

**Dual Anion-Cation Crosslinked Poly(ionic liquid) Composite
Membranes for Enhanced CO₂ Separation**

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ABSTRACT

Herein, we propose a strategy of developing novel dual anionic-cationic crosslinked poly(IL)-IL composite membranes via a photopolymerization method for enhanced CO₂ separations. These are the first examples of dually photopolymerized anionic-cationic poly(IL)-IL composite systems, in which the backbones of poly(IL)s feature both pendant anions and cations without any mobile counterions unlike poly(IL) reported so far in the literature. A new type of dual photopolymerizable anionic-cationic IL (DIL) monomer having methacrylate functional group tethered with highly delocalized sulfonimide anion ($-\text{SO}_2-\text{N}^{(-)}-\text{SO}_2-\text{C}_7\text{H}_7$) and a vinylimidazolium counterion ($[\text{C}_4\text{vim}]^{+}$) was successfully synthesized and photopolymerized with four distinct amounts of free IL with a structurally analogous cation ($[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$) and 20 wt% PEGDA crosslinker, offering novel composite matrices. Further, the structure-property relationships as well as gas separation behaviors of the four newly developed dual anionic-cationic poly(IL)-IL composite membranes were extensively characterized by FT-IR, DSC, and XRD. All of the newly developed dual anionic-cationic poly(IL)-IL composite membranes displayed outstanding permselectivities for CO₂/CH₄, CO₂/N₂, and CO₂/H₂ gas pairs together with reasonable CO₂ permeabilities. As a result, all the dual anionic-cationic poly(IL)-IL composite membranes outperformed the common poly(IL)-IL systems in the upper bound limit plots with best CO₂ permeability of 40 barrer and CO₂/CH₄ permselectivity of 85. This study may pave a new platform to explore countless potential poly(IL)-IL composites for selective separation of CO₂ from flue gas, natural gas, and syngas streams.

INTRODUCTION

Global climate change or global warming caused by greenhouse gases has been considered as a serious environmental threat because of its severe impacts such as floods, droughts, cyclones and other extreme weather conditions.¹⁻³ It has been estimated that the current emission of major greenhouse gas, CO₂ (9-26%), per year from industries, automobiles, and coal-fired power plants is approximately 30 billion tons, a figure that is expected to increase by a factor of 3 to 4 within the next 100 years.^{1, 4} To reduce the climate change-derived environmental and economic threats, CO₂ capture and storage (CCS), a technology for isolating and collecting CO₂ emissions from point sources and storing them in underground reservoirs or utilize as a chemical feedstock has received intense research interest.^{5, 6} There have been several types of separation processes developed to separate CO₂ from gas mixtures at various pressures and compositions including absorption,^{7, 8} pressure swing adsorption,^{9, 10} cryogenic distillation,¹¹ and membrane-based separation.¹²⁻¹⁴

Considerable attention has been given to ionic liquids (ILs), a class of low temperature molten salts with large and asymmetric organic cations and organic or inorganic anions, due to their selectivity for CO₂ gas over other light gases (e.g., N₂ and CH₄) together with excellent chemical, thermal, and electrochemical stability, and lack of volatility.¹⁵⁻¹⁸ Over the past two decades, the combination of ILs with membrane technology has emerged as a promising class of materials for membrane-based gas separations. The earliest form of IL-derived membranes was though their immobilization into microporous polymers, forming supported ionic liquid membranes (SILMs).¹⁹⁻²¹ Given the “tunable” properties of ILs, opportunities for preparing a large array of functional groups and possible cation/anion types, bestowed a greater utility for the design of SILMs with ideal CO₂ permeabilities > 1000 Barrers and CO₂/N₂ permselectivity >

20.²⁰ Nevertheless, the leaching or “blow-out” of immobilized ILs limits the practical use of SILMs in industrial applications at even small pressure differentials < 1 atm.²²

To overcome the mechanical stability issues associated with SILMs, we (and others) have prepared polymerized IL (poly(IL)) membranes through a direct polymerization of IL monomers containing styrene, acrylate or vinyl groups appended to imidazolium cations.²³⁻²⁷ Fundamentally, poly(ILs) stand for a subset of polyelectrolytes in which the polymer repeat unit has IL moieties and share many features with ILs, such as their higher CO₂ solubility. The research in poly(IL)s become of greater interest than SILMs for CO₂ separation because of moderate gas separation properties and superior mechanical properties. It also reported that poly(IL)s exhibit a high CO₂ sorption capacity and high sorption and desorption rates compared to their low molecular IL counterparts.^{28, 29} These research efforts were mainly driven to combine the characteristic properties and functions of ILs and typical polymers to enhance the overall properties and performance of the separation material.

