Supporting information for

High Performance Membranes Based on Ionic Liquid Polymers for CO_2 Separation from the Flue Gas

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Experimental

1. Monomer Synthesis

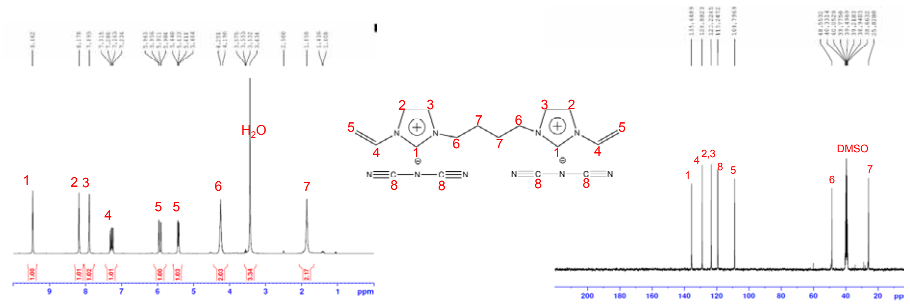
Silver Dicyanamide

Silver nitrate (76.32 g, 449.2 mmol) was dissolved in deionized water (100 mL). Sodium dicyanamide (40 g, 449.2 mmol) was also dissolved in deionized water (100 mL). The two solutions were mixed together with mega-stirred overnight at room temperature. A white precipitate (silver dicyanamide) was formed, filtered and collected. The white precipitate was washed with deionized water twice to eliminate the residual sodium nitrate. The resulting material was dried in a vacuum oven at 80 °C overnight to remove the trace amount of water. Silver dicyanamide (77 g) was obtained as a white powder with a yield of 99 %.

1-ethyl-3-methylimidazolium dicyanamide ([emim][dca])

1-methylimidazole (10 g, 121.8 mmol) was mixed with bromoethane (14.6 g, 134 mmol) in a 250 mL flask. The mixture was mega-stirred and heated at 40 °C in an oil bath for 24 hours. A yellowish material was formed. The compound was dissolved in 50 mL deionized water and then extracted five times using ethyl acetate (10 mL each time). The aqueous phase was collected, vacuum evaporated and placed in a vacuum oven at 50 °C for 24 hours to remove the trace amount of water. 1-ethyl-3-methylimidazolium bromine (20 g) was acquired as a slightly yellowish liquid with a yield of 86 %. 1-ethyl-3-methylimidzolium bromine (20 g, 104.7 mmol) was dissolved in 100 mL deionized water in a 250 mL flask and silver dicyanamide (20 g, 115 mmol) was added to this solution. The slurry was magnetically stirred and heated at 50 °C for 24 hours. During this process, the color of solid changed to yellow indicating the formation of silver bromide. The slurry was filtered and the liquid phase was collected as well as vacuum evaporated to obtain a slight yellowish liquid. The product was dried in a vacuum oven at 50 °C for 24 hours to remove the trace amount of water and give a yield of 91 % (16.9 g).

Using the same approach, the following vinyl-functional ionic liquids including [veim][dca], [vbim][dca], [vhim][dca] and [C_4(dvim)$_2$][dca] were successfully synthesized. The molecular structures of all synthesized monomers were verified using Nuclear Magnetic Resonance (NMR) spectra that were given in Figure 1.



