Design and Synthesis of Imidazolium-Mediated Tröger’s Base-Containing Ionene Polymers for Advanced CO₂ Separation Membranes

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Deposited 08/30/2018

Citation of published version:
DOI: https://dx.doi.org/10.1021%2Facsomega.8b03700
Design and Synthesis of Imidazolium-Mediated Tröger’s Base-Containing Ionene Polymers for Advanced CO2 Separation Membranes

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1. INTRODUCTION

Membrane-based gas separation utilizing polymeric materials has undoubtedly been at the forefront of separation processes such as hydrogen recovery in ammonia manufacture (H2/N2 and H2/CH4), CO2 capture and sequestration (CO2/H2, CO2/N2, and CO2/CH4), N2 or O2 enrichment of air (O2/N2), and olefin/paraffin separations in petrochemical industries (C3H6/C4H8). In general, polymeric membrane-based gas separation is flexible, easy to scale up, and energy-efficient. However, for a given gas pair, a strong inherent trade-off between permeability (the product of the diffusivity and solubility coefficients) and selectivity (the product of the diffusivity and solubility selectivities) invariably affects the polymer membranes and limits the gas separation performance. Improving separation performance of polymeric membranes in aggressive feeds such as natural gas upgrading (i.e., CO2/light gas separations) is of great interest and an enduring challenge in gas separation processes. To prepare highly CO2-permeable membranes, polymers with a high diffusivity coefficient and/or a high solubility coefficient must be designed.

Polymers consisting of high-free-volume elements often yield high diffusion coefficients and enhance the permeability. A class of soluble microporous polymers having rigid ladder-like chains containing sites of contortion, so-called polymers of intrinsic microporosity (PIMs), is well known for their high fractional free volume (FFV) and high gas permeabilities.

Recent developments in the design of microporous polymers have turned to the use of Tröger’s base (TB) derivatives as versatile new building blocks for the synthesis of extraordinary gas separation membranes. Several approaches such as TB polymerization and TB-based copolymers have been proposed to incorporate TB units into the polymer backbone. In general, the TB moiety is a nitrogen-containing kinked heterocycle with a V-shaped bridged bicyclic linking group, a chiral molecule with a site of contortion that can rigidify the polymer chain and generate microporosity in polymer matrixes. Results revealed that TB-containing polymer backbones can obtain much higher CO2 permeabilities due to the large disruptions in chain packing (i.e., increased FFV) caused by V-shaped tertiary amine diazocine bridges and improve the overall gas transport properties, particularly for CO2/CH4 separation with the performance surpassing the Robeson upper bound curves.

On the other hand, polymeric membranes either containing or built from ionic liquids (ILs) have recently emerged as promising CO2 separation materials due to their high CO2 solubility and high CO2 gas selectivities over N2 and CH4. Several promising approaches have been applied toward combining ILs with polymer membranes, including supported...
ionic liquid membranes (SILMs)\textsuperscript{,21−23} polymerized IL monomers, \textsuperscript{24} IL copolymers, \textsuperscript{25} pendant-IL functionalization, \textsuperscript{26} and IL composite membranes. \textsuperscript{27} Initial interest in the use of ILs essentially focused on the examination of SILMs, in which ILs are impregnated into microporous polymers to achieve high CO\textsubscript{2} permeability as well as high CO\textsubscript{2}/N\textsubscript{2} selectivity.\textsuperscript{22} The use of SILMs in practical gas separation processes, however, is hindered by stability issues as ILs can easily leach out from the membranes at pressure differences below 1 atm.\textsuperscript{28} Meanwhile, membranes prepared from polymeric ILs, also known as poly(IL)s, have become of greater interest than SILMs for CO\textsubscript{2} separation because of their moderate gas separation properties and superior mechanical properties. Poly(IL)s are not specifically ILs but rather are polymers containing several forms of ionic salts with many features shared with ILs, such as their high CO\textsubscript{2} solubility. Poly(IL)s also offer a high CO\textsubscript{2} sorption capacity and high sorption and desorption rates compared to ILs.\textsuperscript{29,30}

We have recently focused on the design and synthesis of various imidazole-functionalized monomers that are integrated into a different type of poly(IL), called ionenes, an IL-inspired platform where the polymer backbone contains cationic groups. In our previous work, we have successfully demonstrated the introduction of imidazolium cations into the rigid polyimide (PI) backbone via Menshutkin reactions to form PI–ionene hybrids or “ionic polyimides”.\textsuperscript{31} Membranes prepared from these newly developed ionic polyimides displayed high CO\textsubscript{2} separation properties, together with excellent mechanical and thermal stabilities.