Although polymerized ILs seemed to be a promising strategy, concerning to the gas transport through the solid poly(IL) membranes were impeding with a substantial drop in their gas diffusivities and hence permeabilities compared to their analogous liquid phase in SILMs. To improve the gas diffusivity coefficients in poly(IL)s, we (and others) successfully introduced the incorporation of “free” (i.e., unreactive) ILs into poly(IL)s matrix, acting as nonvolatile selective plasticizing agents while maintaining the mechanical integrity of the resultant composite films.³⁰⁻
³³ More dramatic improvements in CO₂ permeability were accomplished by these poly(IL)-IL hybrid materials with little-to-no sacrifice in CO₂/light gas selectivity. It is also noteworthy to mention here that “free” ILs within poly(IL)s are different from traditional plasticizers in conventional polymers because of their extremely low volatility at ambient conditions and ability

to interact strongly with the charged poly(IL) matrix whilst yield an increment in free volume distribution in the membrane.

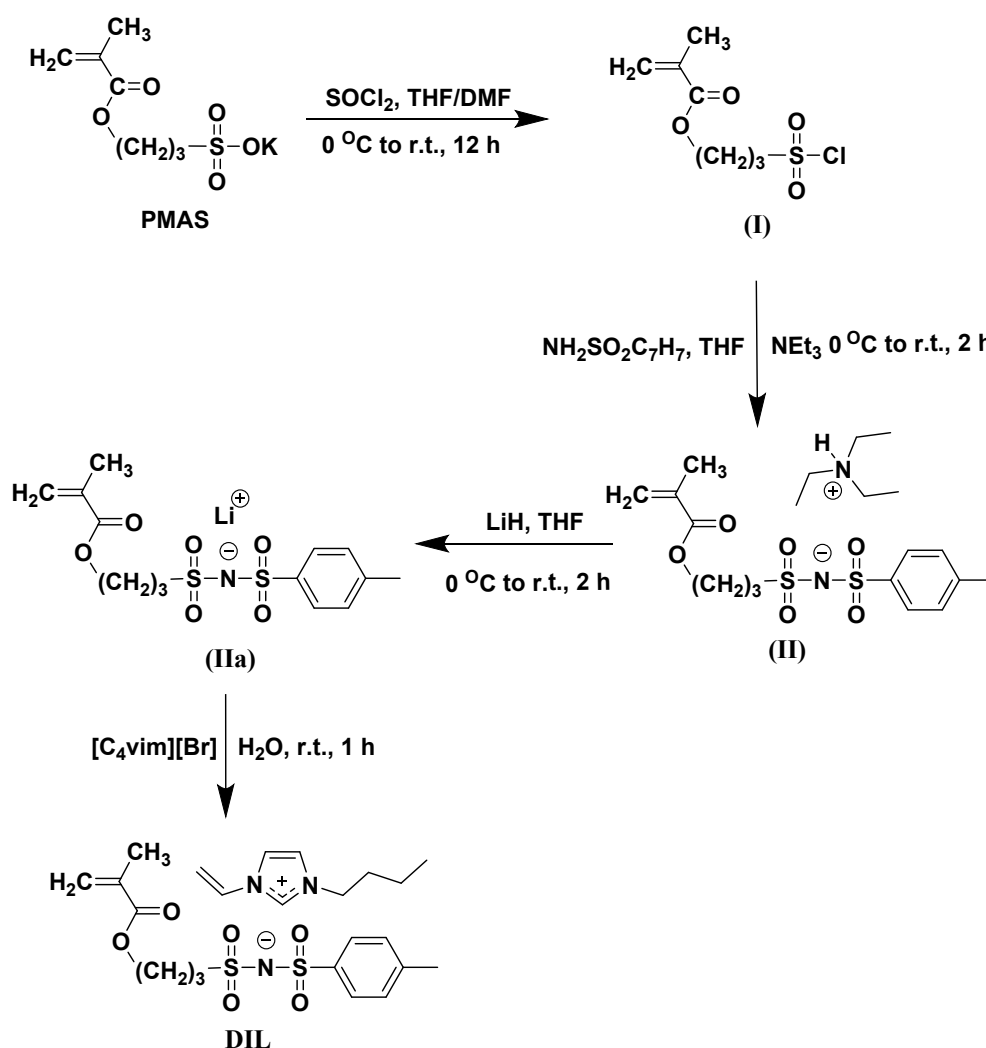
There were more studies inspired on poly(IL)-IL composites including cross-linked poly(IL)-IL to prepare gel membranes having large amounts of “free” IL loading,^{34, 35} step-growth poly(IL)-IL networks to enable facilitative CO₂ transport membranes,³⁶ and poly(IL)-IL blends with solid microporous additives to obtain mixed matrix membranes,³⁷⁻³⁹ etc. Despite various extensive studies to date involving poly(IL)-IL composite membranes for gas separation, poly(IL)s are mostly employed with imidazolium moieties although some other exceptional works reported with pyrrolidinium-based poly(IL)s. In other words, the published data for poly(IL)-IL composite membranes have largely been limited to polycations (i.e., polymer-bound cations), whereas anions are strictly serving as mobile counterions and not covalently bounded to the polymer chain. A comprehensive scope of understanding of the structure-property relationships and gas separation behaviors based on macromolecular structure and molecular composition is still significant to exploiting the use of poly(IL)s in membrane-based gas separation application.