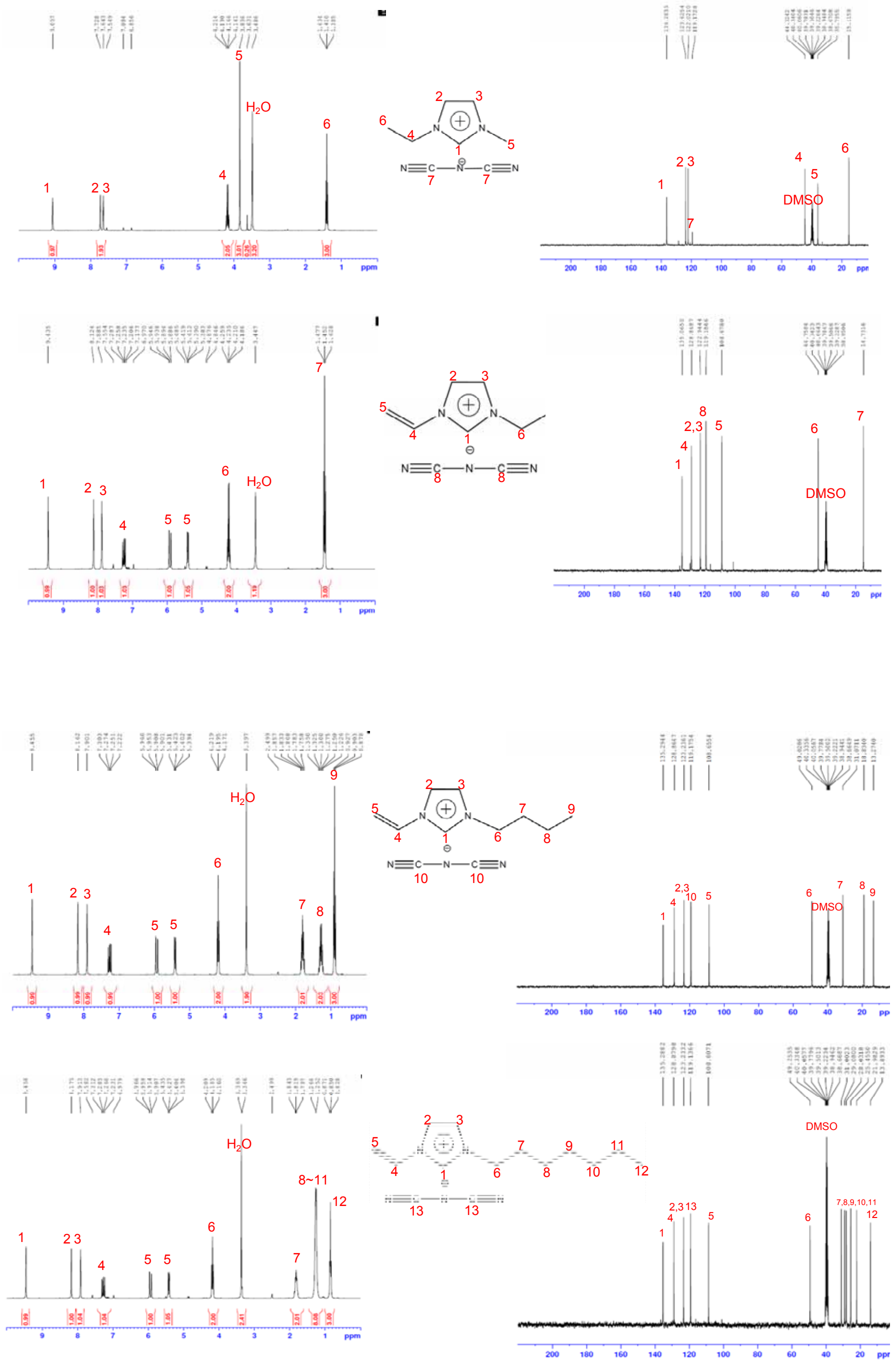


Figure 1: ^{1}H-NMR spectra (left) and ^{13}C-NMR spectra (right) of the synthesized RTILs.

2. Polymer Composite Synthesis

Synthesis of the Pristine Poly (RTIL) and Poly (RTIL) Films

4.5 g of vinyl-RTIL ([veim][dca], [vbim][dca] or [vhim][dca]) were mixed with 0.5 g of the crosslinker [C_4(dvim)$_2$][dca] and 0.05 g of the photo initiator 1-hydroxycyclohexyl phenyl ketone in a flask. 10 mL of ethanol was added into the flask to facilitate mixing. The solution was vacuum evaporated to remove ethanol. Then the RTIL solution was placed between a silicon wafer and a quartz glass. The thickness of the RTIL solution was controlled by a few pieces of alumina tapes inserted between them (i.e., wafer and quartz plate). The wafer-RTIL-quartz sandwich was placed in a UV-crosslinker purchased from Vilber Lourmat Corporation (Marne-la-vallée Cedex1, France) where the quartz face was kept 5 cm away from the UV-bulb (BLX-312 5×8w-312nm). The UV-polymerization was carried out for 30 min. Once the poly (RTIL) film was formed, it was peeled off from the silicon wafer using a razor blade. The thicknesses of all films were controlled from 150 to 200 um.

