Supporting Information

Protic imidazolium cation-based ionic liquids show unexpected interfacial properties

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IL synthesis

1-Propyl-3-methylimidazolium bromide. Under inert atmosphere, in an oven dried round bottom flask , (250 mL) a solution of 1-methylimidazole (16.0 g, 195 mmol) in anhydrous toluene (15 mL) is treated with 1-bromopropane (24.5 g, 199 mmol) via cannula. The reaction is stirred at room temperature for 20 minutes and 70 ºC for 8 h. After completion the reaction mixture is concentrated, dissolved in acetonitrile and washed with diethyl ether to removed organic impurities to obtain the product as a viscous oil (38.0 g, 185 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.63 (s, 1H), 8.14 (d, *J* = 1.8 Hz, 1H), 8.06 (d, *J* = 1.8 Hz, 1H), 4.42 (t, *J* = 7.1 Hz, 2H), 4.13 (s, 3H), 2.04 (q, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

1-Pentyl-3-methylimidazolium bromide. Under inert atmosphere, in an oven dried round bottom flask, (250 mL) a solution of 1-methylimidazole (10.2 g, 124 mmol) in anhydrous toluene (10 mL) is treated with 1-bromopentane (19.0 g, 126 mmol) via cannula. The reaction is stirred at room temperature for 20 minutes and 70 ºC for 5 h. After completion the reaction mixture is concentrated, dissolved in acetonitrile and washed with diethyl ether to removed organic impurities to obtain the product as a viscous oil (28.1 g, 120 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 1H), 1.76 (q, *J* = 7.6, 2H), 1.22 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H).

1-Heptyl-3-methylimidazolium bromide. Under inert atmosphere, in an oven dried round bottom flask, (250 mL) a solution of 1-methylimidazole (10.0 g, 122 mmol) in anhydrous toluene (10 mL) is treated with 1-bromoheptane (22.0 g, 123 mmol) via cannula. The reaction is stirred at room temperature for 20 minutes and 70 ºC for 5 h. After completion the reaction mixture is concentrated, dissolved in acetonitrile and washed with diethyl ether to removed organic impurities to obtain the product as a viscous oil (30.0 g, 115 mmol, 94%).^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s,1H), 7.84 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.75 (q, *J* = 7.4 Hz, 2H), 1.20 (m, 8H), 0.81 (t, *J* = 7.2 Hz, 3H).

1-Methyl-3-octylimidazolium bromide. Under inert atmosphere, in an oven dried round bottom flask, (250 mL) a solution of 1-methylimidazole (7.00 g, 85.0 mmol) in anhydrous toluene (15 mL) is treated with 1-bromooctane (16.8 g, 87.0 mmol) via cannula. The reaction is stirred at room temperature for 20 minutes and 70 ºC for 8 h. After completion the reaction mixture is concentrated, dissolved in acetonitrile and washed with diethyl ether to removed organic impurities to obtain the product as a viscous oil (21.7 g, 79.0 mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.27 (s, 1H), 7.82 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 1.5 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.75 (q, *J* = 7.3 Hz, 2H), 1.21 (m, 10H), 0.82 (t, *J* = 7.2 Hz, 3H).

1-Methyl-3-nonylimidazolium bromide. Under inert atmosphere, in an oven dried round bottom flask, (250 mL) a solution of 1-methylimidazole (7 g, 85 mmol) in anhydrous toluene (10 mL) is treated with 1-bromononane (18 g, 87 mmol) via cannula. The reaction is stirred at room temperature for 20 minutes and 70 ºC for 8 h. After completion the reaction mixture is concentrated, dissolved in acetonitrile and washed with diethyl ether to removed organic impurities to obtain the product as a viscous oil (23.4 g, 81.0 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.84 (d, *J* = 1.8 Hz, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.75 (q, *J* = 7.4 Hz, 2H), 1.21 (m, 12H), 0.80 (t, *J* = 7.2 Hz, 3H).

1-Decyl-3-methylimidazolium bromide. Under inert atmosphere, in an oven dried round bottom flask, (250 mL) a solution of 1-methylimidazole (7.29 g, 89.0 mmol) in anhydrous toluene (10 mL) is treated with 1-bromodecane (20.0 g, 90.0 mmol) via cannula. The reaction is stirred at room temperature for 20 minutes and 70 ºC for 8 h. After completion the reaction mixture is concentrated, dissolved in acetonitrile and washed with diethyl ether to removed organic impurities to obtain the product as a viscous oil (23.4 g, 81.0 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.29 (s, 1H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 2H), 1.75 (q, *J* = 7.4 Hz, 2H), 1.21 (m, 14H), 0.82 (t, *J* = 7.2 Hz, 3H).

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-ethyl-3-methylimidazolium bromide (5.00 g, 26.2 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (7.60 g, 26.5 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (9.50 g, 24.3 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 3.82 (s, 3H), 1.39 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-propyl-3-methylimidazolium bromide (3.50 g, 17.1 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethyl)sulfonyl)amide (5.00 g, 17.4 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane and washed with water (3 * 30 mL) and concentrated down. The product is obtained as a clear liquid (6.67 g, 16.3 mmol, 95%).^{1}H NMR (400 MHz, DMSO-d_6) δ

9.08 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 4.10 (t, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 1.78 (q, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-butyl-3-methylimidazolium bromide (5.20 g, 23.7 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (7.00 g, 24.4 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (9.05 g, 21.5 mmol, 90%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.75 (q, *J* = 7.3 Hz, 2H), 1.24 (q, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-pentyl-3-methylimidazolium bromide (7.20 g, 30.9 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (9.00 g, 31.3 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (12.5 g, 28.8 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.78 (q, *J* = 7.2 Hz, 2H), 1.26 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-hexyl-3-methylimidazolium bromide (6.00 g, 24.3 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (7.00 g, 24.4 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (8.05 g, 22.4 mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.2 Hz, 2H), 1.25 (m, 6H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Heptyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-heptyl-3-methylimidazolium bromide (5.35 g, 20.5 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (6.00 g, 20.9 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (9.03 g, 19.5 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.77 (q, *J* = 7.4 Hz, 2H), 1.24 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-methyl-3-octylimidazolium bromide (4.20 g, 15.3 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (4.54 g, 15.7 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated

down. The product is obtained as a clear liquid (6.91 g, 14.5 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.3 Hz, 2H), 1.24 (m, 10H), 0.84 (s, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Methyl-3-nonylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-methyl-3-nonylimidazolium bromide (4.10 g, 14.2 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (4.10 g, 14.3 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (6.52 g, 13.3 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.24 (m, 12H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-decyl-3-methylimidazolium bromide (4.50 g, 14.8 mmol) is dissolved in water (100 mL), followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (4.30 g, 14.9 mmol). The reaction is stirred for 12 hr. the organic layer is extracted with dichloromethane, washed with water (3 * 30 mL), and concentrated down. The product is obtained as a clear liquid (7.03 g, 13.9 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.22 (m,14H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.84.

1-Ethyl-3-methylimidazolium methanesulfonate. In a round bottom flask (250 mL) a solution of 1-ethyl-3-methylimidazolium bromide (6.10 g, 31.9 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (79.3 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-ethyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (4.38 g, 31.9 mmol, 70% sol.) and stirred for 1 day. The solution is concentrated to obtain the product as a clear oil (6.40 g, 31.0 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21 (s, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 4.18 (q, *J* = 7.3 Hz, 2H), 3.84 (s, 3H), 2.33 (s, 3H), 1.38 (t, *J* = 7.3 Hz, 3H).

1-Propyl-3-methylimidazolium methanesulfonate. In a round bottom flask (250 mL) a solution of 1-propyl-3-methylimidazolium bromide (6.13 g, 29.9 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (79.5 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-propyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (4.10 g, 29.9 mmol, 70% sol.) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (6.40 g, 29.1 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 1.8 Hz, 1H), 4.11 (t, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.30 (s, 3H), 1.78 (q, *J* = 7.3 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).

1-Butyl-3-methylimidazolium methanesulfonate. In a round bottom flask (250 mL) a solution of 1-butyl-3-methylimidazolium bromide (6.00 g, 27.4 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (77.6 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-butyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (3.76 g, 27.4 mmol, 70% sol.) and stirred for 1 day. The solution is concentrated to obtain the product as a white solid (6.20 g, 26.5 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 7.78 (d, *J* = 1.4 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.31 (s, 3H), 1.74 (q, *J* = 7.2 Hz, 2H), 1.22 (h, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

1-Hexyl-3-methylimidazolium methanesulfonate. In a round bottom flask (250 mL) a solution of 1-hexyl-3-methylimidazolium bromide (6.00 g, 24.3 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (75.1 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-hexyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (3.33 g, 24.3 mmol, 70% sol.) and stirred for 1 day. The solution is concentrated to obtain the product as a clear oil (6.06 g, 22.9 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.31 (s, 3H), 1.75 (q, *J* = 7.5 Hz, 2H), 1.24 (m, 6H), 0.83 (t, 3H).

1-Heptyl-3-methylimidazolium methanesulfonate. In a round bottom flask (250 mL) a solution of 1-heptyl-3-methylimidazolium bromide (7.00 g, 26.8 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (77.1 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-heptyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (3.68 g, 26.8 mmol, 70% sol.) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (7.02 g, 25.3 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.30 (s, 3H), 1.75 (q, *J* = 7.2 Hz, 2H), 1.324 (m, 8H), 0.82 (t, *J* = 7.2 Hz, 2H).