In the present work, we combine the benefits of the abovementioned TB-based polymers and ILs to produce a novel imidazolium-mediated Tröger’s base-containing ionene polymer for enhanced CO\textsubscript{2} separation. To the best of our knowledge, this is the first example of using sterically hindered TB-based-imidazole monomers (Im-TB(\textit{\sigma}) and Im-TB(\textit{\rho}), Figure 1) to synthesize ionene polymers for selective CO\textsubscript{2} separation. The newly designed ionenes yielded high-molecular-weight polymers and displayed excellent thermal and mechanical properties, together with enhanced separation performance for CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} gas pairs. We also investigated the effects of two different aliphatic and aromatic monomers (\textit{\alpha,\alpha’}-dichloro-\textit{p}-xylene and 1,10-dibromocane, respectively) used in these TB-Ionene polymers, which impacted the physical properties as well as the gas separation behaviors of the corresponding polymer membranes.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Tröger’s Base-Containing Imidazole Monomers (Im-TBs, III). The Tröger’s base monomers (III) having “ortho”- and “para”-substituted imidazole were synthesized via a three-step synthetic route, starting from commercially available imidazole and either 2-fluoronitrobenzene (2-FNB) or 4-fluoronitrobenzene (4-FNB) to afford III\textit{\alpha} and III\textit{\beta}, respectively (Figure 1). The intermediates (imidazole–aniline derivatives, II\textit{\alpha} and II\textit{\beta}) were first synthesized through the reaction between imidazole and 2-FNB or 4-FNB in the presence of K\textsubscript{2}CO\textsubscript{3} in DMSO at 110 °C, followed by the Pd/C-catalyzed H\textsubscript{2} reduction in EtOH at ambient temperature. The purity and molecular structures of compounds II\textit{\alpha} and II\textit{\beta} were confirmed by \textsuperscript{1}H NMR (Figures S1 and S2, Supporting Information). The desired Im-TBs were further synthesized by the condensation reaction between II\textit{\alpha} and paraformaldehyde in the presence of trifluoroacetic acid (TFA) under ambient conditions. As previously reported, a mixture of enantiomers (\textit{R,R} and \textit{S,S}) can be possible for Im-TBs (III) due to the presence of a V-shaped 3° amine diazocine bridge.\textsuperscript{32} Direct comparisons of III\textit{\alpha} and III\textit{\beta} with their enantiomers, however, were not considered in this study as Im-TBs exclusively prepared for polymerization. Nevertheless, both III\textit{\alpha} and III\textit{\beta} were purified via recrystallization with DCM–MeOH mixtures. The purity and structures of Im-TBs were confirmed by \textsuperscript{1}H NMR (Scheme 1).

2.2. Synthesis and Characterization of Imidazolium-Mediated TB-Based Ionene Polymers (Im-TB-Ionene). As summarized in Scheme 2, a series of four novel imidazolium-mediated Tröger’s base-containing ionene polymers (Im-TB-Ionenes) were synthesized. The two imidazolide-functionalized Tröger’s base monomers synthesized from ortho- and para-substituted imidazole anilines were first polymerized with equimolar amounts of two different aromatic and aliphatic comonomers (\textit{\alpha,\alpha’}-dichloro-\textit{p}-xylene and 1,10-dibromodane, respectively) via Menshutkin reactions to form four corresponding ionene polymers ([Im-TB(\textit{\alpha,p})-Xy][Cl] and ([Im-TB(\textit{\alpha,p})-C\textsubscript{10}][Br]), respectively. The resulting ionene polymers having halide anions were further exchanged with [\textit{Tf}\textsubscript{2}N]\textsuperscript{−} anions, yielding novel Tröger’s base-containing ionene materials Im-TB-Ionenes. All the Im-TB-Ionene polymers were found to have very high number average molecular weights (e.g., \textit{m}/\textit{z} = 169843.8 for [Im-TB(p)-C\textsubscript{10}][\textit{Tf}\textsubscript{2}N]) as confirmed by high-resolution MALDI-TOF, Figures S3–S6), and similarly, high number average molecular weights were also reported in our previous works.\textsuperscript{31,33} The qualitative and quantitative characterizations of newly developed Im-TB-Ionene polymers were further analyzed by \textsuperscript{1}H NMR, FTIR, and thermogravimetric analysis (TGA) measurements.