All the above-mentioned aspects motivated us to explore a new possibility of poly(IL)-IL composites in which poly(IL)s comprise both anions and cations covalently bounded to the polymer backbone. To the best of our knowledge, this is the first example of tailoring a dual anion-cation photopolymerization for the development of poly(IL) material in CO₂ separation membrane applications. A new dual polymerizable anionic-cationic IL (DIL) monomer containing methacryloxy-based negatively charged *para*-toluenesulfonimide (i.e., a delocalized anion of –SO₂–N^(–)–SO₂–C₇H₇) group and 1-vinyl-3-butyylimidazolium ([C₄vim]⁺) counterion has been designed and prepared for the synthesis of novel dual anion-cation photopolymerized poly(IL)-

IL membranes (Scheme 1). 1-butyl-3-methylimidazolium bistriflimide ($[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$) was chosen as the “free” IL due to its structural similarity to the cationic monomer unit of the novel poly(IL) matrix and also because of its wide range use in the CO_2 separation. On the other hand, including our previous investigations, it is well-known that imidazolium poly(IL)s required a porous support as they are too brittle/fragile to form free-standing membranes.^{23, 26} Therefore, in this work, we have focused on the ability to form free-standing membrane materials by introducing a poly(ethylene glycol) (PEG) crosslinking structure into the poly(IL) macrostructure for achieving better mechanical stability as well as high “free” IL loadings ranging from 0.5 to 2 molar equivalents. Unambiguously, the objective of grafting ethylene glycol (EG) units (i.e., $-(\text{CH}_2\text{CH}_2\text{O})_n-$) network was to make the newly developed anionic-cationic poly(IL)-IL membranes less brittle rather than utilizing PEG contents for separation requirements as reported elsewhere.⁴⁰ Therefore, the CO_2 separation properties, together with physical properties of the novel dual anionic-cationic poly(IL)-IL composite membranes containing a minimal amount (i.e., 20 wt%) of crosslinked PEO content were analyzed, and a comparative study on crosslinker contents was not considered. The chemical structures of the materials used in this study are depicted in Figure 1.

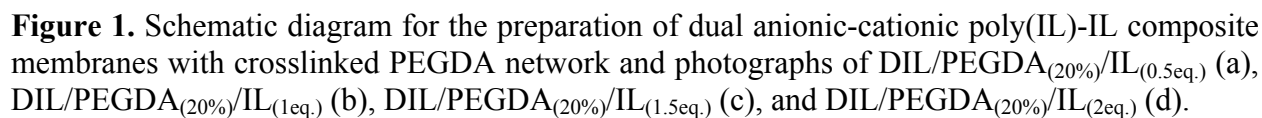
Synthesis and characterization of dual anionic-cationic poly(IL)-IL composite membranes with crosslinked PEGDA network (DIL/PEGDA_(20%)/IL). As summarized in Scheme 1, the dual polymerizable anionic-cationic IL having a pendant sulfonimide anion ($-\text{SO}_2-\text{N}^{(-)}-\text{SO}_2-\text{C}_7\text{H}_7$) and $[\text{C}_4\text{vim}]^+$ counterion was synthesized through four reaction steps. The purity and structure of newly synthesized DIL monomer were qualitatively analyzed by ^1H NMR and FTIR spectroscopic measurements and depicted in the Supporting Information (Figure S2 and Figure S3, respectively). The ^1H NMR spectra of DIL was unambiguously consistent with the proposed

chemical structure, revealing all the characteristic signals of imidazolium ring protons (at δ 9.47, 8.19, and 7.92 ppm) and vinyl protons (at δ 6.03-5.92 and 5.75-5.67 ppm) along with the well resolved signals at δ 4.26, 3.89, 3.27, 2.27, 1.93, and 1.54 ppm for alkyl chains. In addition, the presents of aromatic protons at δ 7.60 and 7.18 ppm were also confirmed the negatively charged $-\text{SO}_2-\text{N}^{(-)}-\text{SO}_2-\text{C}_7\text{H}_7$ substituent, indicating the successful synthesis of newly developed dual polymerizable anionic-cationic IL monomer (Figure S2).



Scheme 1. Synthesis of dual polymerizable anionic-cationic ionic liquid monomer (DIL).

