estimate the atomic charge of COFs for calculating electrostatic interactions, which were determined by the Ewald summation. N₂ molecules were modeled as three-sites including two sites with N atoms and the third one with the center of mass [30]. He and CH₄ molecules were modeled as a single atom, respectively. The detailed parameters of gas molecules were listed in Table S2.

The cut-off is set to 13 Å, and the number of crystal cells is automatically generated which means that the size of the crystal cell along the x, y and z dimensions should at least exceed twice the cut-off. For He, because its adsorption is weak and the initial state of MD simulation is taken from the adsorption results, there may be no He molecules in MD simulation. In this case, we will increase the size of crystal cells until there are He molecules in them. All simulations are conducted independently for three times, and the final results are the average of the three simulations.

3. Results and discussion

3.1. Separation performance of COF membranes at infinite dilution

Firstly, Henry coefficient K_i^0 and self-diffusion coefficient D_i^0 of 665 COFs at infinite dilution and 298 K were calculated, and the permeability P_i^0 of COF membranes were estimated, as well as the He/N₂ and He/CH₄ selectivity of COF membrane. The distribution of adsorption-, diffusion-, and membrane-selectivity of COFs at infinite dilution is shown in Fig. 2. Because the adsorption of He is very weak, it was calculated that the $S_{ads,He/N_2}^0$ and $S_{ads,He/CH_4}^0$ of COFs are less than 1, while the strong adsorption of N₂ and CH₄ leads to slower diffusion, so the $S_{diff,He/N_2}^0$ and $S_{diff,He/CH_4}^0$ of most COFs are greater than 2. Based on selectivity equation, a high selectivity can be obtained from the combination of both high adsorption- and diffusion-selectivity. However, these two parameters are generally against each other: bulkier molecule tends to be adsorbed more but diffuse slower, compared to small molecule, which is the case for He/CH₄ and He/N₂. Therefore, the highly selective COFs among these 665 COFs have $S_{ads,He/N_2}^0$ ($S_{ads,He/CH_4}^0$) in the range of 0.4–0.8 (0.3–0.7), and $S_{diff,He/N_2}^0$ ($S_{diff,He/CH_4}^0$) in the range of 4.6–8.9 (3.9–10.5).

The He permeability and He/N₂ and He/CH₄ selectivity of 665 COF membranes at infinite dilution and 298 K are shown in Fig. 3. In order to compare the He purification performance of COF membranes with that of traditional polymers, the Robeson's upper bounds of corresponding gas pairs are also presented in the figure. It can be seen that for both He/N₂ and He/CH₄ gas pairs, most of the COF membranes exceed the upper limit, which is mainly due to the high He permeability of the COF membranes. In addition, the COF membrane shows a different trend from the well-known trade-off between permeability and selectivity existed in polymers, that is, the He permeability of the COF membranes increases with their He/N₂ and He/CH₄ selectivity. Interestingly, the MOF membranes studied by Daglar et al. also showed a similar trend [26]. To further understand this trend, these COF membranes were classified based on their porosity (Φ). Clearly seen from Fig. 3, increasing porosity improves both He permeability and He selectivity over N₂ or CH₄. Therefore, the synthesis of COFs with higher porosity is of great significance for He purification.

It is well known that pore size plays an important role in the separation performance of membranes. Besides the porosity, the relationship between another parameter, PLD, of these COF membranes and their He separation performance was evaluated, as shown in Fig. 4. Clearly, there exists a positive relationship between the PLD and the He permeability, since COFs with larger PLD tends to have higher He permeability. The same trend is also observed for the He/N₂ and He/CH₄ selectivity, until they reach about 4.0 and 3.6, respectively. It seems that once the PLD is greater than 10 Å, the pore size has marginal effects on selectivity. Since the interested gases in this work only have a kinetic size of 2.6–3.8 Å, overlarge pore size does not benefit the selectivity.