The \textsuperscript{1}H NMR spectra of all four Im-TB-Ionene polymers were consistent with their proposed chemical structures. As shown in Figure 2, the \textsuperscript{1}H NMR spectra of the Im-TB-Ionene polymers display characteristic peaks of imidazolium protons (H\textsubscript{a}) at 10.0 ppm and the bicyclic ring of Tröger’s base protons (H\textsubscript{b}) in the region of 3.5–5.5 ppm, indicating the successful incorporation of imidazolium–TB groups in the polymer backbone. At the same time, benzyllic protons (H, at 5.5 ppm) of [Im-TB(\textit{\alpha,p})-Xy][\textit{Tf}2N], as confirmed by high-resolution MALDI-TOF, Figures S3–S6), and alkyl chain protons (H, at 1.2 ppm) of [Im-TB(\textit{\alpha,p})-C\textsubscript{10}][\textit{Tf}2N] were confirmed due to the presence of aromatic and aliphatic groups in the respective polymer backbones, proving the structures of newly developed Im-TB-Ionene polymers (Figure 2).

As shown in Figure 3, the chemical structures of Im-TB-Ionene polymers were further verified by FT-IR. All four Im-TB-Ionene polymers showed the corresponding peaks of aromatic TB groups (C–H, C–N, and C=C stretching vibrations at 3082, 1690, and 1480 cm\textsuperscript{−1}, respectively) as well as...
as ionic moieties such as imidazolium cations (C–N vibrations at 1320 cm$^{-1}$) and [$\text{Tf}_2\text{N}$]$^-$ anions (SO$_2$ and SNS stretching vibrations at 1190 and 1050 cm$^{-1}$, respectively), indicating that the imidazolium-based TB-Ionene polymers having [$\text{Tf}_2\text{N}$]$^-$ counteranions were successfully formed.$^{34,35}$ On the other hand, the new peaks corresponding to the aliphatic groups (C–H stretching vibrations at 2860 cm$^{-1}$) were only found for $[\text{Im-TB(o}$&$\text{p}]-\text{C}_{10}]$$[\text{Tf}_2\text{N}]$ polymers, confirming the structural variations in newly developed Im-TB-Ionene polymers.

The thermal stabilities of Im-TB-Ionene polymers were evaluated by thermogravimetric analysis (TGA) under a N$_2$ atmosphere (Figure 4). All six Im-TB-Ionene polymers exhibited very similar thermograms with two-stage degradations, the first of which occurring between 350 and 480 °C was attributed to the decomposition of the major ionene backbone, followed by the evolution of the residual ionic char at approximately 480–650 °C. In general, the TGA results showed that Im-TB-Ionene polymers are highly stable and adequate for gas separation applications.

2.3. Membrane Fabrication of Im-TB-Ionene Polymers. The Im-TB-Ionene polymers displayed high solubility in common polar aprotic solvents including DMAc, DMSO, and NMP (Table S1, Supporting Information). The excellent solubility indicated the compatibility of the newly developed ionene materials to form thin films. The corresponding membranes were prepared by casting a DMAc solution of respective Im-TB-Ionene polymers, followed by vacuum drying to give dense, transparent, and flexible membranes (the optical images are shown in Figure 5). Before use for characterization tests, the membranes were washed with hexane and dried for 24 h under ambient conditions to remove any residual solvents. The thickness of the Im-TB-Ionene membranes was controlled to be 90 to 110 μm.

