Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Data

Ionic liquids mediated solvothermal synthesis of the 4, 4′-methylenediphenyl diisocyanate (MDI) – an efficient and environment friendly process

Characterization of the reagents

4,4′-Diaminodiphenylmethane

Analysis of 4,4′-Diaminodiphenylmethane by ^{1}H NMR resulted in a spectrum containing the following peaks: 6.98(4 H, d, C=CH), 6.51 (4 H, d, *N*-C=CH), 6.27 (4 H, s, NH_2), 3.96 (2 H, s, CH_2); IR (neat): 3,415cm^{-1} (NH), 3,210cm^{-1} (CH ring), 3,033cm^{-1} (CH alkyl), 2,901cm^{-1} (CH alkyl), 2,866cm^{-1} (CH alkyl), 1,615cm^{-1} (C=C, N-H), 1,582cm^{-1} (C=C), 1,434cm^{-1} (CH alkyl deform.), 1,317cm^{-1} (C-N), 1,127cm^{-1} (CH ring deform.), 909 and 749cm^{-1} (Ar-H).

Dimethyl carbonate(DMC)

Analysis of dimethyl carbonate (DMC) by ^{1}H NMR resulted in a spectrum containing the following peaks: δ (ppm) = 3.78 (6 H, s, O-CH_3); IR (neat): 2,963cm^{-1} (CH alkyl), 2,857cm^{-1} (CH alkyl), 1,894cm^{-1} (O=C), 1,606cm^{-1} (O=C), 1,120 and 1,1023cm^{-1} (C-O).

Synthesis of the ionic liquids

N-methylimidazole was distilled under reduced pressure prior to use and stored at room temperature. bromobutane, bromooctane, ethylchloroacetate and sodium tetrafluoroborate were used as received. other chemicals such as acetone and acetonitrile was dried and deoxygenated using a solvent purification system.

The synthesis of the ionic liquids was performed in a high pressure polyethylene reactor. The reactions were performed in polyethylene vessels (150 to 250 mL) sealed with a septum. The pressure of the system was controlled by a load cell connected to the pressure vessel and the temperature of the reaction mixture was monitored using a calibrated infrared sensor, which is located at the side of the reaction vessel. All experiments were performed using a Teflon-coated magnetic stirring bar.

An Infra-Red Vortex-Evaporator connected to a PoleStar Coldtrap System was used for drying the ionic liquids under vacuum. In this system the samples and a steel rack holder are heated by infrared light. The drying temperature was measured with a sensor connected to the steel rack. The maximum temperature for this system is 393K. To remove water after the anion exchange process a freeze dryer Alpha 1-2 LD from Christ was used. The dried ionic liquids were stored under dry conditions in an Ar-filled glove box.

Production and characterization of the synthesized ionic liquids

1-butyl-3-methylimidazolium bromide

[C_4mim]Br was prepared by the reaction of N-methylimidazole and bromobutane. N-methylimidazole(0.2 mol) and bromobutane (0.2 mol) were mixed and stirred in a high pressure polyethylene reactor at 80°C for 4h. The resultant yellow liquid product then was dried in a vacuum at 80 °C for 4 h.

Analysis of [C_4mim]Br by ^{1}H NMR (neat sample, dried, ppm) resulted in a spectrum containing the following peaks: δ (ppm) = 9.329 (1 H, s), 7.831 (1 H, s), 7.752(1 H, s), 4.169 (2 H, t, *N*-CH_2), 3.863 (3 H, s, *N*-CH_3), 1.772 (2 H, m, CH_2), 1.248 (2 H, m, CH_2), 0.895 (3 H, t, CH_3); IR (neat): 3,424cm^{-1} (OH), 3,116cm^{-1} (CH ring), 3,043cm^{-1} (CH alkyl), 2,987cm^{-1} (CH alkyl), 2,864cm^{-1} (CH alkyl), 2,121cm^{-1} (N=C), 1,667cm^{-1} (C=C, C=N), 1,556cm^{-1} (C-C, C-N), 1,432cm^{-1} (CH alkyl deform.), 1,125cm^{-1} (CH ring deform.).

1-butyl-3-methylimidazolium tetrafluoroborate

Sodium tetrafluoroborate (0.02 mol) was added into [bmim]Br (0.02mol) in a high pressure polyethylene reactor equipped with a stirrer. Next, the solution was stirred for 4 h at 80°C. The precipitate of NaBr was filtered out, and the remaining water in the filtrate was removed by vacuum distillation at 120°C for 4h. Finally, the resultant neutral ionic liquid [bmim]BF_4 was dried in vacuum.