For further screening, we specified that the He permeability of COF membranes should be greater than 5 × 10⁵ Barrer, and then we screened out 30 COFs with the highest selectivity for both gas pairs. For He/N₂ gas pair, the selectivity range of COF membranes is 2.9–4.0, and for He/CH₄ gas pair, the selectivity range of COF membranes is 2.1–3.6. Finally, we

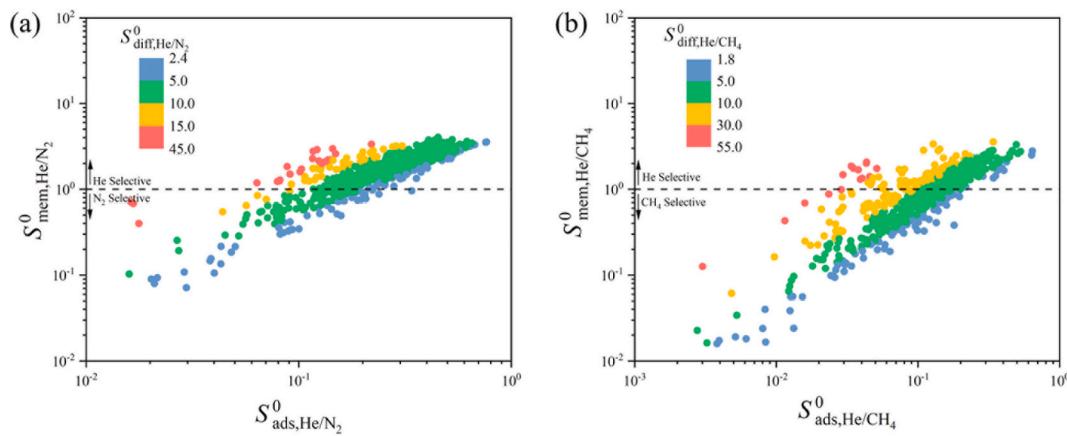


Fig. 2. Adsorption, diffusion and membrane selectivity of COFs at infinite dilution and 298 K.

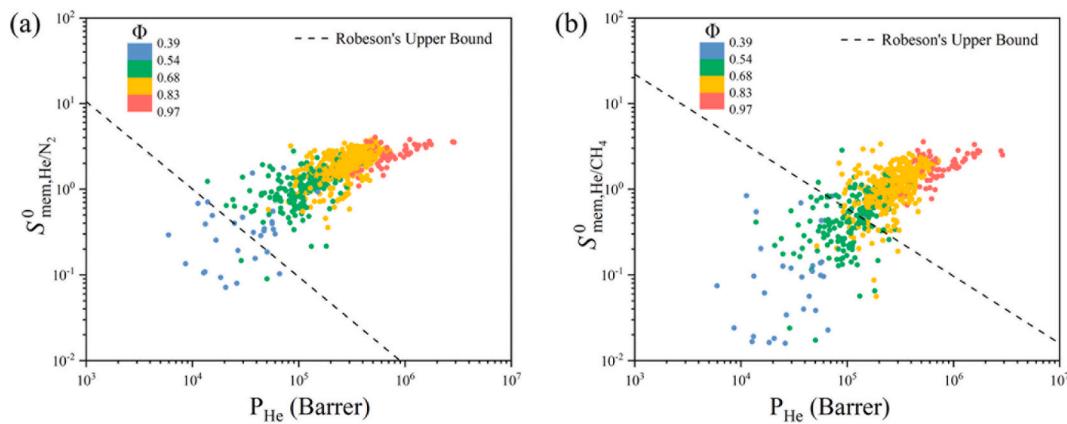


Fig. 3. He permeability and He/N₂ (a) and He/CH₄ (b) selectivity of pure COF membranes at infinite dilution and 298 K. Φ Indicates porosity.