Synthesis of the Poly(RTIL)-RTIL Composite Films

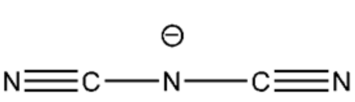
To synthesize the poly ([veim][dca])-[emim][dca] composite film, 4.5 g of [veim][dca] was mixed with 0.5 g of [C_4(dvim)$_2$][dca], 5 g of [emim][dca] and 0.05 g of 1-hydroxycyclohexyl phenyl ketone in a 50 mL flask. 10 mL of ethanol was first added in the solution to facilitate mixing and then it was removed using a Rota evaporator. The RTIL mixture formed a composite film by a UV-polymerization through the same procedure of the synthesis for the pristine poly (RTIL) films. The composite membrane consisted of polymerized [veim][dca]-[C_4(dvim)][dca] (crosslinker), while [emim][dca] remained as the free ionic liquid within the polymer matrix. Using this method, a series of poly (RTIL)-RTIL composite films with a concentration of free RTILs at 50 wt % were synthesized including: poly ([veim][dca])-[emim][dca], poly ([vbim][dca])-[emim][dca], poly ([vhim][dca])-[emim][dca], poly ([veim][dca])-[emim][$B(CN)_4$], poly ([vbim][dca])-[emim][$B(CN)_4$], poly ([vhim][dca]) -[emim][$B(CN)_4$], poly ([veim][dca])-[emim][BF_4], poly ([vbim][dca])-[emim][BF_4] and poly ([vhim][dca])-[emim][BF_4]. In addition, two poly(RTIL)-RTIL composites with 66.6 wt % free RTILs were also synthesized which were poly ([vbim][dca])-[emim][$B(CN)_4$] and poly ([vbim][dca])-[emim][dca].

3. Calculation the van der Waals volumes of RTILs

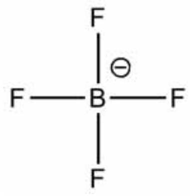
Polymer van der Waals volumes were calculated using Bondi's group contribution method.[1] As listed in Table 1, the van der Waals volumes of –H, -CH-, -CH_2-, CH_2=CH- are from Bondi's.[1] The van der Waals volume of [dca]$^-$ was calculated using the following method. As shown in Figure 2, the [dca]$^-$ anion contained two –CN groups and one –N- group. According to Bondi's report [1], the van der Waals volumes of –C≡N and –N- groups were 14.7 and 4.33 cm^3/mol respectively. Therefore, the van der Waals volume of [dca]$^-$ anion was $14.7 \times 2 + 4.33 = 33.73$ cm^3/mol. The van der Waals volume of imidazole group was acquired in literature[2] in which the van der Waals volume of imidazole was reported to be 90 Å^3. And the value in unit of cm^3/mol was $6.02 \times 10^{23} \times 90 \times (10^{-8})^3 = 54.2$ cm^3/mol. The van der Waals volume of the imidazolium (imidazole without the H attached to N in the imidazole ring) was $54.2 - 3.44 = 50.76$ cm^3/mol.

Table 1: Van der Waals volumes of groups used in this study

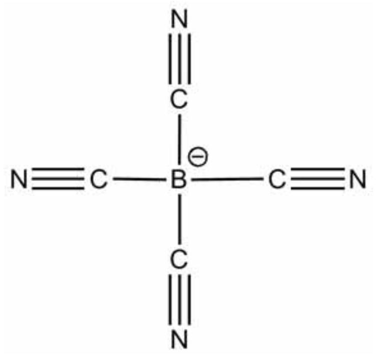
Group	V_w (cm^3/mol)
-H	3.44
-CH-	6.79
$-CH_2-$	10.23
$CH_2=CH-$	20.41
imidazolium	50.76
$[BF_4]^-$	31.70
$[dca]^-$	33.73
$[B(CN)_4]^-$	69.33



DCA anion



BF_4 anion



$[B(CN)_4]$ anion

Figure 2: The molecular structures of [dca], BF_4 and $[B(CN)_4]$ anions.

The van der Waals volume of the $[BF]_4^-$ group was not found in Bondi's report.[1] Therefore, it was calculated using the van der Waals radii of the atoms of Boron, Fluorine and the covalent bond distance of the B-F bond according to Bondi's method for the calculation of van der Waals volume of diatomic molecules.

