

Rapid communication

# Improving CO<sub>2</sub> selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents

Jason E. Bara<sup>a,b</sup>, Christopher J. Gabriel<sup>b</sup>, Evan S. Hatakeyama<sup>a</sup>, Trevor K. Carlisle<sup>a</sup>,  
Sonja Lessmann<sup>b</sup>, Richard D. Noble<sup>a,\*</sup>, Douglas L. Gin<sup>a,b,\*\*</sup>

<sup>a</sup> Department of Chemical & Biological Engineering, University of Colorado, Boulder, CO 80309-0424, United States

<sup>b</sup> Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO 80309-0215, United States

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## Abstract

Solid, polymer membranes fabricated from room-temperature ionic liquid monomers containing oligo(ethylene glycol) or nitrile-terminated alkyl substituents tethered to imidazolium cations were found to exhibit ideal CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation factors significantly greater than those with comparable length *n*-alkyl substituents, with similar CO<sub>2</sub> permeability. Polymers containing these functional groups exhibited CO<sub>2</sub>/N<sub>2</sub> gas separation performance exceeding the “upper bound” of a “Robeson Plot”.

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## 1. Introduction

The purification of flue gas streams (CO<sub>2</sub>/N<sub>2</sub>) and sweetening of natural gas (CO<sub>2</sub>/CH<sub>4</sub>) have been carried out in industry and researched using many different methods and materials [1,2]. In recent years, room-temperature ionic liquids (RTILs) have gained notoriety as “green” solvents and materials for these applications [3–6]. As neat fluids, RTILs could be used as non-volatile [7], inflammable [8] solvents for gas absorption [3–6] or processed into supported ionic liquid membranes for gas or liquid separations (SILMs) [9,10]. Given the modular nature of RTILs (especially imidazolium salts), they can be also formed into a thin, solid film when polymerized together via the cation and/or anion [11–13] and used as gas separation membranes [13]. Previously, we reported on the use of a series of polymerized RTILs (poly(RTILs)) for this application [13]. These polymers featured varying alkyl-imidazolium salts

tethered to a polystyrene or polyacrylate backbone. Gas pair separation was achieved through a favorable solubility difference for CO<sub>2</sub>/N<sub>2</sub> separation and solubility and diffusion selectivity contributions for CO<sub>2</sub>/CH<sub>4</sub> [13]. A trade-off between flux and selectivity was observed for increasing lengths of alkyl substituents. While these membranes exhibited lower gas fluxes than SILMs, poly(RTILs) also featured increased mechanical strength [9,13,14]. Separately, we identified that the inclusion of a polar, oligo(ethylene glycol) (i.e. OEG) substituent on the cation of imidazolium-based RTILs significantly increased separation selectivity relative to imidazolium salts with pendant alkyl chains [15], which have typically been studied for gas separation applications [3–6]. OEG chains are not the only polar groups that can be easily tethered to imidazolium cations [16]. Alkyl-terminated nitrile groups (C<sub>*n*</sub>CN) are another polar group of interest that can have pronounced effects on gas separations in polymer membranes [17]. Herein, we demonstrate improved performance in poly(RTIL) gas separation membranes by synthesizing and evaluating the gas separation performance of a second-generation of functionalized poly(RTIL)s using imidazolium-based monomers containing either OEG or C<sub>*n*</sub>CN units (Fig. 1).

These poly(RTIL)s functionalized with polar groups were found to have ideal CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation factors

\* Corresponding author. Tel.: +1 303 492 6400.

\*\* Corresponding author at: Department of Chemical & Biological Engineering, and Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO 80309-0424, United States. Tel.: +1 303 735 1107.

E-mail addresses: [NobleR@colorado.edu](mailto:NobleR@colorado.edu) (R.D. Noble),  
[Gin@spot.colorado.edu](mailto:Gin@spot.colorado.edu) (D.L. Gin).

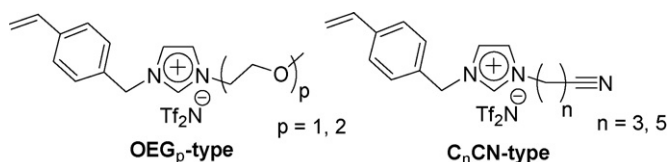


Fig. 1. Polymerizable RTIL monomers functionalized with polar substituents.

ca. 50% greater than those with comparable length alkyl substituents, with similar levels of  $\text{CO}_2$  permeability [13]. For both classes of poly(RTIL) membranes, the  $\text{CO}_2/\text{N}_2$  gas separation performance exceeds the “upper bound” of a “Robeson Plot” [18]. The inclusion of polar groups on poly(RTILs) and their impact on gas separations demonstrates that opportunities exist for the tailoring of polymerizable imidazolium cations to obtain new RTIL-based materials with enhanced gas separation capabilities.