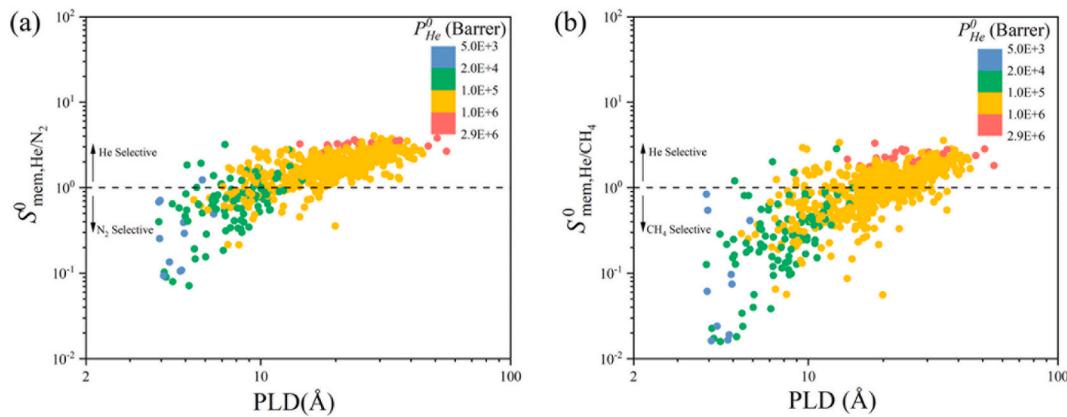


Fig. 4. Relationship between selectivity of COF membranes and PLD at infinite dilution and 298 K. The dotted lines refer to selectivity of 1.

took the intersection of these two groups of COFs and obtained 23 high-performance COFs for further screening. Details information about these 23 COFs can be found in Table S3.

3.2. Separation of the He/N₂/CH₄ mixture

The 23 pre-screened COFs were further examined for the adsorption, diffusion and permeation of three gases in mixture (He/CH₄/N₂: 5/4/1 molar ratio) at 298 K and a pressure of 1.2 bar. Table 2 lists the adsorption capacity N_i^{MIX} , self-diffusion coefficient D_i^{MIX} and

permeability P_i^{MIX} of each gas in 23 COFs, as well as adsorption selectivity, diffusion selectivity and membrane selectivity. Although the composition of N₂ in the mixture is less than that of He, N₂ obtains the maximum adsorption capacity in all 23 COFs, which should be attributed to the strongest affinity of N₂. As in the case of infinite dilution, all 23 COFs showed a diffusion selectivity over He of larger than 1. In addition, $D_{\text{CH}_4}^{\text{MIX}}$ is larger than $D_{\text{N}_2}^{\text{MIX}}$ in all 23 COFs, which is consistent with the adsorption results. After calculating the permeability from the results of adsorption and diffusion, we compared it with the permeability at infinite dilution (i.e., pure gas), as shown in Fig. 5. It can be

Table 2

Adsorption, diffusion and permeation of He/N₂/CH₄ mixture in 23 prescreened COFs at 298 K and 1.2 bar. The shaded ones are the 5 best COFs.