Further, the dual cross-linked anionic-cationic poly(IL)-IL membranes were prepared via a UV-photopolymerization according to our previously reported method.^{30, 31} In this work, we have synthesized a series of novel photopolymerized dual anionic-cationic poly(IL)-IL composite membranes with an equimolar ratio to incorporate non-polymerizable ILs (i.e., free ILs) ranging from 0.5 to 2 equivalents in order to equilibrate the number of free anions and cations within poly(IL) matrix. Consequently, as depicted in Figure 1, four blend solutions were prepared from the newly designed polymerizable dual anionic-cationic IL (DIL) with corresponding amount of free IL ([C₄mim] [Tf₂N]), and the crosslinker (PEGDA) was added at 20 wt.% to each blend solution and cast into composite membranes under UV irradiation to yield DIL/PEGDA_(20%)/IL_(0.5eq.), DIL/PEGDA_(20%)/IL_(1eq.), DIL/PEGDA_(20%)/IL_(1.5eq.), and DIL/PEGDA_(20%)/IL_(2eq.). All the anionic-cationic poly(IL)-IL composites displayed as solid highly flexible free-standing membranes, which is desirable for gas separation applications (Figure 1).



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Physical properties of dual anionic-cationic poly(IL)-IL composite membranes. As shown in Figure 1, all the dual anionic-cationic poly(IL)-IL composite membranes were optically transparent and highly flexible regardless to the amount of free IL present. Therefore, their polymer chain packing conditions were examined by wide angle X-ray diffraction (WAXD) analysis as depicted in Figure 2. It was surprisingly observed that there were no sharp peaks exhibited in all XRD pattern, revealing the interpenetrating crosslinked networks are amorphous and the tendency to crystallize due to PEG contents does not occur. This further proves that the amount of PEGDA used in the newly developed anionic poly(IL)-IL composite membranes is minimum and appropriate to form flexible free standing membranes. On the other hand, two distinct peak distributions were found for the dual anionic-cationic poly(IL)-IL composite membranes on the addition of free IL. While 0.5 equivalent of free IL containing membrane (i.e., DIL/PEGDA_(20%)/IL_(0.5eq.)) displayed a bimodal diffraction peak, all other three membranes obtained a single broad peak distribution (Figure 2). This is mainly attributed to the average inter-chain distance diminishes occurred in the minimum amount of free IL (0.5 eq.) blends and causing non-uniformity in chain packing of resultant DIL/PEGDA_(20%)/IL_(0.5eq.) membrane. The inter-chain spacing values of all the four composite membranes were calculated from the main halo and summarized in the Table 1. An increasing trend on d-spacing values was also found in the dual anionic-cationic poly(IL)-IL membranes as increasing the amount of free ILs.

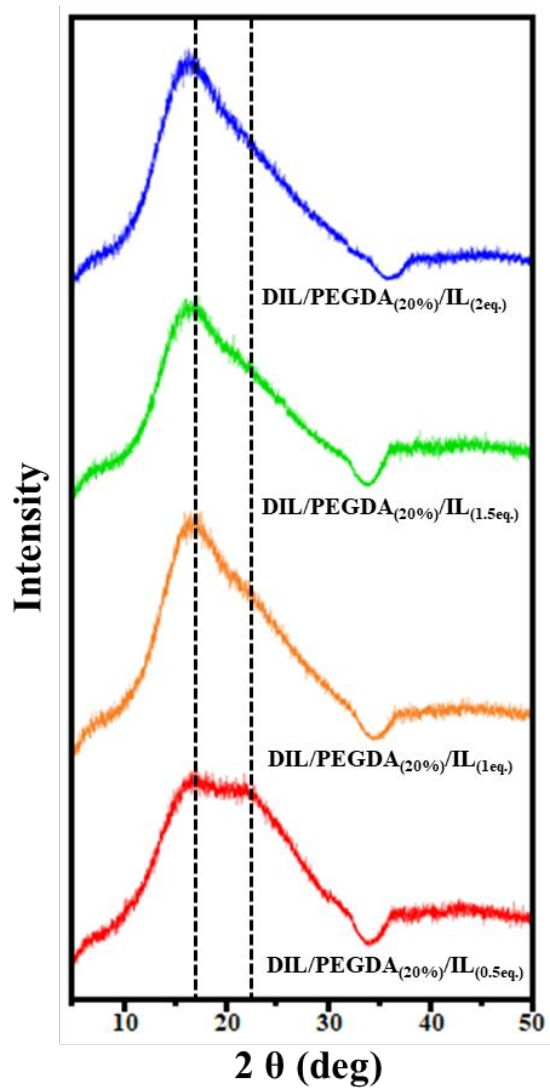


Figure 2. Wide-angle X-ray diffraction plots obtained from the dual anionic-cationic poly(IL)-IL composite membranes with crosslinked PEGDA network.