1-Methyl-3-octylimidazolium methanesulfonate. In a round bottom flask (250 mL) a solution of 1-methyl-3-octylimidazolium bromide (7.00 g, 25.4 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (77.5 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-methyl-3-octylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (3.49 g, 25.4 mmol, 70% sol.) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (7.10 g, 24.5 mmol, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.30 (s, 3H), 1.75 (q, *J* = 7.3 Hz, 2H), 1.23 (m, 10H), 0.83 (t, *J* = 7.3 Hz, 3H).

1-Propyl-3-methylimidazolium trifluoromethanesulfonate. In a round bottom flask (250 mL) a solution of 1-propyl-3-methylimidazolium bromide (6.13 g, 29.9 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (79.7 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-propyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL

round bottom flask and treated with trifluoromethanesulfonic acid (4.49 g, 29.9 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (7.81 g, 28.4 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 4.11 (t, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.79 (h, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Pentyl-3-methylimidazolium trifluoromethanesulfonate. In a 250 mL flask, 1-pentyl-3-methylimidazolium bromide (7.20 g, 30.9 mmol)) in methanol (100 mL) is treated with Amberlite IRN-78 (89.0 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-Pentyl-3-methylimidazolium hydroxide. . The mixture is filtered to a 500 mL round bottom flask and treated with trifluoromethanesulfonic acid (4.64 g, 30.9 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (8.78 g, 93%).^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.78 (q, *J* = 7.2 Hz, 2H), 1.26 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Hexyl-3-methylimidazolium trifluoromethanesulfonate. In a round bottom flask (250 mL) a solution of 1-hexyl-3-methylimidazolium bromide (9.25 g, 20.3 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (40.8 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-hexyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (5.62 g, 37.4 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (11.1 g, 35.1 mmol, 94%) ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 1H), 1.76 (q, *J* = 7.2 Hz, 2H), 1.24 (m, 6H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Heptyl-3-methylimidazolium trifluoromethanesulfonate. In a round bottom flask (250 mL) a solution of 1-heptyl-3-methylimidazolium bromide (3.00 g, 14.7 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (40.6 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-heptyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (2.20 g, 14.7 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (4.51 g, 13.6 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.90 (s, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.77 (q, *J* = 7.2 Hz, 2H), 1.24 (m, 8H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Methyl-3-octylimidazolium trifluoromethanesulfonate. In a round bottom flask (250 mL) a solution of 1-methyl-3-octylimidazolium bromide (6.21 g, 22.6 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (82.5 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-methyl-3-octylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (3.39 g, 22.6 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (7.30 g, 21.2 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.24 (m, 10H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Methyl-3-nonylimidazolium trifluoromethanesulfonate. In a round bottom flask (250 mL) a solution of 1-methyl-3-nonylimidazolium bromide (6.17 g, 21.3 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (77.5 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-methyl-3-nonylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with trifluromethanesulfonic acid (3.20 g, 21.3 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (7.31 g, 20.4 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.24 (m, 12H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Decyl-3-methylimidazolium trifluoromethanesulfonate. In a round bottom flask (250 mL) a solution of 1-decyl-3-methylimidazolium bromide (6.15 g, 20.3 mmol) in methanol (100 mL) is treated with Amberlite IRN-78 (40.4 g) and oscillated for 17 hr, when no residual halide precipitation is observed by $AgNO_3$ test, to obtain 1-decyl-3-methylimidazolium hydroxide. The mixture is filtered to a 500 mL round bottom flask and treated with methanesulfonic acid (3.04 g, 20.3 mmol) and stirred for 1 day. The solution is concentrated to obtain the product as clear oil (7.21 g, 19.4 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.24 (m, 12H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.93.

1-Ethylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-ethylimidazole (3.56 g, 37.0 mmol) is dissolved in methanol (20 mL). Nitric acid (3.33 g, 2.36 mL, 37.0 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-ethylimidazole and stirred for 10 minutes, followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (10.6 g, 37.0 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (13.1 g, 35.8 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 4.19 (q, *J* = 7.3 Hz, 2H), 1.41 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Propylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-propylimidazole (2.00 g, 18.2 mmol) is dissolved in methanol (20 mL). Nitric acid (1.63 g, 1.16 mL, 18.2 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-propylimidazole and stirred for 10 minutes, followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (5.21 g, 18.2 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (6.83 g, 17.4 mmol, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 4.13 (t, *J* = 7.1 Hz, 2H), 1.80 (h, *J* = 7.3 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96. ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Butylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-butylimidazole (2.90 g, 23.3 mmol) is dissolved in methanol (20 mL). Nitric acid (2.10 g, 1.48 mL, 23.3 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-butylimidazole and stirred for 10 minutes, followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (6.70 g, 23.3 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (13.1 g, 35.8 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.63 (d, *J* = 1.7 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 1.77 (q, *J* = 7.2 Hz, 2H), 1.23 (h, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Pentylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-pentylimidazole (2.50 g, 18.1 mmol) is dissolved in methanol (20 mL). Nitric acid (1.63 g, 1.41 mL, 18.1 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-pentylimidazole and stirred for 10 minutes, followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (5.19 g, 18.1 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (13.1 g, 35.8 mmol, 97%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 4.17 (t, *J* = 7.3 Hz, 2H), 1.81 (q, *J* = 7.4 Hz, 2H), 1.28 (m, 2H), 1.24 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Hexylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-hexylimidazole (4.40 g, 28.9 mmol) is dissolved in methanol (20 mL). Nitric acid (2.60 g, 1.84 mL, 28.9 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-hexylimidazole and stirred for 10 minutes, followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (8.30 g, 28.9 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (12.1 g, 27.7 mmol, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.62 (d, *J* = 1.7 Hz, 1H), 4.15 (t, *J* = 7.3 Hz, 2H), 1.79 (q, *J* = 7.3 Hz, 2H), 1.21 (m, 6H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Heptylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-heptylimidazole (4.50 g, 27.1 mmol) is dissolved in methanol (20 mL). Nitric acid (2.44 g, 1.73 mL, 27.1 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-heptylimidazole and stirred for 10 minutes, followed by the addition of lithium bis((trifluoromethyl)sulfonyl)amide (7.77 g, 27.1 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (11.2 g, 25.0 mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.63 (d, *J* = 1.7 Hz, 1H), 4.15 (t, *J* = 7.3 Hz, 2H), 1.79 (q, *J* = 7.3 Hz, 2H), 1.24 (m, 8H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Octylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-octylimidazole (4.10 g, 22.7 mmol) is dissolved in methanol (20 mL). Nitric acid (2.05 g, 1.45 mL, 22.74 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-octylimidazole and stirred for 10 minutes, followed by the addition of lithium bis((trifluoromethyl)sulfonyl)amide (6.53 g, 22.7 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (10.1 g, 21.9 mmol, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.10 (t, *J* = 1.5 Hz, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.66 (t, *J* = 1.7 Hz, 1H), 4.16 (t, *J* = 7.3 Hz, 2H), 1.78 (q, 7.0 Hz, 2H), 1.22 (m, 12H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Nonylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-nonylimidazole (4.31 g, 22.2 mmol) is dissolved in methanol (20 mL). Nitric acid (1.99 g, 1.42 mL, 22.18 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-nonylimidazole and stirred for 10 minutes, followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (6.37 g, 22.2 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (10.2 g, 21.4 mmol, 97%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 14.20 (s, 1H), 9.12 (s, 1H), 7.78 (d, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 1.7 Hz, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 1.80 (q, *J* = 7.3 Hz, 2H), 1.24 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Decylimidazolium bis(trifluoromethylsulfonyl)imide. In a 250 mL flask, 1-decylimidazole (4.30 g, 20.6 mmol) is dissolved in methanol (20 mL). Nitric acid (1.86 g, 1.32 mL, 20.6 mmol, 70%), previously dissolved in 20 mL of methanol, is slowly added to the solution of 1-decylimidazole and stirred for 10 minutes, followed by the addition of lithium bis((trifluoromethyl)sulfonyl)amide (5.93 g, 20.6 mmol). The reaction is stirred for 12 hr, followed by concentration and dissolution in dichloromethane to precipitate $LiNO_3$. The salt is filtered out and the IL washed with water (3x * 5 mL), dried, and concentrated. The product is obtained as a clear liquid (9.60 g, 19.6 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.10 (s, 1H), 7.76 (d, *J* = 1.7 Hz, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 4.16 (t, *J* = 7.3 Hz, 2H), 1.78 (q, *J* = 7.3 Hz, 2H), 1.22 (m, 14H), 0.84 (t, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.96.

1-Hexylimidazole. In a flame dried 500 mL flask, under argon atmosphere, sodium hydride (6.46 g, 162 mmol, 60%) is slowly added to a solution of dry imidazole (10.0 g, 147 mmol) in dry THF (250 mL) at 0 °C. The reaction is left stirring at room temperature for 30 minutes and cooled again to 0 °C to add 1-bromohexane (24.2 g, 147 mmol). The reaction is quenched with water, extracted with THF, and concentrated. The concentrate is distilled at 90 °C and 0.75 mbar to obtain the product as a clear liquid (20.5 g, 135 mmol, 92%).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 (s, 1H), 7.10 (d, *J* = 1.3 Hz, 1H), 6.84 (d, *J* = 1.1 Hz, 1H), 3.89 (t, *J* = 7.1 Hz, 2H), 1.65 (q, *J* = 7.1 Hz, 2H), 1.19 (m, 5H), 0.80 (t, *J* = 7.1 Hz, 3H).

1-Heptylimidazole. In a flame dried 500 mL flask, under argon atmosphere, sodium hydride (7.05 g, 176 mmol, 60%) is slowly added to a solution of dry imidazole (10 g, 147 mmol) in dry THF (250 mL) at 0 °C.