COF	PLD	Φ	N^{MIX} (mol/kg)			$D^{MIX}(10^{-8} \text{ m}^2/\text{s})$			$P^{MIX}(10^4 \text{ Barrer})$			S_{ads}^{MIX}		S_{diff}^{MIX}		S_{mem}^{MIX}	
			N ₂	He	CH ₄	N ₂	He	CH ₄	N ₂	He	CH ₄	He / N ₂	He/CH ₄	He/N ₂	He/CH ₄	He/N ₂	He/CH ₄
20481N3	35.99	0.969	0.573	0.350	0.079	30.15	242.20	79.77	69.85	273.61	101.69	0.76	0.64	8.03	3.04	3.92	2.69
19531N2	34.81	0.895	0.519	0.104	0.027	2.53	60.17	8.01	16.44	62.29	10.81	0.50	0.34	23.77	7.51	3.79	5.76
19456N2	31.43	0.811	0.207	0.051	0.014	2.44	44.84	9.26	10.93	39.48	11.09	0.48	0.29	18.38	4.84	3.61	3.56
20480N3	34.79	0.969	0.615	0.370	0.083	34.88	190.41	71.29	82.60	216.88	91.18	0.76	0.63	5.46	2.67	2.63	2.38
15100N2	36.16	0.814	0.197	0.046	0.013	1.64	27.80	8.15	7.89	24.84	10.05	0.47	0.28	16.94	3.41	3.15	2.47
19510N2	38.64	0.840	0.230	0.060	0.016	2.34	31.51	11.27	10.56	29.70	13.82	0.51	0.32	13.47	2.80	2.81	2.15
18143N3	30.44	0.941	0.450	0.207	0.050	8.63	62.82	27.33	26.61	71.08	37.11	0.65	0.51	7.28	2.30	2.67	1.92
19002N3	20.29	0.929	0.455	0.159	0.041	6.72	62.63	23.55	26.82	69.84	33.58	0.58	0.42	9.31	2.66	2.60	2.08
16061N2	18.50	0.939	0.434	0.194	0.047	9.09	63.28	24.44	28.49	71.11	33.55	0.64	0.49	6.96	2.59	2.50	2.12
20310N2	28.44	0.891	0.538	0.100	0.028	1.29	19.41	4.73	8.97	20.08	6.83	0.45	0.30	15.05	4.11	2.24	2.94
18020N3	14.36	0.918	0.378	0.141	0.037	7.19	53.72	15.45	26.44	59.00	21.99	0.56	0.41	7.47	3.48	2.23	2.68
16250N3	21.57	0.928	0.500	0.162	0.041	5.74	44.64	16.10	25.00	50.29	23.10	0.54	0.39	7.77	2.77	2.01	2.18
20430N3	46.91	0.945	0.615	0.207	0.051	9.40	67.71	31.94	39.13	76.03	43.89	0.61	0.44	7.21	2.12	1.94	1.73
20110N3	24.62	0.949	0.513	0.237	0.055	8.62	45.23	21.56	26.46	51.34	28.40	0.67	0.53	5.25	2.10	1.94	1.81
20113N3	24.11	0.944	0.506	0.221	0.053	9.41	49.25	22.13	30.40	55.47	29.96	0.65	0.50	5.23	2.23	1.82	1.85
20311N2	33.83	0.906	0.614	0.127	0.034	3.66	40.44	7.03	23.69	43.15	9.97	0.49	0.32	11.04	5.75	1.82	4.33
12024N2	32.08	0.792	0.196	0.041	0.011	1.68	17.84	6.40	8.80	15.68	7.85	0.44	0.26	10.65	2.79	1.78	2.00
20100C3	50.92	0.860	0.220	0.061	0.015	3.15	25.27	16.13	14.20	25.15	20.42	0.53	0.34	8.02	1.57	1.77	1.23
17160N3	18.71	0.921	0.455	0.134	0.035	5.94	43.76	21.38	27.89	48.33	31.23	0.53	0.38	7.36	2.05	1.73	1.55
11002N2	32.27	0.821	0.179	0.050	0.013	2.31	17.62	11.56	8.94	15.17	13.14	0.51	0.32	7.62	1.52	1.70	1.15
15201N3	22.38	0.941	0.474	0.180	0.044	4.15	21.21	13.84	15.78	24.48	19.69	0.60	0.45	5.11	1.53	1.55	1.24
20116N3	23.74	0.943	0.552	0.210	0.051	7.24	36.78	30.16	27.09	41.85	41.62	0.62	0.46	5.08	1.22	1.54	1.01
16130N3	22.10	0.933	0.463	0.157	0.040	5.58	29.34	16.02	23.55	33.52	23.55	0.57	0.42	5.26	1.83	1.42	1.42

seen that the permeability at infinite dilution generally overestimates that in the mixture, which should be attributed to the fact that competitive adsorption and collaborative diffusion are not considered at infinite dilution, similar conclusions have been drawn in other high-throughput screening studies [9,31].