Analysis of [C_4mim]BF_4 by H NMR (neat sample, dried, ppm) resulted in a spectrum containing the following peaks: δ (ppm) = 9.082 (1 H, s), 7.738 (1 H, s), 7.673 (1 H, s), 4.152 (2 H, t, *N*-CH_2), 3.836 (3 H, s, *N*-CH_3), 1.739 (2 H, m, CH_2), 1.245 (2 H, m, CH_2), 0.893 (3 H, t, CH_3); IR (neat): 3,665 (OH), 3,574 (OH), 3,142 (CH ring), 3,110 (CH ring), 2,954 (CH alkyl), 2,933 (CH alkyl), 2,866 (CH alkyl), 1,654 (C=C, C=N), 1,562 (C-C, C-N), 1,467(CH deform. alkyl), 1,155 (CH deform. ring), 1,060 (B-F) cm^{-1}.

1-octyl-3-methylimidazolium bromide

The same procedure was used as for [C_4mim]Br with the substitution of bromooctane for bromobutane. N-methylimidazole(0.2 mol) and bromooctane (0.2 mol) were mixed and stirred in a high pressure polyethylene reactor at 80°C for 4h. The resultant liquid product then was dried in a vacuum at 80°C for 4h.

Analysis of [C_8mim]Br by H NMR resulted in a spectrum containing the following peaks: δ (ppm) = 9.012 (1 H, s), 7.635 (1 H, s), 7.562 (1 H, s), 4.105 (2 H, t, *N*-CH_2), 3.756 (3 H, s, *N*-CH_3), 1.711 (2 H, m, CH_2), 1.092 (2 H, m, CH_2), 1.045 (2 H, m, CH_2), 0.676 (3 H, t, CH_3).

1-octyl-3-methylimidazolium tetrafluoroborate

The same procedure was used as for [C_4mim]BF_4. Analysis of [C_8mim]BF_4 by H NMR gave spectra containing no extraneous peaks that were not assigned to the [C_8mim]Br sample. However, analysis of [C_8mim]BF_4 by IR gave a spectrum identical to that for [C_8mim]BF_4 with the addition of a small, broad peak at 1,060 (B-F) cm^{-1}.

1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate ([EAmim]BF_4)

Analysis of [EAmim]BF_4 by ^{13}C NMR ($CDCl_3$, 101 MHz) resulted in a spectrum containing the following peaks: δ (ppm) = 166.2, 138.5, 123.6, 123.0, 62.4, 50.3, 36.6 and 14.2 ppm.

Isothermal gravimetrical analyses of ionic liquids

Isothermal analyses of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate at various temperatures are shown in Fig. S1. It can be seen that in 2 hours just 1 % can be lost at temperatures of 230°C. With the temperature raised to 330°C, weight loss of ionic liquids can get 2.5% after heating for the same time. When temperature is furthermore up to 330°C, the weight loss corresponding increased to 4.8% after heated at 120min.