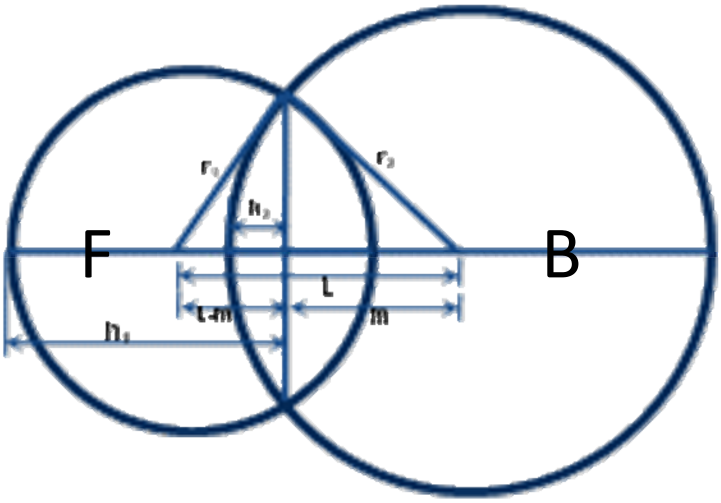


Figure 3: The molecular structure of B-F group from $[BF]_4^-$ anion. r_1, r_2 – van der Waals radii of Fluorine and Boron, L- covalent bond distance (distance between two centers of the circles), m- auxiliary parameter, h_1, h_2- height of sphere segments.

The van der Waals radii of Boron (B), Fluorine (F) and the bond distance of B-F of the $[BF]_4^-$ anion [3] were 2 Å, 1.47 Å and 1.43 Å respectively. The volume of Boron atom was $\frac{4}{3} \times \pi \times (r_2)^3 = \frac{4}{3} \times 3.142 \times (2)^3 = 33.41$ Å^3. And that of Fluorine was $\frac{4}{3} \times \pi \times (r_1)^3 = \frac{4}{3} \times 3.142 \times (1.47)^3 = 13.27$ Å^3. The overlapped volumes were calculated as $\Delta V_{2-L} = \pi {h_2}^2 \left(r_2 - \frac{h_2}{3}\right) = 3.142 \times 0.64^2 \times \left(2 - \frac{0.64}{3}\right) = 2.3$ Å^3 and $\Delta V_{1-L} = \pi(2r_1 - h_1)^2 \left(r_1 - \frac{2r_1 - h_1}{3}\right) = 3.142 \times 1.4^2 \times \left(1.47 - \frac{1.4}{3}\right) = 6.1$ Å^3. Therefore, the van der Waals volume of $[BF]_4^-$ anion was $33.41 + 4 \times 13.27 - 4 \times (2.3 + 6.16) = 52.65$ Å^3 which was equal to $6.02 \times (10)^{23} \times 52.65 \times (10^{-8})^3 = 31.70$ cm^3/mol. For $[B(CN)_4]^-$ anion, the van der Waals radii of C and B-(CN) bond distance was 1.70 and 1.59 Å.[4] The overlapped volume of Boron atom could be calculated as $\Delta V_{2-L} = \pi {h_2}^2 \left(r_2 - \frac{h_2}{3}\right) = 3.142 \times 0.86^2 \times \left(2 - \frac{0.86}{3}\right) = 3.98$ Å^3. The volume of un-overlapped Boron atom was $33.41 - 4 \times 3.98 = 17.49$ Å^3 which was equal to $6.02 \times (10)^{23} \times 17.49 \times (10^{-8})^3 = 10.53$ cm^3/mol. The van der Waals volume of -(CN) was 14.7 cm^3/mol reported by Bondi.[1] Therefore, the van der Waals volume of $[B(CN)_4]^-$ anion was $10.53 + 4 \times 14.7 = 69.33\ cm^3/mol$.

References

1 A. Bondi, *J. Phys. Chem.* 1964, **68**, 441-451.

2 U. Constantino, M. A. Massucci, A. Ginestra, A. M. Tarola and L. J. Zampa, *Incl. Phenom.* 1986, **4**, 147-151.

3 J. L. Hoard and V. Blair, *J. Am. Chem. Soc.*, 1935, **57**, 1985-1988.

4 Bond distance of B-(CN) bond is estimated using the software “ChemBioOffice 2008”.