In order to obtain the COFs with the best performance that can be applied to He recovery for ternary mixture, we sorted the COF membrane selectivity of the two gas pairs individually, and took the first five COFs that appear in the two groups at the same time, which are Yuan's COF-2 [32], TAH-COF2 [33], COF-1-tbo [34], COF-2-tbo [34] and TfPBHD [35]. They provide a $S_{mem,He/N_2}^{MIX}$ of 2.63–3.92, a $S_{mem,He/CH_4}^{MIX}$ of 2.38–5.76, and high He permeability of 2.5×10^{-5} – 2.7×10^{-6} Barrer. We note that the PLD of these five COFs is about 35 Å and the porosity of them is more than 0.8. In addition, two similar COFs with tbo topology (COF-1-tbo and COF-2-tbo) show great He permeability. This information may have important guiding significance for the experimental

synthesis of COFs for He purification. Among the five COFs, only Yuan's COF-2 has been used for membrane application, which served as fillers in MMMs for selectively amino acids transport [32]. Up to present, the usage of the other four COFs are limited in fluorescence chemosensor (TfpBDH), photocatalysis (COF-1-tbo, COF-2-tbo), and catalyst in amination reaction (TAH-COF2).

3.3. Separation performance of COF/polymer MMMs

In the previous parts, we discussed the He purification performance of pure COF membrane. However, the reliable fabricating large-scale and defect-free pure COF membranes is not yet mature [36]. Recent experimental works have shifted the attention from pure COF membranes to COF/polymer MMMs due to the excellent processability of the latter. Polymer membranes usually have low He permeability (22–3600 Barrer) and high selectivity (4–622 for He/N₂ and 4–3041 for He/CH₄).

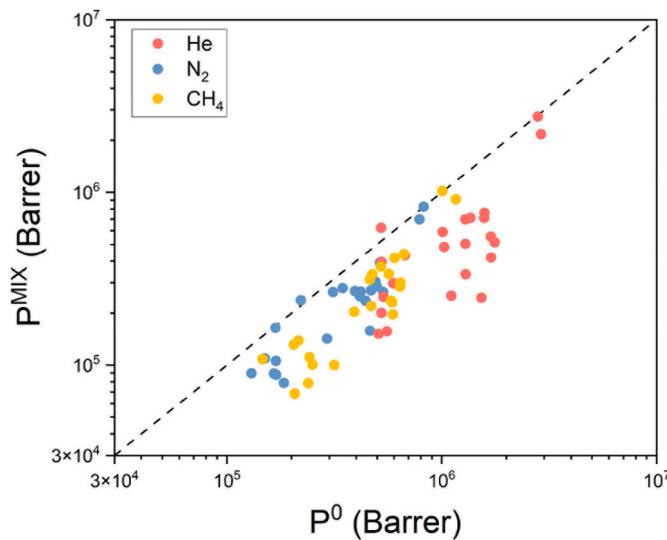


Fig. 5. Comparison of permeability of the prescreened 23 COF membranes computed at infinite dilution and at mixture conditions.

Before predicting the performance of MMMs, we first verified the accuracy of the method. We compared the collected experimental data with the permeability data simulated at the same conditions, as shown in Fig. 6. It can be seen that our simulation data are in good agreement with the experimental data [37–41]. Therefore, we applied this method to simulate the permeability of 55 MMMs, which are composed from the 5 top COFs and 11 polymers, respectively.

Fig. 7 shows the permeability of 55 MMMs we simulated. For both gas pairs, the addition of COF filler into polymer has greatly improved overall He separation performance, and some of them even exceed the Robeson's upper bound, such as Homo AF and HFP-TFE based MMMs. However, for most polymers, the addition of COF filler does not increase the He/N₂ and He/CH₄ selectivity, due to the relatively low He selectivity over N₂ or CH₄ of the selected COFs. Only polymers with a lower intrinsic He selectivity than that of COFs, such as PTMSP, can gain benefits from blending with COFs in terms of selectivity. Therefore, the improvement of He separation performances induced by adding COF filler into polymer matrix is mainly reflected by the increase of He permeability.