2.4. Physical Properties of Im-TB-Ionene Polymers. The effect on thermal transitions of Im-TB-Ionene polymers as
a function of imidazolium groups as well as hard and soft segments (aromatic and aliphatic comonomers, respectively) was investigated using DSC analysis (Table 1 and Figure 6). The ionic polymers often yield lower glass transition temperature ($T_g$) values, which is proportional to the ratio of the counterion charge to the distance between the centers of cations and anions. Interestingly, in the newly developed Im-TB-Ionenes, the aromatic hard segments containing ionenes ([Im-TB(o)-Xy][Tf$_2$N]) possessed a similar high $T_g$ around 100 °C, which was even much higher than those obtained from other imidazolium–ionenes. Although slightly lower $T_g$ values ($\leq$80 °C) were observed for the aliphatic soft segment [Im-

Figure 2. $^1$H NMR spectra of the Im-TB-Ionene polymers.

Figure 3. FT-IR spectra of the Im-TB-Ionene polymers.

Figure 4. TGA curves of the Im-TB-Ionene polymers.

Figure 5. Photographs of Im-TB-Ionene polymer membranes (diameter = 47 mm).
Table 1. Physical Parameters Characterizing the Im-TB-Ionene Polymer Membranes

<table>
<thead>
<tr>
<th>membrane</th>
<th>$T_g$ (°C)</th>
<th>d spacing (Å)</th>
<th>density</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Im-TB(o)-XY][Tf$_2$N]</td>
<td>104</td>
<td>4.8</td>
<td>1.41</td>
</tr>
<tr>
<td>[Im-TB(o)-C$_{10}$][Tf$_2$N]</td>
<td>55</td>
<td>5.9</td>
<td>1.29</td>
</tr>
<tr>
<td>[Im-TB(p)-XY][Tf$_2$N]</td>
<td>98</td>
<td>4.7</td>
<td>1.39</td>
</tr>
<tr>
<td>[Im-TB(p)-C$_{10}$][Tf$_2$N]</td>
<td>80</td>
<td>4.6</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Figure 6. DSC curves of the Im-TB-Ionene polymers.

Table 2. Pure Gas Permeabilities ($P$) and Permselectivities ($\alpha$) of Im-TB-Ionene Polymer Membranes

<table>
<thead>
<tr>
<th>membrane</th>
<th>$P_{CO_2}$ ($\times 10^{-10}$ cm$^3$ STP cm)/(cm$^2$ s cmHg)</th>
<th>$P_{N_2}$</th>
<th>$P_{CH_4}$</th>
<th>$\alpha_{CO_2/N_2}$</th>
<th>$\alpha_{CO_2/CH_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Im-TB(o)-XY][Tf$_2$N]</td>
<td>2.69</td>
<td>0.91</td>
<td>0.047</td>
<td>29.6</td>
<td>57.2</td>
</tr>
<tr>
<td>[Im-TB(o)-C$_{10}$][Tf$_2$N]</td>
<td>1.99</td>
<td>0.077</td>
<td>0.026</td>
<td>25.8</td>
<td>76.5</td>
</tr>
<tr>
<td>[Im-TB(p)-XY][Tf$_2$N]</td>
<td>2.02</td>
<td>0.084</td>
<td>0.038</td>
<td>24.1</td>
<td>53.2</td>
</tr>
<tr>
<td>[Im-TB(p)-C$_{10}$][Tf$_2$N]</td>
<td>3.47</td>
<td>0.55</td>
<td>0.053</td>
<td>33.9</td>
<td>82.5</td>
</tr>
</tbody>
</table>

$P$ in barrer, where 1 barrer = 10$^{-10}$ (cm$^3$ STP cm)/(cm$^2$ s cmHg).

Figure 7. Wide-angle X-ray diffraction plots obtained from the Im-TB-Ionene membranes.

TB(o&p)-C$_{10}$][Tf$_2$N] ionenes, similar values were also reported for imidazolium ionenes with butyl chains. The lower $T_g$ values were attributed to a looser packing of the ionene groups within the flexible aliphatic networks, suggesting that chain mobility of the ionenes was high, and hence, enhanced gas permeability was expected for the membrane with this combinational series. Most notably, a much lower $T_g$ of 55 °C was observed for the ortho-positioned aliphatic Im-TB-ionene polymer, [Im-TB(o)-C$_{10}$][Tf$_2$N].