## 2. Experimental

### 2.1. Materials

All chemicals were used as received, except anhydrous THF, which was prepared by passing it through a column of activated  $\text{Al}_2\text{O}_3$ . 4-Chloromethylstyrene was purchased as a yellow liquid from TCI America (Portland, OR, USA). Lithium bis(trifluoromethane)sulfonimide ( $\text{LiTf}_2\text{N}$ ) was purchased from 3 M (St. Paul, MN, USA). All other chemicals were purchased from Sigma–Aldrich (Milwaukee, WI, USA). All gases were purchased from AirGas (Radnor, PA, USA) and were of at least 99.99% purity.

### 2.2. Synthesis of RTIL monomers

RTIL monomers were synthesized according to the following Scheme 1.

#### 2.2.1. Synthesis of functionalized imidazoles (**1a,b** & **2a,b**): general procedure

OEG-functionalized imidazoles (**1a,b**) were prepared according to a procedure we have detailed in a prior work [15].

$\text{C}_n\text{CN}$ -functionalized imidazoles (**2a,b**) were prepared similarly by the following method.

$\text{NaH}$  (3.67 g, 91.8 mmol, 60 wt% in mineral oil) was added to an air and water free 250 mL, 3-neck round bottom flask equipped with stir bar, reflux condenser and argon purge. Anhydrous THF (~125 mL) was added to the vessel. Imidazole (5.00 g, 73.4 mmol) was slowly added to the stirring mixture. Upon addition of imidazole, gas bubbles became visible in the reaction, indicating evolution of  $\text{H}_2$  as a consequence of the acid–base neutralization occurring. The reaction was warmed to  $40^\circ\text{C}$ , sealed under argon and stirred for 1 h. After this time had passed, a bromoalkylnitrile (73.4 mmol) was added to the reaction via syringe. The reaction was heated to reflux ( $65^\circ\text{C}$ ) and stirred under argon for an additional 16 h.

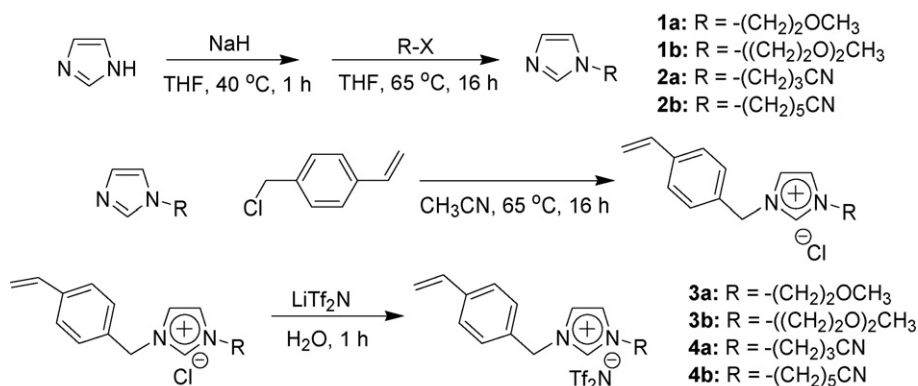
The reaction was then allowed to cool to room temperature, and the solids filtered and washed with THF (250 mL). The solvent was removed via rotary evaporation until a viscous oil remained. MeOH (250 mL) was added to the crude product and the MeOH phase washed with hexanes ( $3 \times 125$  mL). MeOH was removed via rotary evaporation and the remaining brown oils further dried under vacuum (100 mTorr) at room-temperature overnight.

*1-Butanenitrileimidazole 2a*: yield = 5.75 g, 57.8%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.31 (pentet, 2H), 2.0 (m, 2H), 2.19 (m, 2H), 3.99 (t, 2H), 4.17 (t, 2H), 6.83 (dd, 1H), 6.95 (dd, 1H), 7.38 (dd, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.4, 26.8, 45.0, 118.5, 118.8, 130.1, 137.3.

*1-Hexanenitrileimidazole 2b*: yield = 8.29 g, 69.2%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.39 (m, 2H), 1.60 (m, 2H), 1.75 (m, 2H), 2.28 (t, 2H), 3.90 (t, 2H), 6.85 (s, 1H), 6.98 (s, 1H), 7.41 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  17.2, 25.0, 25.8, 30.5, 46.8, 118.9, 119.6, 129.6, 137.2.

#### 2.2.2. Synthesis of functionalized imidazolium-based RTIL monomers (**3a,b** & **4a,b**): typical procedure

Photopolymerizable RTIL monomers were also synthesized according to previous procedures that our group has developed [13,14], but with additional purification steps added. The synthetic method and thorough purification are outlined here for the convenience of the reader.



Scheme 1. Synthesis of RTIL monomers containing polar substituents.

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