Table 1. Physical parameters that characterized the dual anionic-cationic poly(IL)-IL composite membranes

Membrane	T_g (°C)	d-spacing (Å)
DIL/PEGDA _(20%) /IL _(0.5eq.)	-13.9	6.09
DIL/PEGDA _(20%) /IL _(1eq.)	-19.8	6.16
DIL/PEGDA _(20%) /IL _(1.5eq.)	-26.6	6.39
DIL/PEGDA _(20%) /IL _(2eq.)	-36.8	6.51

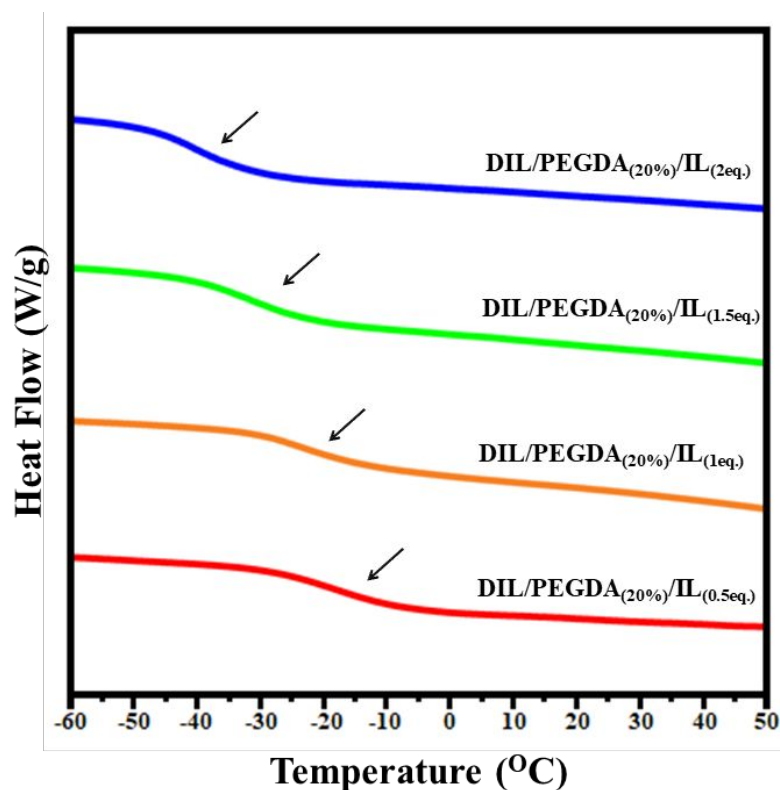


Figure 3. DSC curves of the dual anionic-cationic poly(IL)-IL composite membranes with crosslinked PEGDA network.

The thermal transition properties of newly developed dual anionic-cationic poly(IL)-IL composite membranes were further investigated by DSC analysis as a function of their chain packing architectures with respect to the increasing amount of free ILs, as showed in Figure 3. DSC measurements generally reflect the polymer chain mobility as well as phase behavior of polymer blends.⁴² Interestingly, in this study, all the dual anionic-cationic poly(IL)-IL composite membranes exhibited a single T_g , suggesting that there were no appreciable phase separation and crystallinity behaviors although we used PEO networks as one of the composite matrices (Figure 3). This observation is consistent with the XRD results that the free IL was completely miscible within the crosslinked DIL and PEO network, forming a compatible system. At the same time, as summarized in Table 1, all the dual anionic-cationic poly(IL)-IL composite membranes found obtaining reduced T_g values as increasing the amount of free ILs. In other words, the

incorporation of free ILs drastically increased the chain mobility of the resultant composites, expecting an enhancement in their gas diffusivities and hence permeabilities. The detailed discussion of gas permeation behaviors is well described below.

Gas permeation behaviors and CO₂ separation performance of dual anionic-cationic poly(IL)-IL composite membranes. The gas permeation properties of all the newly developed dual anionic-cationic poly(IL)-IL composite membranes were measured at 3 atm and 20 °C using a lab-made high-vacuum time-lag unit according to constant volume/variable-pressure method, as we reported hitherto.^{43, 44} The pure gas permeabilities of CO₂ and other light gases including H₂, N₂, and CH₄, and permselectivities of CO₂/H₂, CO₂/N₂, and CO₂/CH₄ are summarized in Table 2. To better understand a qualitative and quantitative separation performance of newly developed poly(IL)-IL systems, we calculated the diffusivity coefficients using the time lag equation (eq. S2 in Supporting Information) and subsequently determined the solubility coefficients by assuming solution-diffusion model ($P = SD$), as reported in Table 3.

Typically, the CO₂-preferential separation membranes yield much higher CO₂ solubility which is even one to two orders of magnitude higher than that of the other common light gases (N₂ and CH₄), because they are either built from rubbery polymers with lower glass transition temperature (T_g) or contain certain polar functional groups which have direct interaction with the quadrupolar CO₂ molecules.^{45, 46} On the other hand, many studies have proved that incorporation of free ILs into poly(IL)s increases diffusivity and consequently improve gas permeabilities without any permselectivity impairments.^{30, 32, 47} This trend of diffusivity increment in poly(IL)-IL composites can be mainly attributed to increase in free volume elements and higher polymer chain mobility mediated by non-volatile free IL contents. Interestingly, our experiments demonstrated that the incorporation of free IL into novel dual anionic-cationic poly(IL) matrix

anticipated to have a double effect of high CO₂ solubility and an increase in the diffusivity, leading to the favorable reverse-selectivity behavior for CO₂/H₂ gas pair. The obtained results revealed that the permeability of each single gas for the composite membranes are in the order of CO₂ (3.3 Å) > H₂ (2.89 Å) > N₂ (3.6 Å) > CH₄ (3.8 Å) (see Table 2).