To further investigate the chemical structures and chain packing architectures of the newly developed ionenes, wide-angle X-ray diffraction (WAXD) was performed. As shown in Figure 7, there were no sharp peaks exhibited in all X-ray diffraction patterns, indicating the amorphous structures of Im-TB-Ionenes. Whereas both the aromatic copolymers [Im-TB(o&p)-XY][Tf$_2$N] displayed a single-peak distribution, a bimodal distribution was obtained for aliphatic copolymers [Im-TB(o&p)-C$_{10}$][Tf$_2$N], which is plausible because of the enhanced chain mobility of ionenes caused by alkyl chains. However, the intersegmental d spacing values of Im-TB-Ionenes calculated from the main halo ($2\theta = 21–22°$) remained constant irrespective of their molecular structure, except for [Im-TB(o)-C$_{10}$][Tf$_2$N] (Table 1). The main halo in [Im-TB(o)-C$_{10}$][Tf$_2$N] was shifted from 2$\theta$ of 21.5 to 17.2° and resulted in a high d spacing of 5.9 Å. The relatively higher d spacing of [Im-TB(o)-C$_{10}$][Tf$_2$N] can be attributed to the introduction of the alkyl groups into the ortho positions of the imidazolium–TB unit, which disrupts the chain packing of ionenes and increases the d spacing.

Generally, the d spacing represents the distance between the polymer chain segments, and the increase in the d spacing values of [Im-TB(o)-C$_{10}$][Tf$_2$N] might lead to a decrease in the density. The [Im-TB(o)-C$_{10}$][Tf$_2$N] yielded the lowest density among the four Im-TB-Ionene polymers (Table 1). These results clearly suggested an increased free volume distribution and hence enhanced gas transport properties in the [Im-TB(o)-C$_{10}$][Tf$_2$N] membrane (see below).

2.5. Gas Transport Properties of Im-TB-Ionene Polymers. The pure gas permeabilities and permselectivities of the Im-TB-Ionene membranes were measured at 3 atm and 20 °C using a lab-made high-vacuum time-lag unit according to the constant volume–variable pressure method, as summarized in Table 2. The permeability of Im-TB-Ionenes follows the sequence of the kinetic diameter of the respective gas molecules: CO$_2$ (3.3 Å) > N$_2$ (3.6 Å) > CH$_4$ (3.8 Å), a trend that indicates the size-selective chain packing of the newly developed ionenes due to the presence of TB units. As shown in Table 2, the gas permeabilities of aromatic segments containing ionenes displayed a similar result irrespective of their ortho and para substructures; for example, the CO$_2$ permeabilities of [Im-TB(o)-XY][Tf$_2$N] and [Im-TB(p)-XY][Tf$_2$N] were 1.99 and 2.02 barrer, respectively. In contrast, the aliphatic segments containing ionenes exhibited a dramatic increase in permeabilities, especially the ortho-positioned [Im-TB(o)-C$_{10}$][Tf$_2$N] ionene, due to the enhanced diffusion as well as solubility coefficients (Table 3). [Im-TB(o)-C$_{10}$][Tf$_2$N] showed the best permeabilities among the four Im-TB-Ionenes; for example, the CO$_2$ permeability of [Im-TB(o)-C$_{10}$][Tf$_2$N] was 4.37 barrer (increased by about 2-fold). This provides further evidence that the alkyl groups in the ortho position of the imidazolium–TB unit effectively improve the flexibility in the polymer chain, which is consistent with the d spacing data and the thermal transition properties (lower $T_g$ was obtained for [Im-TB(o)-C$_{10}$][Tf$_2$N]).
provide a novel approach to introducing imidazolium-TB groups into a variety of polymer structures for use in gas separations, CO₂ capture, catalysis, and electrochemical applications.

3. CONCLUSIONS

We prepared a series of novel imidazolium-mediated Tröger’s base-containing ionenes and successfully demonstrated the potential utility of the corresponding membranes for CO₂ gas separation. This is the first example of the incorporation of Tröger’s base groups into the imidazolium–ionene polymers to serve as a CO₂ selective separation membrane. We investigated the effects of Im-TB-ionenes on the structures and properties of the polymers as well as the gas separation properties of the corresponding polymer membranes by varying the regiochemistry of imidazolium groups in TB units and the presence of aromatic and aliphatic co-monomers. All newly developed Im-TB-Ionene polymers exhibited high molecular weight, excellent solubility in polar organic solvents, and high thermal stability. The Im-TB-Ionene membranes showed superior CO₂/CH₄ and CO₂/N₂ selectivities with reasonable gas permeability yields. This simple strategy may be readily applied toward preparing more extraordinary polymer membranes for CO₂ separation applications.