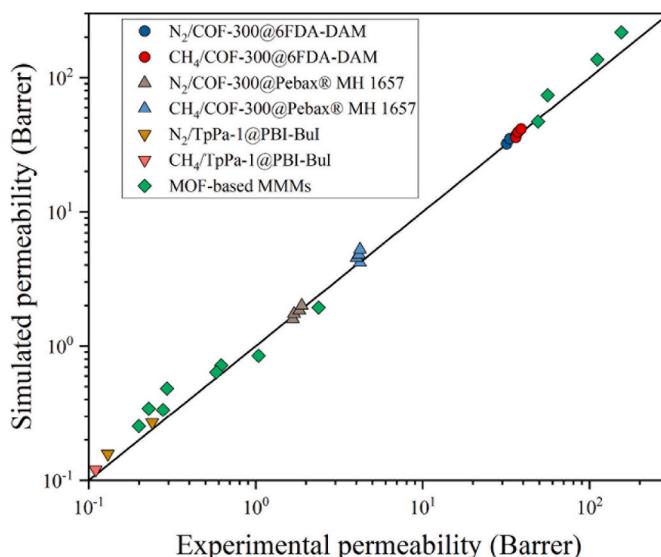


Fig. 6. Comparison of experimental and simulated permeability of MMMs [37–43].

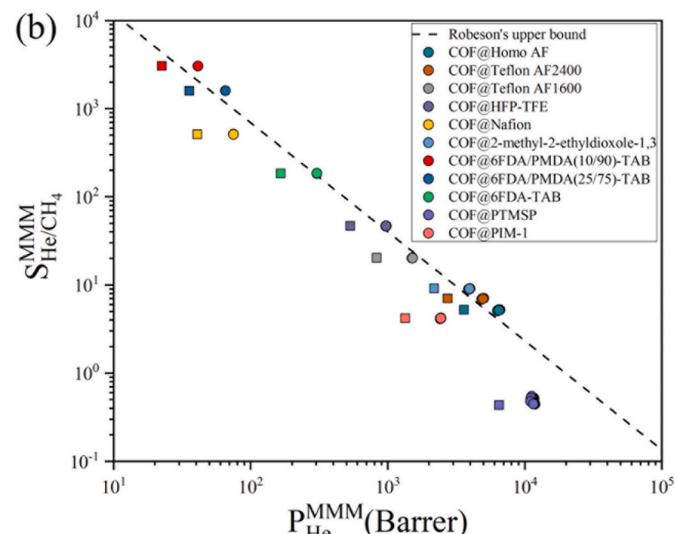
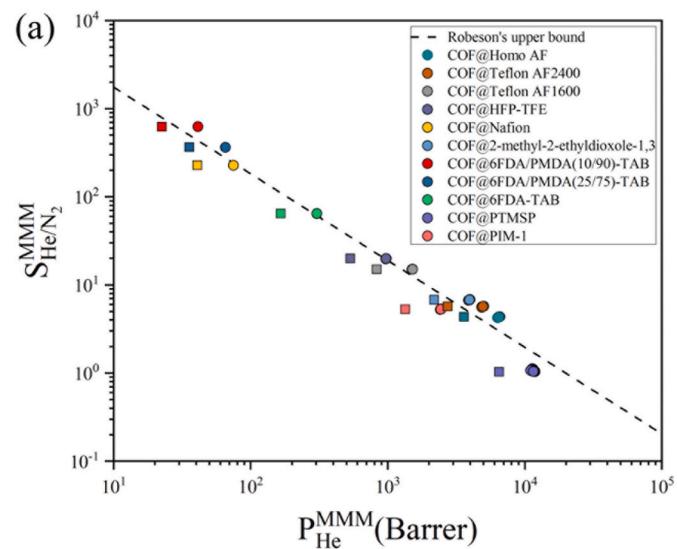


Fig. 7. Simulated permeability of 55 MMMs, and the block represents the corresponding polymer [2,14–20].