The reaction is left stirring at room temperature for 30 minutes and cooled again to 0 °C to add 1-bromoheptane (26.3 g, 147 mmol). The reaction is quenched with water, extracted with THF, and concentrated. The concentrate is distilled at 94 °C and 0.75 mbar to obtain the product as a clear liquid (23.0 g, 138 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 (s, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 6.83 (d, *J* = 2.9 Hz, 1H), 3.89 (t, *J* = 7.1 Hz, 2H), 1.64 (q, *J* = 7.2 Hz 2H), 1.27 (m, 8H), 0.81 (t, *J* = 6.7 Hz, 3H).

1-Octylimidazole. In a flame dried 500 mL flask, under argon atmosphere, sodium hydride (6.46 g, 162 mmol, 60%) is slowly added to a solution of dry imidazole (10.0 g, 147 mmol) in dry THF (250 mL) at 0 °C. The reaction is left stirring at room temperature for 30 minutes and cooled again to 0 °C to add 1-bromooctane (26.3 g, 147 mmol). The reaction is quenched with water, extracted with THF, and concentrated. The concentrate is distilled at 98 °C and 0.75 mbar to obtain the product as a clear liquid (24.1 g, 133 mmol, 91%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 (s, 1H), 7.12 (d, *J* = 1.3 Hz, 1H), 6.85 (d, *J* = 1.1 Hz, 1H), 3.91 (t, *J* = 7.1 Hz, 2H), 1.66 (q, *J* = 7.2 Hz, 2H), 1.21 (m, 10H), 0.82 (t, *J* = 7.2 Hz, 3H).

1-Nonylimidazole. In a flame dried 500 mL flask, under argon atmosphere, sodium hydride (6.56 g, 164 mmol, 60%) is slowly added to a solution of dry imidazole (10.2 g, 149 mmol) in dry THF (250 mL) at 0 °C. The reaction is left stirring at room temperature for 30 minutes and cooled again to 0 °C to add 1-bromononane (30.9 g, 149 mmol). The reaction is quenched with water, extracted with THF, and concentrated. The concentrate is distilled at 108 °C and 0.75 mbar to obtain the product as a clear liquid (27.3 g, 140 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (s, 1H), 7.07 (s, 1H), 6.84 (s, 1H), 3.89 (t, *J* = 7.1 Hz, 2H), 1.64 (p, *J* = 7.1 Hz, 2H), 1.15 (m, 12H), 0.81 (t, *J* = 6.7 Hz, 3H).

1-Decylimidazole. In a flame dried 500 mL flask, under argon atmosphere, sodium hydride (6.46 g, 162 mmol, 60%) is slowly added to a solution of dry imidazole (10 g, 147 mmol) in dry THF (250 mL) at 0 °C. The reaction is left stirring at room temperature for 30 minutes and cooled again to 0 °C to add 1-bromodecane (32.50 g, 147 mmol). The reaction is quenched with water, extracted with THF, and concentrated. The concentrate is distilled at 118 °C and 0.75 mbar to obtain the product as a clear liquid (28.6 g, 137 mmol, 93%).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 (s, 1H), 7.10 (d, *J* = 1.3 Hz, 1H), 6.85 (d, *J* = 1.1 Hz, 1H), 3.91 (t, *J* = 7.1 Hz, 2H), 1.66 (q, *J* = 7.2 Hz, 2H), 1.21 (s, 14H), 0.83 (t, *J* = 7.1 Hz, 3H)

Selected ^{1}H NMR spectra of IL samples

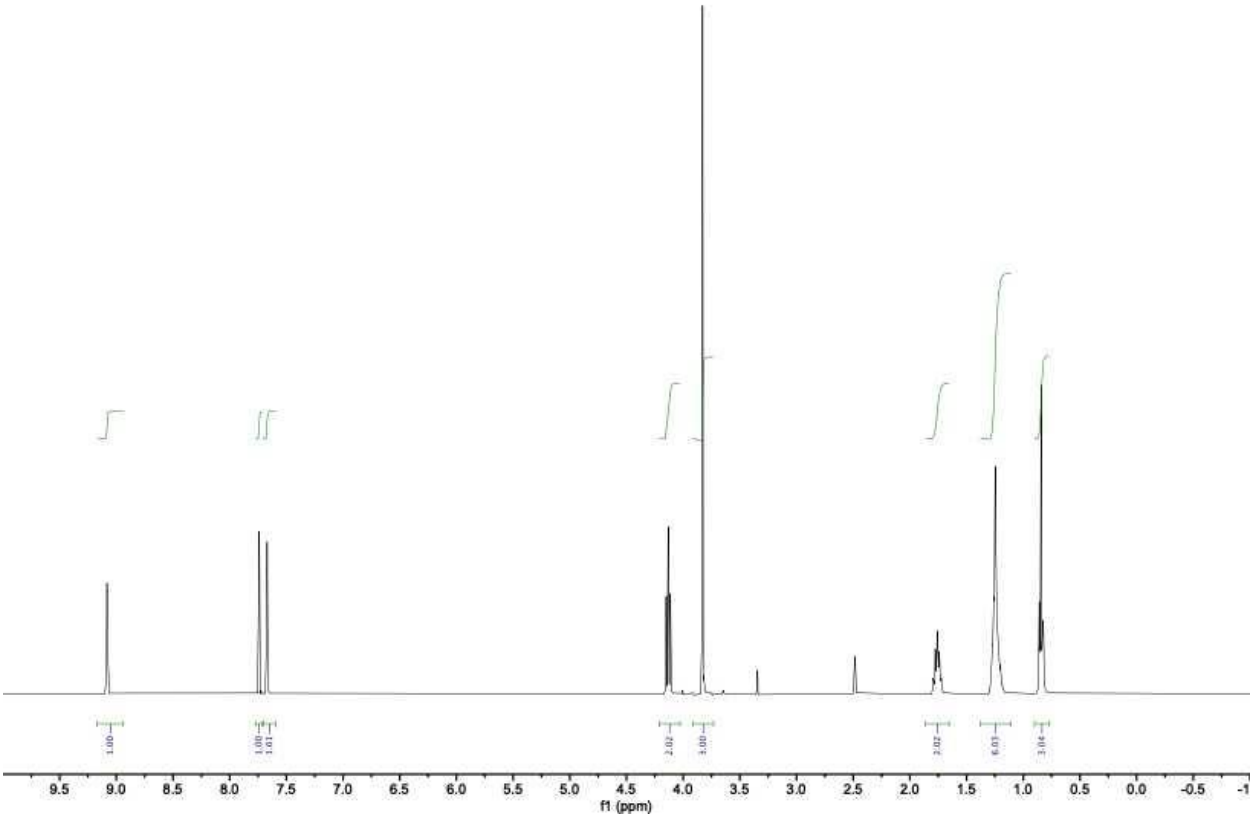

Figure S1. ^{1}H NMR spectrum of [C_6mim][Tf_2N].

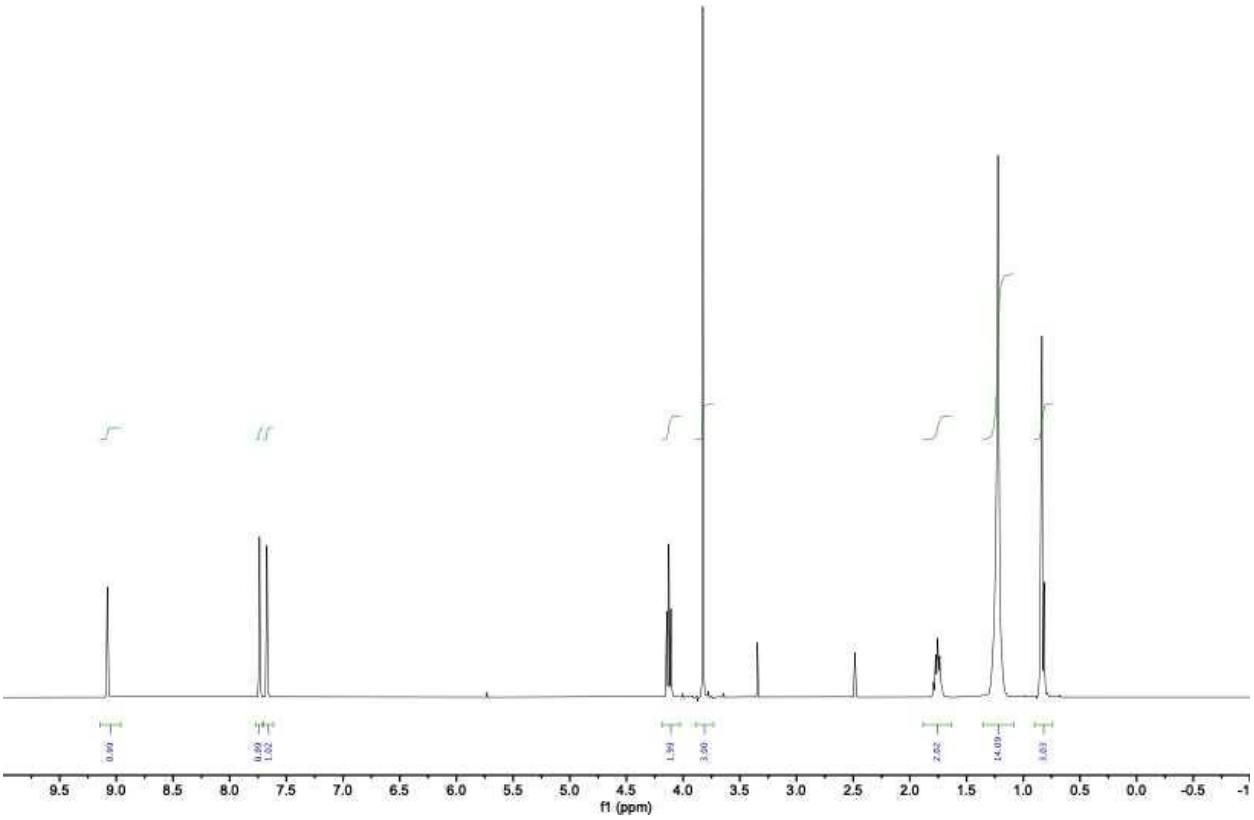

Figure S2. ^{1}H NMR spectrum of $[C_{10}mim][Tf_2N]$.