Table 2. Ideal gas permeabilities (*P*)^a and permselectivities (α) of dual anionic-cationic poly(IL)-IL composite membranes at 3 atm and 20 °C.

^a*P* in barrers, where 1 barrer = 10⁻¹⁰ [cm³ (STP) cm]/(cm² s cm Hg)

Membrane	<i>P</i> _{CO2}	<i>P</i> _{H2}	<i>P</i> _{N2}	<i>P</i> _{CH4}	α _{CO2/H2}	α _{CO2/N2}	α _{CO2/CH4}
DIL/PEGDA _(20%) /IL _(0.5eq.)	9.43	1.95	0.161	0.135	4.85	58.54	69.82
DIL/PEGDA _(20%) /IL _(1eq.)	18.04	5.87	0.337	0.262	3.07	53.53	68.9
DIL/PEGDA _(20%) /IL _(1.5eq.)	27.64	6.71	0.425	0.360	4.12	65.03	76.68
DIL/PEGDA _(20%) /IL _(2eq.)	40.28	11.4	0.592	0.473	3.53	68.05	85.13

Table 3. Ideal gas diffusivity coefficients^a and solubility coefficients^b of dual anionic-cationic poly(IL)-IL composite membranes at 3 atm and 20 °C

Membrane	<i>D</i> _{CO2}	<i>D</i> _{N2}	<i>D</i> _{CH4}	<i>S</i> _{CO2}	<i>S</i> _{N2}	<i>S</i> _{CH4}	<i>D</i> _{CO2/N2}	<i>D</i> _{CO2/CH4}	<i>S</i> _{CO2/N2}	<i>S</i> _{CO2/CH4}
DIL/PEGDA _(20%) /IL _(0.5eq.)	4.60	0.748	0.524	2.05	0.215	0.258	6.15	8.78	9.53	7.95
DIL/PEGDA _(20%) /IL _(1eq.)	7.02	1.34	1.01	2.57	0.252	0.259	5.24	6.95	10.19	9.92
DIL/PEGDA _(20%) /IL _(1.5eq.)	10.19	1.79	1.38	2.71	0.238	0.262	5.69	7.38	11.39	10.34
DIL/PEGDA _(20%) /IL _(2eq.)	14.49	2.86	2.39	2.78	0.206	0.198	5.07	6.06	13.49	14.04

^aDiffusivity coefficient (10⁻⁸ cm²/s). ^bSolubility coefficient (10⁻² cm³ (STP) cm⁻³ cm⁻¹ Hg⁻¹)

As summarized in Table 2, the permeabilities of the dual anionic-cationic poly(IL)-IL composite membranes to all gases increased dramatically as the free IL content increased. For instance, the CO₂ permeabilities of the dual anionic-cationic poly(IL)-IL composite membranes increased by factors of approximately 2, 3, and 4 for DIL/PEGDA_(20%)/IL_(1eq.),

DIL/PEGDA_(20%)/IL_(1.5eq.), and DIL/PEGDA_(20%)/IL_(2eq.), respectively, compared to the DIL/PEGDA_(20%)/IL_(0.5eq.) (Table 2). This trend corresponded to a significant increase in the diffusivity coefficients (Table 3) caused by the irregularity in the interchain spacing and/or the polymer chain flexibility with increasing free IL contents. In fact, the diffusivity coefficients of all the gases to the dual anionic-cationic poly(IL)-IL composite membrane exhibited drastic increase as free IL loading. For instance, the CO₂ diffusivities of the dual anionic-cationic poly(IL)-IL composite membranes increased by factors of 1.5, 2, and 3 for DIL/PEGDA_(20%)/IL_(1eq.), DIL/PEGDA_(20%)/IL_(1.5eq.), and DIL/PEGDA_(20%)/IL_(2eq.), respectively, compared to the DIL/PEGDA_(20%)/IL_(0.5eq.) (Table 3). Therefore, it can be concluded that the increasing amount of non-polymerizable component (i.e., free ILs) served to create and fill more volume within the anionic-cationic poly(IL) matrix and increased the diffusivity of these materials, which also agrees with the XRD and DSC data of newly developed anionic poly(IL)-IL composites (a much lower T_g and higher d-spacing value was obtained for DIL/PEGDA_(20%)/IL_(2eq.)), a similar trend was also reported by Li et. al.³⁴