4. EXPERIMENTAL SECTION

4.1. Materials. 2-Fluoronitrobenzene, 4-fluoronitrobenzene, and trifluoroacetic acid were purchased from Oakwood Chemical. Imidazole (99%) and 1,10-dibromodecane (>97%) were purchased from Aldrich. Potassium carbonate (99%, anhydrous) and Pd/C (10% on C, type 487) were purchased from BeanTown Chemical. Paraformaldehyde (>97%) was obtained from Alfa Aesar. α, α’-Dichloro-p-xylene (>98%) was...
purchased from TCI. Lithium bis-trifluoromethanesulfonylimide (HQ-115) was purchased from 3M. Ethanol (200 proof), N-

methylpyrrolidone (NMP) (ACS grade), and dimethylacetate-

dime (DMAc) (ACS grade) were purchased from VWR. Celite 545 was purchased from Acros Organics. All other chemicals, unless otherwise noted, were obtained from commercial sources and used as received.

4.2. Characterization. 1H NMR spectra were obtained on a Bruker Avance (500 MHz) instrument using DMSO-δ6 as a reference or internal deuterium lock. FT-IR spectra of the materials were recorded using a Perkin Elmer Spectrum 2 ATR-FTIR spectrometer in the range of 4000–400 cm−1. Molar masses were determined by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS, Bruker UltraTRIFT spectrometer).

4.3. Synthesis of Imidazole-Mediated TB-Based Ionone Polymers (Im-TB-Ionenes). 4.3.1. Synthesis of Imidazole–Aniline Derivatives (IIa and IIb). For preparing the ortho derivative (IIa), imidazole (24.125 g, 354 mmol), 2-

fluoronitrobenzene (2-FNB, 25.000 g, 177 mmol), and potassium carbonate (K2CO3, 26.936 g, 195 mmol) were added to the heavy-walled pressure vessel (Ace Glass) sealed with a threaded PTFE cap and a DuPont ask with 250 mL of DMSO to a 1000 mL round-bottom flask equipped with a magnetic stir bar. Then, the vessel was capped with a rubber stopper and vented with a needle through the cap to prevent the buildup of pressure in the flask while stirring for 24 h.

The reaction was set to stir with a H2 feed (30 psi) for 48 h. The contents of the reaction were filtered through Celite to isolate the Pd/C for disposal, and the EtOH filtrate was transferred to a round-bottom flask. The solvent was removed via rotary evaporation, and the reduced product was dried under vacuum at 60 °C overnight to yield an off-white solid (17.621 g, 77%). 1H NMR (500 MHz, DMSO-δ6) δ 8.05 (s, 2H, J = 3.7, 2 × N=N−CH−N), 7.60 (s, 2H, J = 7.4, 2 × N−CH=), 7.21–6.94 (br signal, 2H, 2 × N=CH−N, 6H, 6 × ArH), 4.37–4.29 (br signal, 4H, 2 × N−CH=, 2 × N−CH−N), and 3.24 (s, 2H, 2 × N=CH2−). 4.3.3. Synthesis of Four Im-TB-Ionenes. To a DMF (50 mL) solution of Im-TB IIa or IIb (4 g, 11.29 mmol), the corresponding equimolar cuminomeron (11.29 mmol, 1.98 g for α,α′-dichloro- p-xylene (DCXy) and 3.39 g for 1,10-dibromo-

decane (DBC10) was added into a heavy-walled round-bottom flask (Ace Glass) equipped with a magnetic stir bar. Then, the vessel was sealed with a threaded PTFE cap and a DuPont Kalrez O ring.