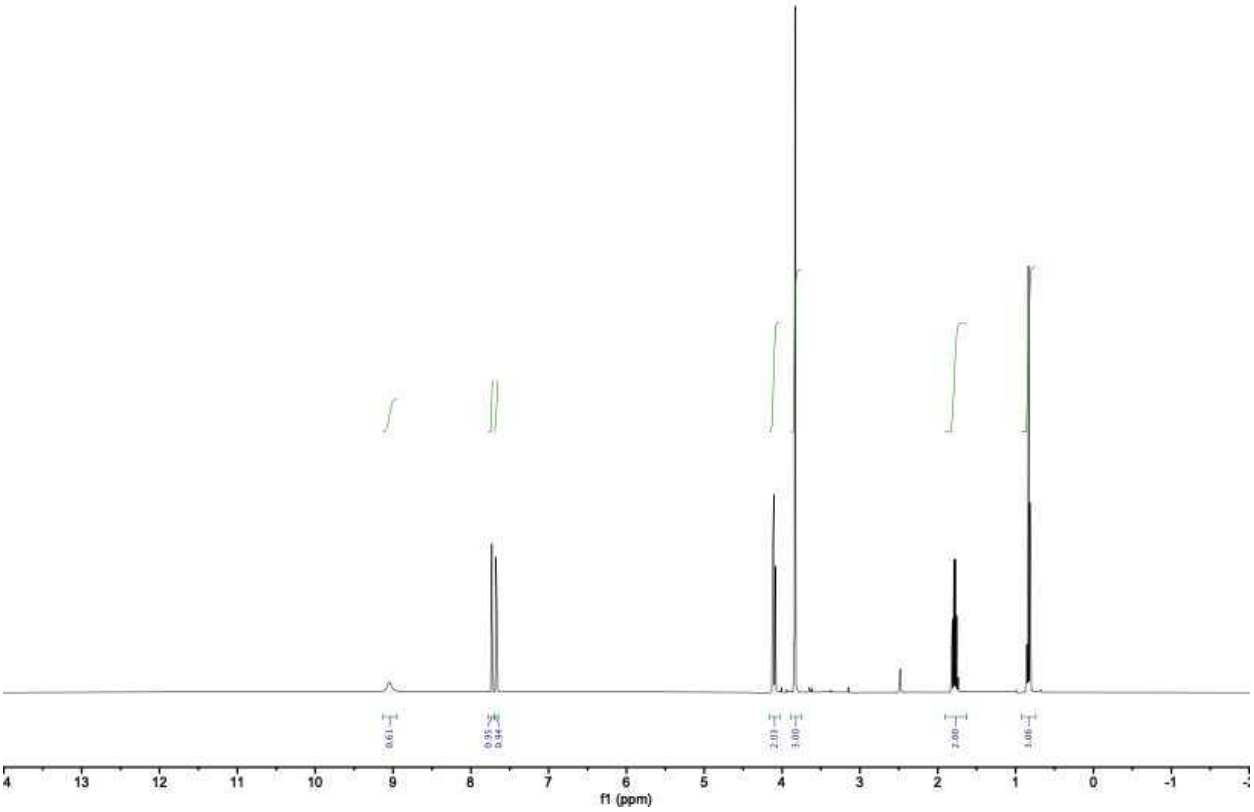

Figure S3. ^{1}H NMR spectrum of $[C_3mim][CF_3SO_3]$.

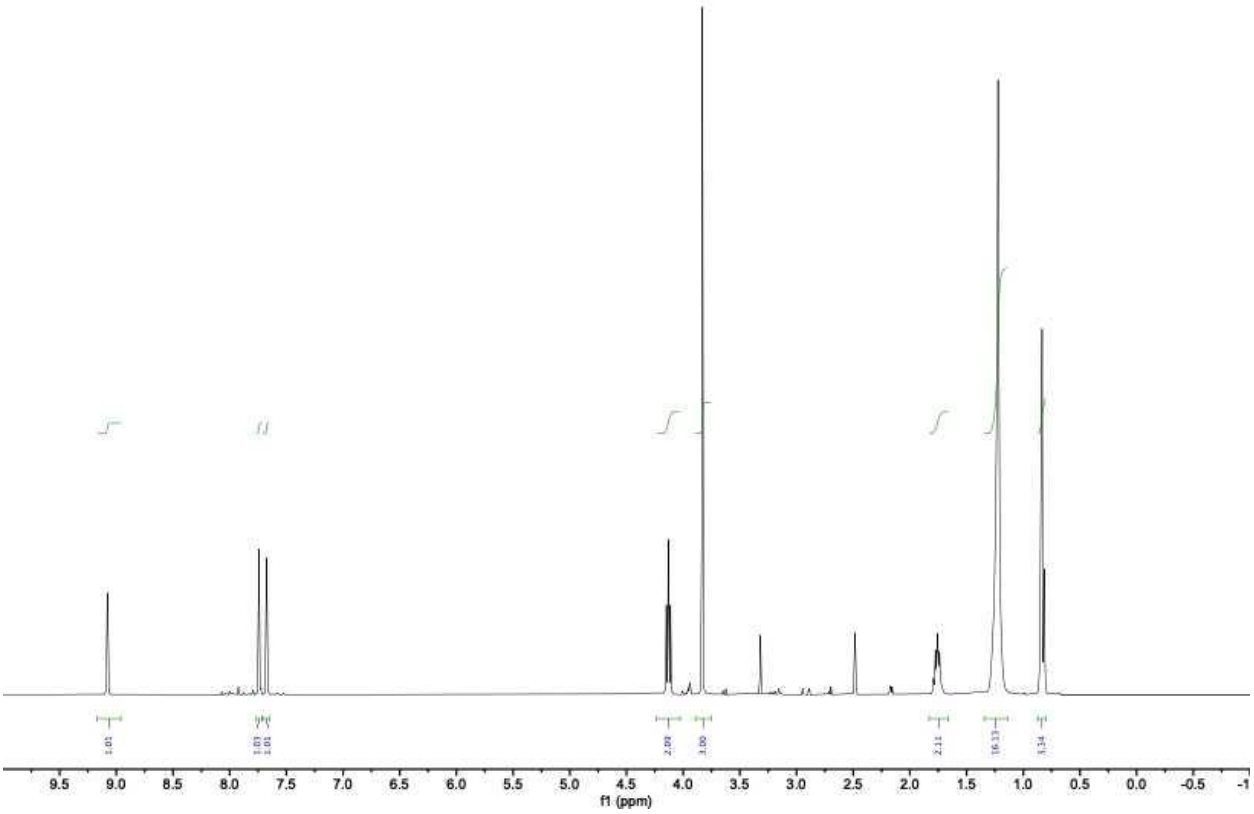

Figure S4. ^{1}H NMR spectrum of $[C_{10}mim][CF_3SO_3]$.

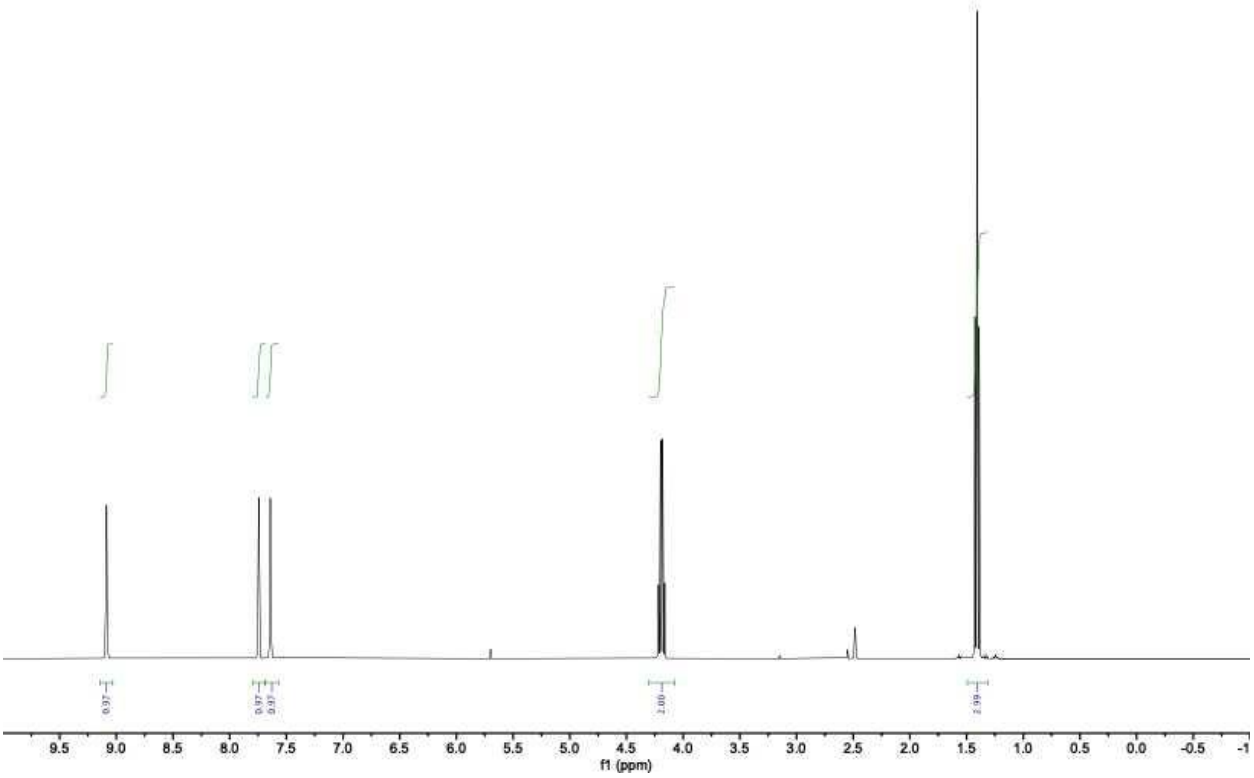

Figure S5. ^{1}H NMR spectrum of $[C_2im][Tf_2N]$.