Although the diffusivity was the primary factor which differentiated the CO₂ permeabilities, all the newly developed dual anionic-cationic poly(IL)-IL composite membranes also favorably showed much higher solubilities toward CO₂ than to other gases (Table 3) due to a stronger affinity between ionic liquid groups and quadrupolar CO₂ molecules. As a result, unlike the nonpolar gas (H₂, N₂ and CH₄) separation trends, the ability of the dual anionic-cationic poly(IL)-IL composite membranes to separate CO₂ appeared to be an extraordinary, and these novel materials yielded excellent CO₂/CH₄, CO₂/N₂ and CO₂/CH₂ permselectivities. For instance, DIL/PEGDA_(20%)/IL_(2eq.) showed high selectivities of 85.13, 68.05, and 3.53 for

CO₂/CH₄, CO₂/N₂ and CO₂/CH₂, respectively, while maintaining a best CO₂ permeability of 40.28 Barrer amongst all the dual anionic-cationic poly(IL)-IL composite membranes. The high permeability and high selectivity of DIL/PEGDA_(20%)/IL_(2eq.) was ascribed to a combination of the boosted diffusivity coefficient and an enhancement in solubility selectivities for CO₂ over other gases in this membrane compared to other counterparts (Table 3), suggesting that higher free IL loading certainly created larger free volume for this composition. As depicted in Table 3, the diffusivity coefficients and CO₂ solubility selectivities of all the dual anionic-cationic poly(IL)-IL composite membranes increased as the free IL content increased whereas the diffusivity selectivity remained almost constant, which in turn is caused by our structure being unique in having a double effect of high CO₂ solubility and an increased diffusivity.

The CO₂ permeability-selectivity tradeoff results obtained for CO₂/CH₄, CO₂/N₂, and CO₂/H₂ gas pairs were then compared by plotting the benchmark upper bound of the Robeson plot and the upper bound proposed by Freeman, et al.⁴⁸⁻⁵⁰ As portrayed in Figure 4, a comparative study of our newly developed dual anionic-cationic poly(IL)-IL composite membranes with the key literature reports related to cationic poly(IL)-IL composites were performed.^{30-33, 35, 47, 51, 52} All the anionic-cationic poly(IL)-IL composite membranes showed outstanding CO₂/CH₄ performances way above the Robeson upper bound of 1991, and the DIL/PEGDA_(20%)/IL_(2eq.) membrane curves even appeared above the 2008 upper bound because of high permeability and extraordinary selectivity of 40.28 and 85.13, respectively (Figure 4(a)). At the same time, all dual anionic-cationic poly(IL)-IL composite membranes found below the upper bound line for CO₂/N₂, but they were comparable and within the general range of other cationic poly(IL)-IL systems (Figure 4(b)). Also, the CO₂ separation performance of these novel

materials reached the reverse CO_2/H_2 upper bound limit (Figure 4(c)). It is noteworthy that all the newly developed anionic-cationic poly(IL)-IL composite membranes showed superlative CO_2 separation factors over other light gases, indicating the remarkable capacities of these materials toward selective CO_2 separation in practical applications.