The reaction mixture was heated to 110 °C and allowed to stir for 24 h. After this time, the precipitated polymer product was cooled to room temperature, the remaining DMF was decanted, and deionized H2O was added directly to the flask. The vessel was heated to 40 °C while stirring to dissolve the dark brown solids. LiTf2N (8.1g, 28.2 mmol) was dissolved in 200 mL of DI water in a 500 mL Erlenmeyer flask, and the dissolved polymer product from the flask was poured into the aqueous LiTf2N solution, whereupon a precipitate immediately formed. The mixture was vigorously stirred with an overhead mechanical stirrer for 1 h, and the polymer was collected by filtration and dried in a vacuum oven for 36 h at 80 °C to give the desired Im-TB-Ionene polymer. 4.3.2. Synthesis of Tröger’s Base-Containing Imidazole Monomers (Im-TB, IIa, and IIIb). Following a literature method for the preparation of ortho and para Im-TBs,8 cooled (−15 °C) trifluoroacetic acid (200 mL) was added to IIa or IIb (10 g, 62.82 mmol) at −15 °C; subsequently, p-toluenesulfonamide (4.72 g, 157.1 mmol) was added to the reaction mixture and allowed to stir at room temperature for 40 h. After the reaction, the resultant mixture was quenched by pouring into it crushed ice (900 g) followed by the addition of 30% aqueous ammonia solution (150 mL). The organic components were extracted with dichloromethane (3 × 200 mL), washed with brine solution, and dried over anhydrous MgSO4, and the solvent was evaporated under reduced pressure to obtain a crude gumy compound. The product was purified by recrystallization from a MeOH–DCM mixture to give off-white crystals.

IIa (off-white crystals): Yield (75%). 1H NMR (DMSO-δ6) δ 8.05 (s, 2H, J = 3.7, 2 × N=N−CH−N), 7.60 (s, 2H, J = 7.4, 2 × N−CH=), 7.21–6.95 (br signal, 2H, 2 × N=CH−N, 6H, 6 × ArH), 4.38–4.30 (br signal, 4H, 2 × N−CH=, 2 × N−CH−N), and 3.24 (s, 2H, 2 × N=CH2−).

IIb (pale yellow crystals): Yield (72%). 1H NMR (DMSO-δ6) δ 8.05 (s, 2H, J = 3.7, 2 × N=N−CH−N), 7.60 (s, 2H, J = 7.4, 2 × N−CH=), 7.21–6.95 (br signal, 2H, 2 × N=CH−N, 6H, 6 × ArH), 4.38–4.30 (br signal, 4H, 2 × N−CH=, 2 × N−CH−N), and 3.24 (s, 2H, 2 × N=CH2−).
2H, 2 × C−CH$_2$−C), and 1.37 (s, 16H, 16 × C−CH$_2$−C); (FT-IR)/cm$^{-1}$ 3082, 2860, 1690, 1480, 1320, 1190, 1050, 750, and 640.

[Im-TB(p)-Xy][Tf$_2$N]: Yield (85%). $^1$H NMR (500 MHz, DMSO-d$_6$) δ 10.17−9.95 (br signal, 2H, 2 × N≡CH−N) 8.63−8.28 (br signal, 4H, 4 × N−CH−C) 8.10−7.62 (br signal, 10H, ArH) 5.53−5.16 (br signal, 8H, 2 × N−CH$_2$−C, 2 × N−CH−N and 4 × ArCH$_2$), and 3.61−3.5 (br signal, 2H, 2 × N−CH$_2$−C); (FT-IR)/cm$^{-1}$ 3082, 1690, 1480, 1320, 1190, 1050, 750, and 640.

[Im-TB(p)-C$_6$][Tf$_2$N]: Yield (82%). $^1$H NMR (500 MHz, DMSO-d$_6$) δ 10.10−9.95 (br signal, 2H, 2 × N≡CH−N) 8.62−8.27 (br signal, 4H, 4 × N−CH−C) 8.09−7.60 (br signal, 10H, ArH) 4.30−4.17 (br signal, 6H, 4 × N−CH$_2$−C, 2 × N−CH−N), 3.58 (br signal, 2H, 2 × N−CH$_2$−C), 1.93 (s, 2H, 2 × C−CH$_2$−C), and 1.35 (s, 16H, 16 × C−CH$_2$−C); (FT-IR)/cm$^{-1}$ 3082, 2860, 1690, 1480, 1320, 1190, 1050, 750, and 640.

4.4. Synthesis Im-TB-Ionene Membranes. All the Im-TB-Ionene membranes were prepared by the solution-casting method using DMAc as solvent. The ionene polymers (1.2 g, 10 wt %) were dissolved in DMAc (10.8 g, 90 wt %) and sonicated at 30 °C until they formed completely homogeneous solutions. The resulting solutions were filtered through a cotton plug to ensure that the solution was free of any dust particles and poured onto a Teflon block. The Teflon plates were then placed in an oven, covered with aluminum foil having small holes, underwent slow solvent evaporation at 40 °C for 96 h, and further dried at 60 °C for 48 h in a vacuum oven. After becoming completely dried, the membranes were peeled off from the Teflon plate and then dried at ambient temperature. The membrane thickness was controlled to be 90 to 110 μm.