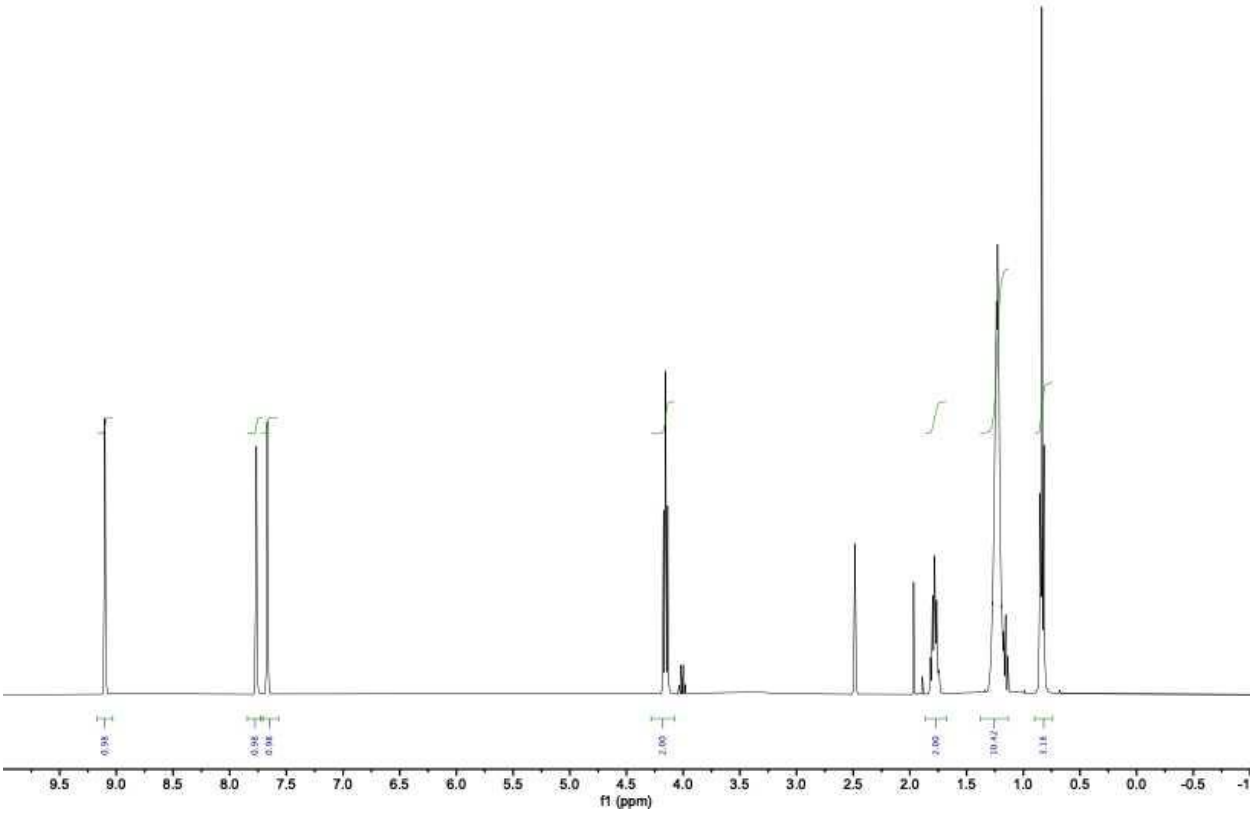

Figure S6. ^{1}H NMR spectrum of $[C_{10}im][Tf_2N]$.

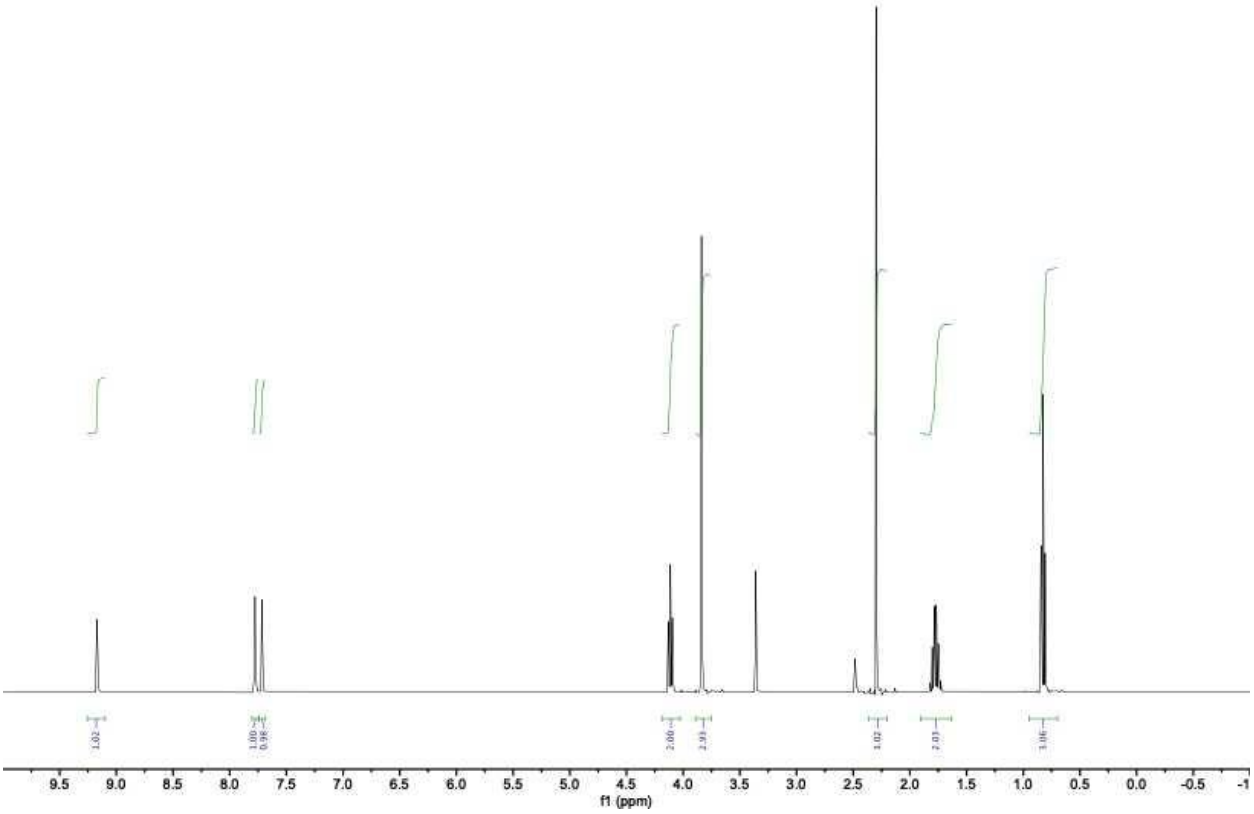

Figure S7. ^{1}H NMR spectrum of $[C_3mim][CH_3SO_3]$.