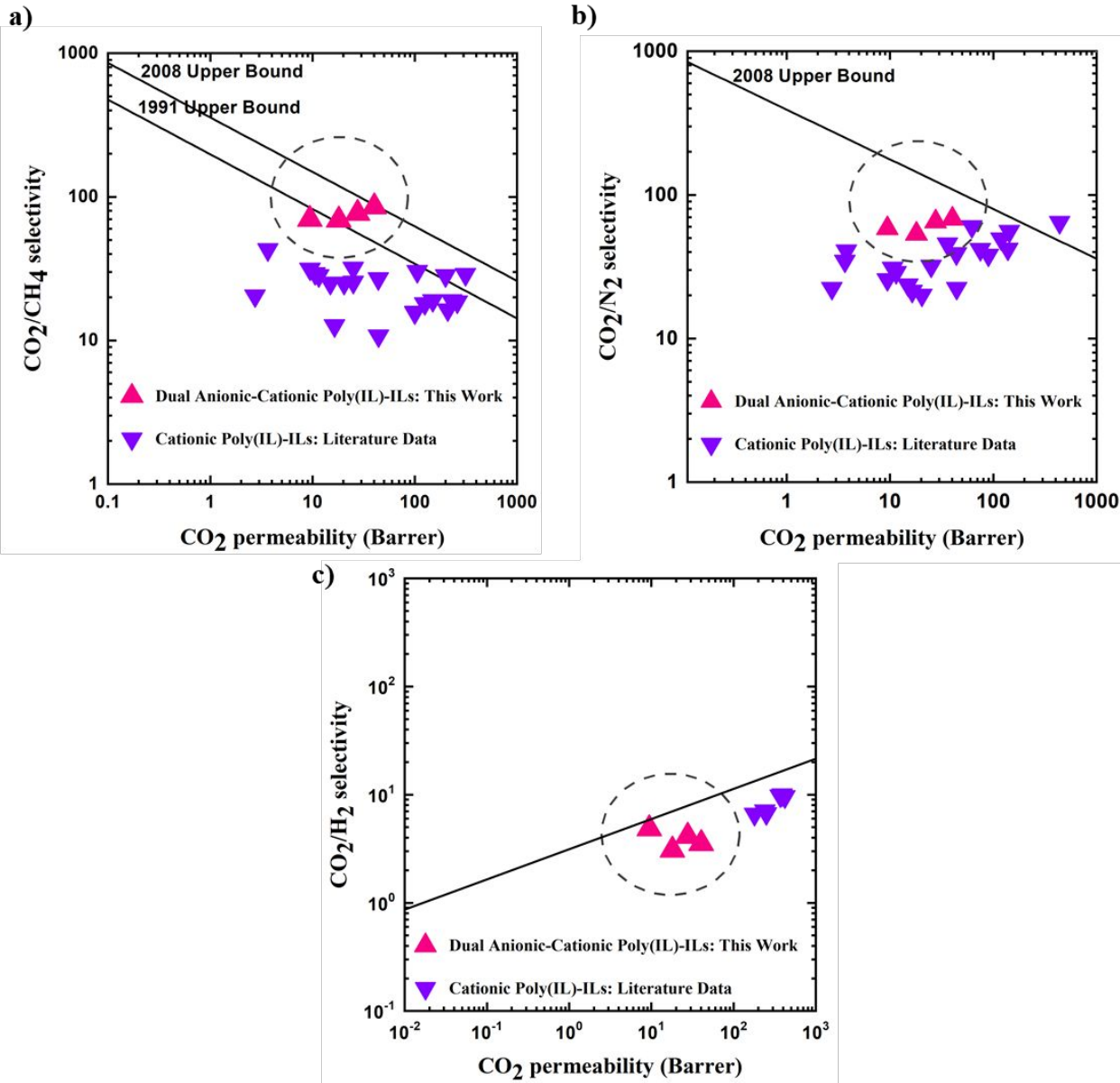


Figure 4. “Upper bound” comparison of the CO_2/CH_4 (a), CO_2/N_2 (b), and CO_2/H_2 (c) separation performances of dual anionic-cationic poly(IL)-IL composites with other (mainly cationic) poly(IL)-ILs reported in the literature.[30-33, 35, 47-52]

CONCLUSIONS

In conclusion, we developed a novel dual polymerized anionic-cationic poly(IL)-IL system for the first time and effectively demonstrated the utility of corresponding membranes for selective CO₂ separation. A new type of dual photopolymerizable anionic-cationic IL (DIL) monomer having methacrylate functional group tethered with highly delocalized anion ($-\text{SO}_2-\text{N}^{(-)}-\text{SO}_2-\text{C}_7\text{H}_7$) and a counterion of vinyl functional group containing imidazolium cation ($[\text{C}_4\text{vim}]^{+}$) was successfully synthesized and used in this work. Further photopolymerization of DIL with four distinct amounts of free IL containing the same structural cation ($[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$) and 20 wt% PEGDA crosslinker, serving as composite matrices obtained stable, transparent, and free-standing membranes. Promising results in gas permeation of the facile synthesized composite membranes were achieved by incorporating various amount of free ion pairs in dual anionic-cationic poly(IL) matrix. All the newly developed anionic-cationic poly(IL)-IL composite membranes exhibited outstanding selectivities for CO₂/CH₄, CO₂/N₂, and CO₂/H₂ gas pairs, while maintaining reasonable CO₂ permeabilities. The upper bound comparative studies further proved that the newly developed anionic-cationic poly(IL)-IL composite membranes have remarkable potential to separate CO₂ from various gas streams such as natural gas/biogas (i.e., CO₂/CH₄), flue gas (i.e., CO₂/N₂), and syngas (i.e., CO₂/H₂).

Many previously reported poly(IL)-IL composite membranes, in which cationic groups were incorporated into the polymer backbone, have demonstrated promising CO₂ separation with high free IL loading, however, none of these studies attempted to introduce anionic groups into the polymer backbone as presented in this work. Facile synthesis and outstanding gas separation properties of robust membranes of newly developed dual anionic-cationic poly(IL)-IL pender

new possibilities to design potential poly(IL) matrices for efficient gas separation processes. We envision a wide-range of development within this novel platform and tailoring countless dual anionic-cationic poly(IL)s with potentially fine-tuned substructures via introducing more flexible insertions (e.g., extended alkyl chains or ethylene oxide chains) into both anionic and cationic groups or fairly preparing high polar delocalized anions (e.g., cyanamide anions). Forthcoming works of our group will also be focused on the amount of crosslinked PEO units to feature the structure-property relationships and the CO₂ separation capacities, which were not aimed in this study.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

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