4.5. Membrane Characterization. The densities of the membranes (g cm$^{-3}$) were determined experimentally using a top-loading electronic Mettler Toledo balance (XP205, Mettler Toledo, Switzerland) coupled with a density kit based on Archimedes’ principle. The samples were weighed in air, and a known-density liquid (high-purity heptane) was used. All measurements were carried out at room temperature by the buoyancy method, and the density was calculated as follows:

$$\rho_{\text{polymer}} = \frac{W_0}{W_0 - W_1}$$

where $W_0$ and $W_1$ are the membrane weights in air and water, respectively. The liquid sorption of the Im-TB-Ionene membranes was not considered due to their extremely low swelling property.

The glass transition temperature ($T_g$) of each Im-TB-Ionene polymer was measured by DSC (TA Instruments, DSC Q20) from 20 to 300 °C with a scan rate of 10 °C min$^{-1}$ under N$_2$.

The wide-angle X-ray diffraction (WAXD) patterns of the membranes were measured using a Bruker D8 Discover diffractometer by employing a scanning rate of 4°/min in a 2θ range from 5 to 60° with a Co Kα1 X-ray (λ = 0.17886) source. The d spacing values were calculated using Bragg’s law ($d = \lambda/2\sin \theta$).

4.6. Gas Separation Measurements. The pure gas permeation measurements were performed to determine the gas separation abilities of the newly developed Im-TB-Ionene polymer membranes using high-vacuum time-lag apparatus based on the constant volume—variable pressure method. The construction and operation of this measurement unit were already discussed in our previous works. The only addition to the construction was that Im-TB-Ionene membranes were “masked” on both sides using adhesive aluminum tape to confine gas permeation through a fixed membrane area of 1/2 in. diameter, as described elsewhere. All measurements were ideal (i.e., single gas) and performed at 20 °C, and the feed pressure was ~3 atm (~45 psia) against an initial downstream vacuum (~0.01 psia). Pressures and temperatures were measured and recorded using the most recent version of LabVIEW software (National Instruments). After each measurement, the unit was held under dynamic vacuum (~0.01 psia) for at least 16 h at ambient temperature. The pressure rise versus time transient signals of the permeate side, equipped with a pressure transducer, were recorded and passed to a desktop computer through a shield data cable. The permeability coefficient was determined from the linear slope of the downstream pressure rise versus time plot (dp/dt) according to the following equation:

$$P = \frac{273}{76} \times \frac{VI}{AT_P} \times \frac{dp}{dt}$$

where $P$ is the permeability expressed in barrer (1 barrer = $10^{-10}$ cm$^3$STP cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$), $V$ (cm$^3$) is the downstream volume, $I$ (cm) is the membrane thickness, $A$ (cm$^2$) is the effective area of the membrane, $T$ (K) is the temperature of measurement, $p_i$ (Torr) is the pressure of the feed gas in the upstream chamber, and dp/dt is the rate of the pressure rise in the steady state. Assuming the solution–diffusion (S–D) mechanism, the diffusivity ($D_i$) of each gas was calculated from the time lag (Ω) and membrane thickness ($l$), and the solubility ($S_i$) of each gas was calculated as the quotient of $P_i$ and $D_i$. The pure gas permeability, solubility, and diffusivity selectivity ($α_{ij}$) for a given gas pair (e.g., CO$_2$/N$_2$) were calculated as $P_i/P_j$, $S_i/S_j$, and $D_i/D_j$, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03700.

Molar masses of ionene polymers with MALDI-TOF-MS spectra, NMR spectra of monomers, and solubility properties (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon the work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Separation Science program under award no. DE-SC0018181. Additional support from the NASA Marshall Space Flight Center (CAN 80MSFC18M0041) and NSF CHE-1726812 from the Major Research Instrumentation...
Program for purchase of the MALDI/TOF-TOF mass spectrometer is gratefully acknowledged.

**REFERENCES**