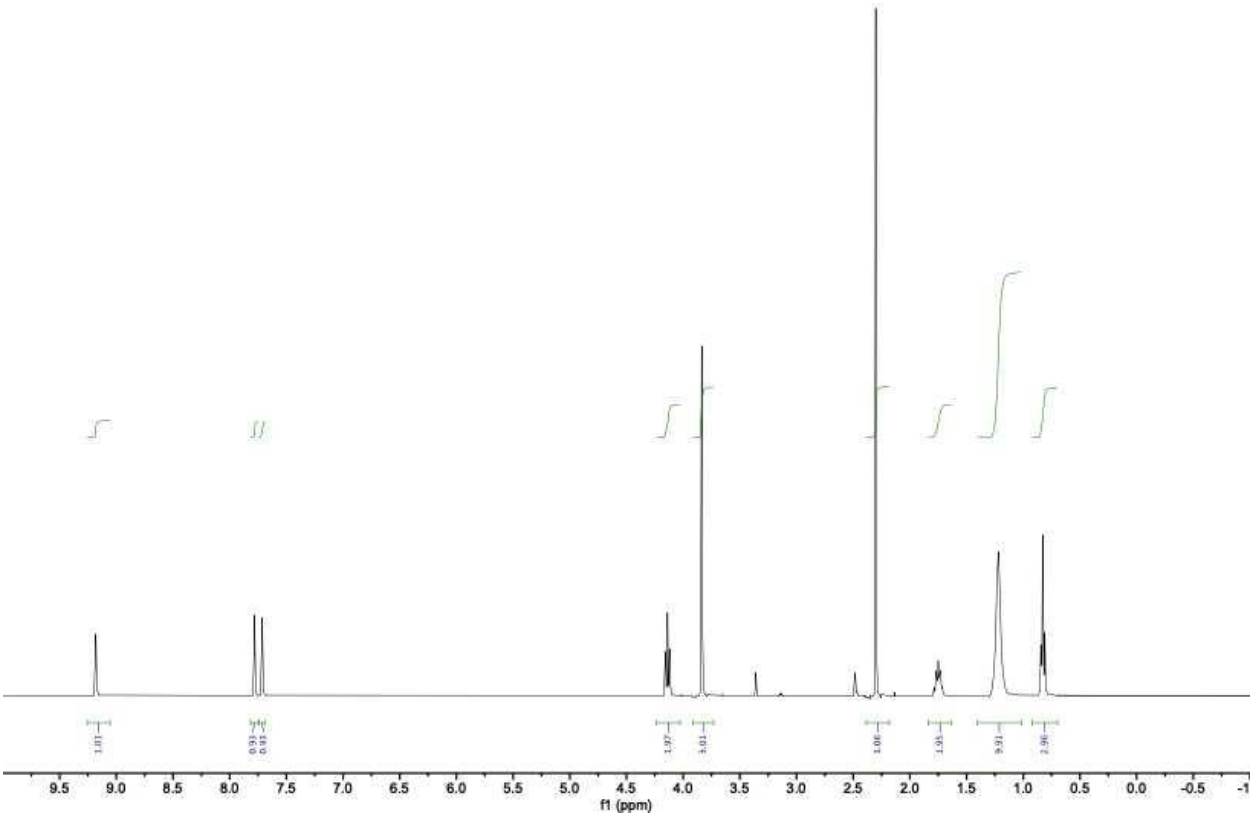

Figure S8. ^{1}H NMR spectrum of $[C_8mim][CH_3SO_3]$.

Table S1. Glass transition temperature (T_g), melting point (T_m) and thermal decomposition temperature (T_d) of the four series of $[C_n mim][CH_3SO_3]$, $[C_n mim][CF_3SO_3]$, $[C_n mim][Tf_2N]$, and $[C_n im][Tf_2N]$ ionic liquids.

ILs	Water Content (ppm)	T_g (K) [a]	T_m (K) [b]	T_d (K) [c]
$[C_2mim][Tf_2N]$	105	181.3, 181[24], 186[27]	261.3, 256[24], 255[27]	709.5
$[C_3mim][Tf_2N]$	60	184.5		703.9
$[C_4mim][Tf_2N]$	120	186.4, 187[24], 186[26-27]	269.0, 271[24], 270[26-27]	703.0, 695[24], 696[26], 700[27]
$[C_5mim][Tf_2N]$	190	187.5	265.0	696.7
$[C_6mim][Tf_2N]$	103	188.3, 189[25], 192[27]	265.2, 266[25], 267[27]	694.7, 700[25], 701[27]
$[C_7mim][Tf_2N]$	181	188.4		692.9
$[C_8mim][Tf_2N]$	60	189.1, 189[25], 193[27]		698.0, 700[25], 701[27]
$[C_9mim][Tf_2N]$	539	189.7		706.5
$[C_{10}mim][Tf_2N]$	700	189.2	276.4	706.6
$[C_2im][Tf_2N]$	262	190.9	280.7	665.5
$[C_3im][Tf_2N]$	277	191.7	279.1	672.2
$[C_4im][Tf_2N]$	150	187.8		676.1
$[C_5im][Tf_2N]$	114	195.1		663.6
$[C_6im][Tf_2N]$	204	196.6		669.4
$[C_7im][Tf_2N]$	74	195.0		656.4
$[C_8im][Tf_2N]$	160	195.7	272.4	668.3
$[C_9im][Tf_2N]$	317	195.2	290.7	678.9
$[C_{10}im][Tf_2N]$	63	195.7	279.9	662.7
$[C_2mim][CF_3SO_3]$	257	179.1	259.0	658.5
$[C_3mim][CF_3SO_3]$	187	185.0	279.1	664.3
$[C_4mim][CF_3SO_3]$	163		288.1, 286[24], 290[26]	662.3, 665[24], 682[26]
$[C_5mim][CF_3SO_3]$	470	195.6		662.2
$[C_6mim][CF_3SO_3]$	326		295.6	658.3
$[C_7mim][CF_3SO_3]$	336	191.6	258.1	663.2
$[C_8mim][CF_3SO_3]$	325	196.3	283.6	661.9
$[C_9mim][CF_3SO_3]$	198	183.1	282.8	660.0
$[C_{10}mim][CF_3SO_3]$	240			660.6
$[C_2mim][CH_3SO_3]$	228	205.5, 211[28]	303.5	608.7
$[C_3mim][CH_3SO_3]$	408	212.4	310.3	609.8
$[C_4mim][CH_3SO_3]$	1000	216.8	334.2, 345[29]	607.2
$[C_6mim][CH_3SO_3]$	657	212.5	309.5	608.2
$[C_7mim][CH_3SO_3]$	332	216.1	310.2	606.5
$[C_8mim][CH_3SO_3]$	1500	212.9	309.1	604.7

[a]Glass transition temperature determined by differential scanning calorimetry. [b]Melting point determined by differential scanning calorimetry. [c]Decomposition temperature determined by thermal gravimetric analysis.

[d]The uncertainties of the reported T_g and T_m values are ±1.0 K. The uncertainties of the reported T_d values are ±2.0 K. The reference numbers in the table are the reference numbers in the main text.

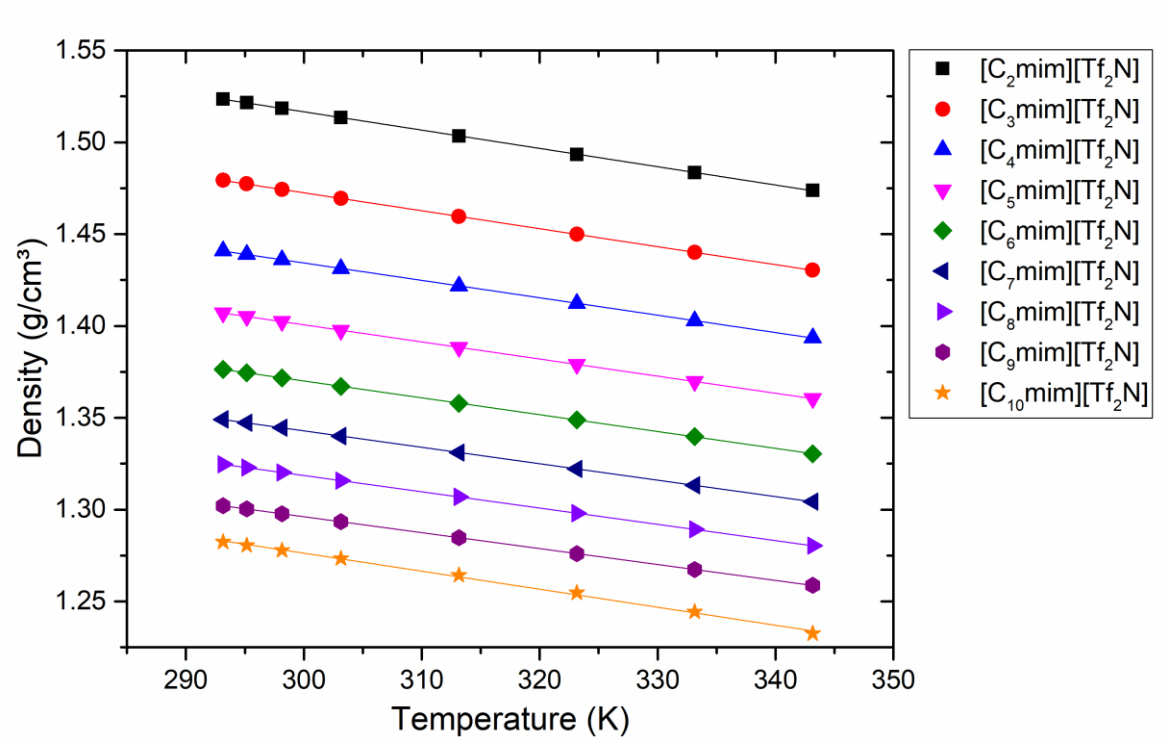

Figure S9. Density of [$C_n$mim][Tf_2N] ILs with n=2 through 10 as a function of temperature. The solid lines are linear fits of the data (see Table S2 for the parameters).