As shown in Fig. 8, we analyzed the influence of the volume fraction of COF fillers on permeability and selectivity of MMMs. Here, we selected Homo AF, Teflon AF2400, and Teflon AF1600 as the model polymers due to their both high He permeability and He selectivity over N₂ or CH₄ arised from the fluorinated nature. Besides, previous results also revealed that MMMs based on these polymers exhibited He separation performances surpassed the upper bounds, as we discussed above. Each line in Fig. 8a represents the permeability of one MMM under different COF volume ratios. It can be seen that for the three gases, He permeability of MMMs increases exponentially when the volume fraction of COF fillers increases, while the selectivity remains constant. These results suggest that the selectivity of polymers and the permeability of COFs dominate the selectivity and permeability of resultant MMMs, respectively. Therefore, in the future screening of COF membranes for helium purification, researchers should focus on those COFs with high permeability.

4. Conclusions

In this study, we studied the performance of COF-based membrane

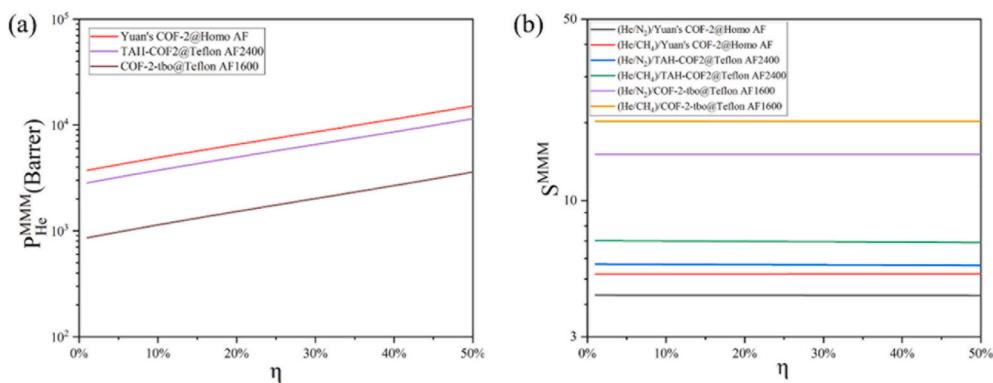


Fig. 8. The influence of the volume fraction of COF fillers on (a)permeability and (b)selectivity of MMMs.

separation of He/N₂ and He/CH₄ by molecular simulation. Firstly, we conducted the simulation at infinite dilution, and selected 23 COFs with the best performance that can be applied to the separation of He/N₂ and He/CH₄ at the same time from 665 COFs. Then, we simulated the performance of these 23 COFs at mixture conditions, and finally obtained 5 COFs with the best performance, which are Yuan's COF-2, TAH-COF2, COF-1-tbo, COF-2-tbo and TfPBHD. Although the selectivity of COF membranes is lower than that of polymer membranes, the He permeability of these COF membranes is much higher than that of polymer membranes, which shows their great potential in large-scale He purification applications. Considering the challenge of producing pure COF membrane, we also studied the He separation performances of 55 COF/polymer MMMs which were composed from the 5 top COFs and 11 polymers. The results showed that the addition of COF filler significantly improves the He permeability of MMMs without sacrificing the selectivity, compared to COF-free membranes. These results can provide valuable guidance for further material development targeted towards He purification membranes.

Credit author statement

Minggao Feng: Conceptualization, Methodology, Software, Writing – original draft. **Min Cheng:** Writing – review & editing, **Jing Deng:** Writing – review & editing. **Xu Ji:** Resources. **Li Zhou:** Resources. **Yagu Dang:** Resources. **Kexin Bi:** Formal analysis. **Zhongde Dai:** Supervision, writing – review & editing. **Yiyang Dai:** Funding acquisition, project administration, supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rineng.2022.100538>.

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