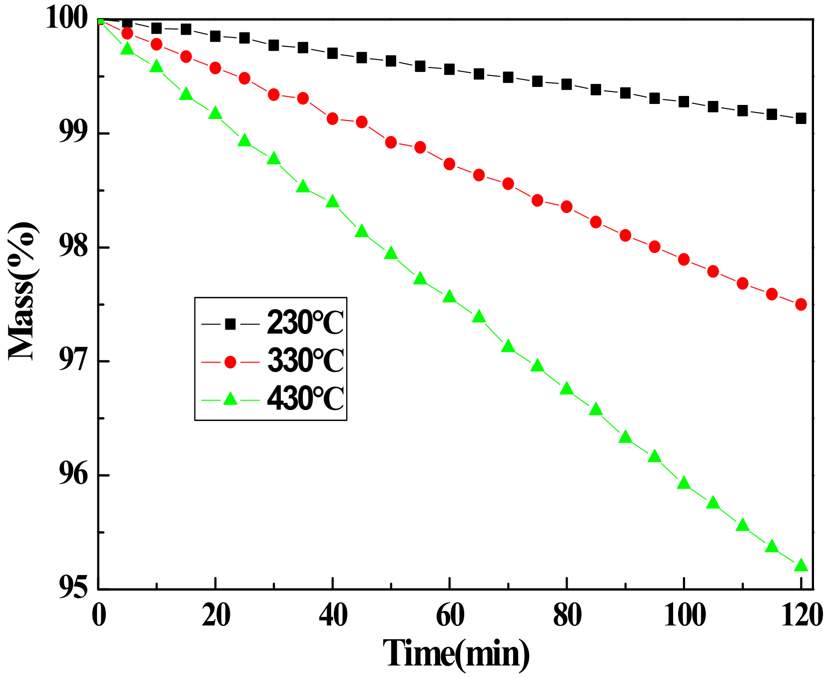

Fig. S1 Isothermal gravimetrical analyses of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate at various temperatures, N_2-atmosphere.

Characterization of the recovered ionic liquids

The peaks at 3,130 and 2,978cm^{-1} are assigned to stretching vibration of C-H and 1,754cm^{-1} corresponds to C=O. Moreover, the peaks at 1,585 and 1,378cm^{-1} are the skeleton vibration of C=C and stretch vibration of C-N. The characteristic peaks at

1034cm^{-1} are attributed to the B-F and the peaks appears at 625-520cm^{-1} are attributed to C-H stretching vibration. To observe the purity of the recycled [EAmim]BF$_4$ ^{1}H NMR analysis was provided and the results were presented in Fig. S2. The ^{1}H NMR data of δ = 9.04 (s, 1H), 7.70 (t, 2H), 5.21 (s, 2H), 4.20 (m, 2H), 3.89 (s, 3H), 2.49 (t, 1H) and 1.24 (m, 3H) correspond respectively to the hydrogen atom in [EAmim]BF$_4$. Based on the IR and ^{1}H NMR analysis, the recovered ionic liquids is identified as [EAmim]BF$_4$ with a higher purity of 99%.

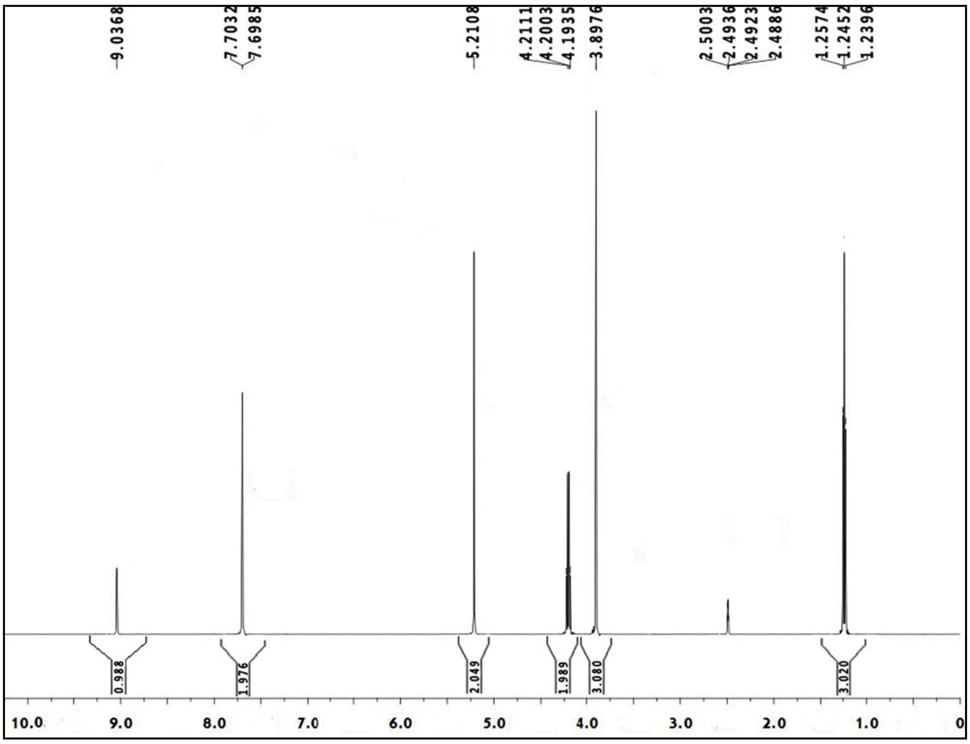

Fig. S2 ^{1}H NMR spectra of recovered [EAmim]BF$_4$ distilled at 90°C and subsequently dried in a vacuum drier at 120°C for 4h.