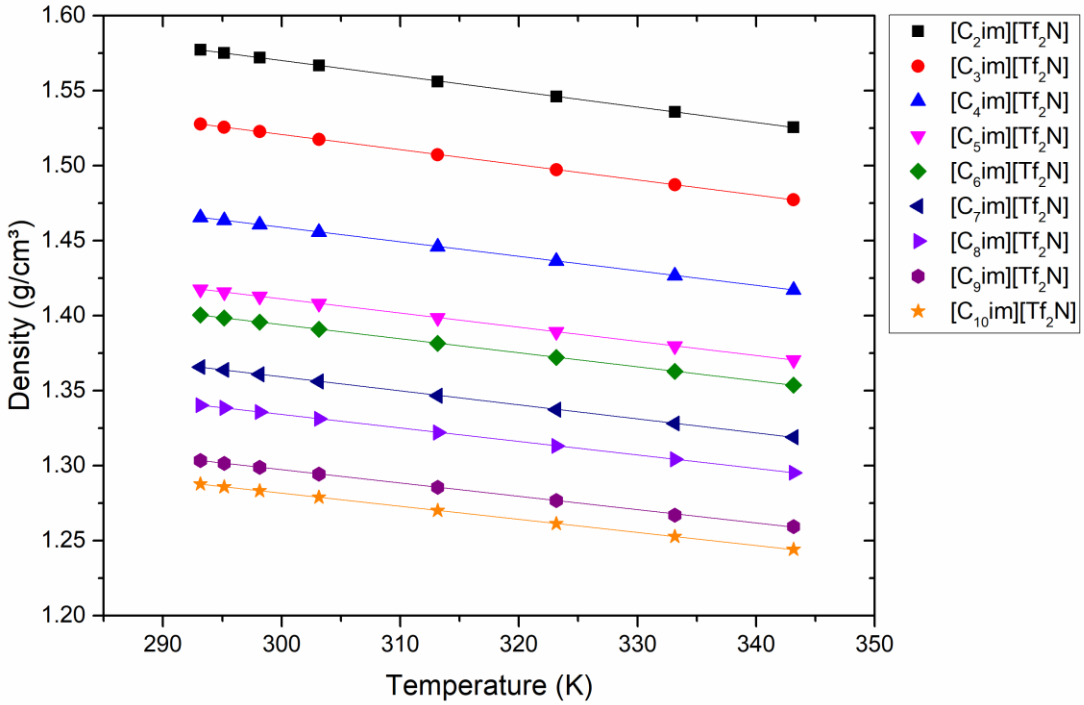

Figure S10. Density of [$C_n$im][Tf_2N] ILs with n=2 through 10 as a function of temperature. The solid lines are linear fits of the data (see Table S2 for the parameters).

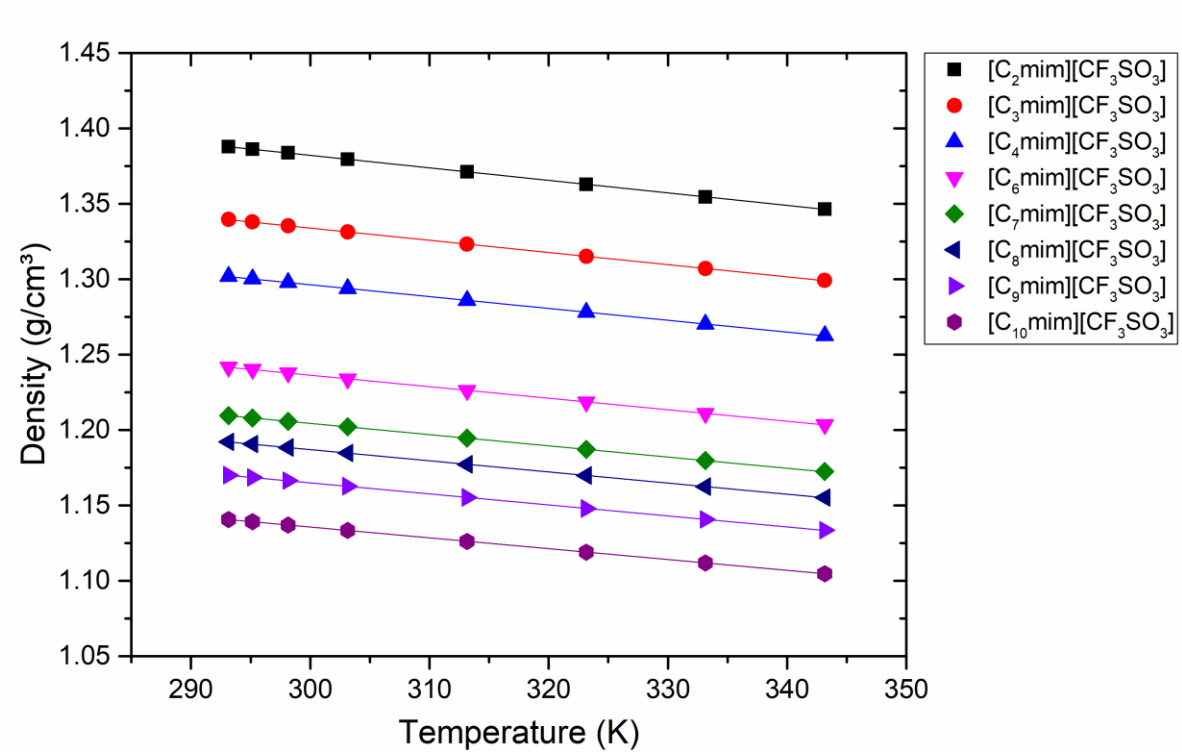

Figure S11. Density of $[C_n mim][CF_3SO_3]$ ILs with n = 2 to 4 and 6 to 10 as a function of temperature. The solid lines are linear fits of the data (see Table S2 for the parameters).

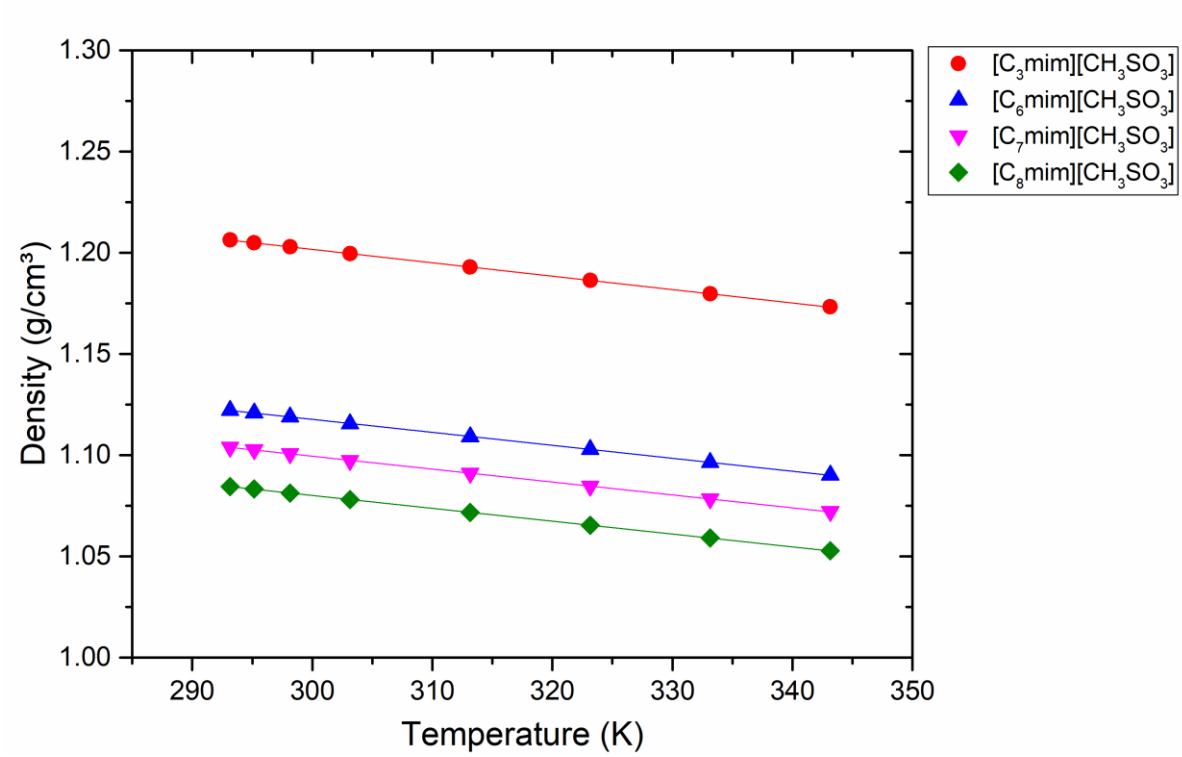

Figure S12. Density of $[C_n mim][CH_3SO_3]$ ILs with n=3, 6, 7 and 8 as a function of temperature. The solid lines are linear fits of the data (see Table S2 for the parameters).

Table S2. Density (g/cm^3) of the four series of [$C_n$mim][CH_3SO_3], [$C_n$mim][CF_3SO_3], [$C_n$mim][Tf_2N], and [$C_n$im][Tf_2N] ionic liquids at various temperatures (K).

ILs \ T (K)	Density (g/cm^3)							
	293.15	295.15	298.15	303.15	313.15	323.15	333.15	343.15
[C_2mim][Tf_2N]	1.524	1.522	1.519	1.513	1.503	1.493	1.484	1.474
[C_3mim][Tf_2N]	1.479	1.477	1.474	1.469	1.460	1.450	1.440	1.430
[C_4mim][Tf_2N]	1.441	1.439	1.436	1.431	1.422	1.412	1.403	1.394
[C_5mim][Tf_2N]	1.407	1.405	1.402	1.398	1.388	1.379	1.370	1.360
[C_6mim][Tf_2N]	1.376	1.375	1.372	1.367	1.358	1.349	1.340	1.330
[C_7mim][Tf_2N]	1.349	1.347	1.345	1.340	1.331	1.322	1.313	1.304
[C_8mim][Tf_2N]	1.325	1.323	1.320	1.316	1.307	1.298	1.289	1.280
[C_9mim][Tf_2N]	1.302	1.300	1.298	1.293	1.285	1.276	1.267	1.259
[C_{10}mim][Tf_2N]	1.282	1.281	1.278	1.273	1.264	1.255	1.244	1.232
[C_2im][Tf_2N]	1.577	1.575	1.572	1.567	1.556	1.546	1.536	1.526
[C_3im][Tf_2N]	1.528	1.526	1.523	1.518	1.507	1.497	1.487	1.477
[C_4im][Tf_2N]	1.466	1.464	1.461	1.456	1.446	1.436	1.427	1.417
[C_5im][Tf_2N]	1.418	1.416	1.413	1.408	1.399	1.389	1.380	1.371
[C_6im][Tf_2N]	1.400	1.399	1.396	1.391	1.382	1.372	1.363	1.354
[C_7im][Tf_2N]	1.366	1.364	1.361	1.356	1.347	1.337	1.328	1.319
[C_8im][Tf_2N]	1.340	1.339	1.336	1.331	1.322	1.313	1.304	1.295
[C_9im][Tf_2N]	1.303	1.302	1.299	1.295	1.286	1.277	1.267	1.260
[C_{10}im][Tf_2N]	1.288	1.286	1.283	1.279	1.270	1.261	1.253	1.244
[C_2mim][CF_3SO_3]	1.388	1.386	1.384	1.380	1.371	1.363	1.355	1.347
[C_3mim][CF_3SO_3]	1.340	1.338	1.335	1.331	1.323	1.315	1.307	1.299
[C_4mim][CF_3SO_3]	1.302	1.300	1.298	1.294	1.286	1.278	1.270	1.263
[C_6mim][CF_3SO_3]	1.242	1.240	1.238	1.234	1.226	1.219	1.211	1.204
[C_7mim][CF_3SO_3]	1.210	1.208	1.206	1.202	1.195	1.187	1.180	1.172
[C_8mim][CF_3SO_3]	1.192	1.191	1.188	1.185	1.177	1.170	1.163	1.155
[C_9mim][CF_3SO_3]	1.170	1.169	1.166	1.163	1.155	1.148	1.141	1.134
[C_{10}mim][CF_3SO_3]	1.141	1.139	1.137	1.133	1.126	1.119	1.112	1.105
[C_3mim][CH_3SO_3]	1.206	1.205	1.203	1.200	1.193	1.186	1.180	1.173
[C_6mim][CH_3SO_3]	1.122	1.121	1.119	1.116	1.109	1.103	1.096	1.090
[C_7mim][CH_3SO_3]	1.104	1.103	1.101	1.097	1.091	1.085	1.078	1.072
[C_8mim][CH_3SO_3]	1.085	1.083	1.081	1.078	1.072	1.065	1.059	1.053

[a]The uncertainty is approximately ±0.012 g/cm^3. The water content for each IL is the same as the one for surface tension measurement.

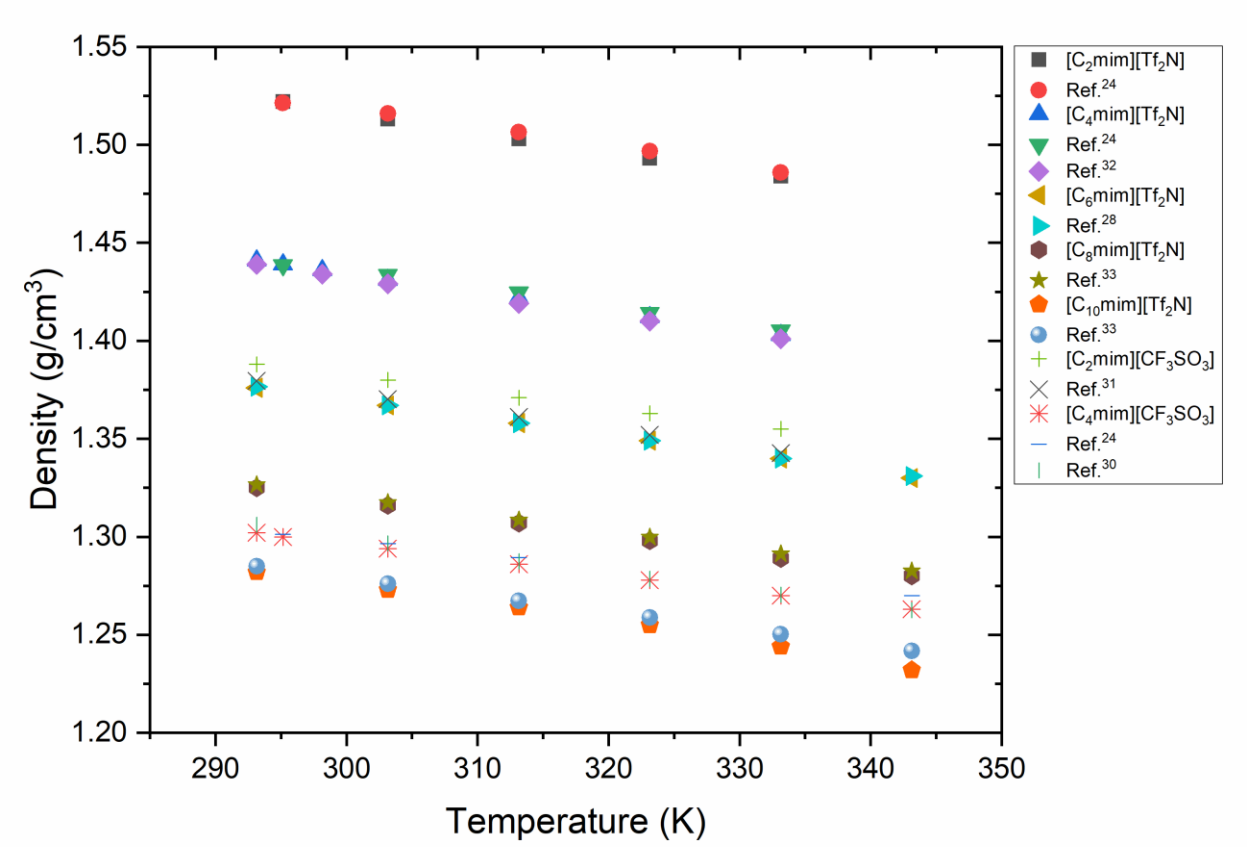

Figure S13. Comparison between the experimental data of density of ILs in this work and the literature data (the reference numbers in the figure are the reference numbers in the main text).

Table S3. Linear fitting parameters for the density of the ionic liquids.

ILs	a (g/cm^3)	b ($10^4*g/(cm^3*K)$)	R^2
$[C_2mim][Tf_2N]$	1.8156 ± 0.0006	-9.97 ± 0.02	1.0000
$[C_3mim][Tf_2N]$	1.7659 ± 0.0003	-9.78 ± 0.01	1.0000
$[C_4mim][Tf_2N]$	1.7186 ± 0.0004	-9.47 ± 0.01	1.0000
$[C_5mim][Tf_2N]$	1.6801 ± 0.0003	-9.31 ± 0.01	1.0000
$[C_6mim][Tf_2N]$	1.6452 ± 0.0002	-9.17 ± 0.01	1.0000
$[C_7mim][Tf_2N]$	1.6114 ± 0.0003	-8.95 ± 0.01	1.0000
$[C_8mim][Tf_2N]$	1.5845 ± 0.0001	-8.86 ± 0.01	1.0000
$[C_9mim][Tf_2N]$	1.5563 ± 0.0004	-8.67 ± 0.01	1.0000
$[C_{10}mim][Tf_2N]$	1.5706 ± 0.0060	-9.81 ± 0.19	0.9977
$[C_2im][Tf_2N]$	1.8800 ± 0.0008	-10.30 ± 0.03	1.0000
$[C_3im][Tf_2N]$	1.8237 ± 0.0007	-10.10 ± 0.03	1.0000
$[C_4im][Tf_2N]$	1.7490 ± 0.0006	-9.67 ± 0.02	1.0000
$[C_5im][Tf_2N]$	1.6943 ± 0.0006	-9.43 ± 0.02	1.0000
$[C_6im][Tf_2N]$	1.6744 ± 0.0006	-9.34 ± 0.02	1.0000
$[C_7im][Tf_2N]$	1.6397 ± 0.0011	-9.35 ± 0.03	0.9999
$[C_8im][Tf_2N]$	1.6042 ± 0.0005	-9.00 ± 0.02	1.0000
$[C_9im][Tf_2N]$	1.5637 ± 0.0022	-8.88 ± 0.07	0.9996
$[C_{10}im][Tf_2N]$	1.5435 ± 0.0005	-8.73 ± 0.02	1.0000
$[C_2mim][CF_3SO_3]$	1.6311 ± 0.0006	-8.29 ± 0.02	1.0000
$[C_3mim][CF_3SO_3]$	1.5764 ± 0.0006	-8.08 ± 0.02	1.0000
$[C_4mim][CF_3SO_3]$	1.5320 ± 0.0005	-7.85 ± 0.02	1.0000
$[C_6mim][CF_3SO_3]$	1.4655 ± 0.0005	-7.63 ± 0.02	1.0000
$[C_7mim][CF_3SO_3]$	1.4276 ± 0.0004	-7.43 ± 0.01	1.0000
$[C_8mim][CF_3SO_3]$	1.4088 ± 0.0004	-7.39 ± 0.01	1.0000
$[C_9mim][CF_3SO_3]$	1.3842 ± 0.0004	-7.30 ± 0.01	1.0000
$[C_{10}mim][CF_3SO_3]$	1.3512 ± 0.0003	-7.18 ± 0.01	1.0000
$[C_3mim][CH_3SO_3]$	1.4003 ± 0.0005	-6.62 ± 0.01	1.0000
$[C_6mim][CH_3SO_3]$	1.3099 ± 0.0005	-6.40 ± 0.02	1.0000
$[C_7mim][CH_3SO_3]$	1.2908 ± 0.0005	-6.37 ± 0.02	1.0000
$[C_8mim][CH_3SO_3]$	1.2707 ± 0.0004	-6.35 ± 0.01	1.0000

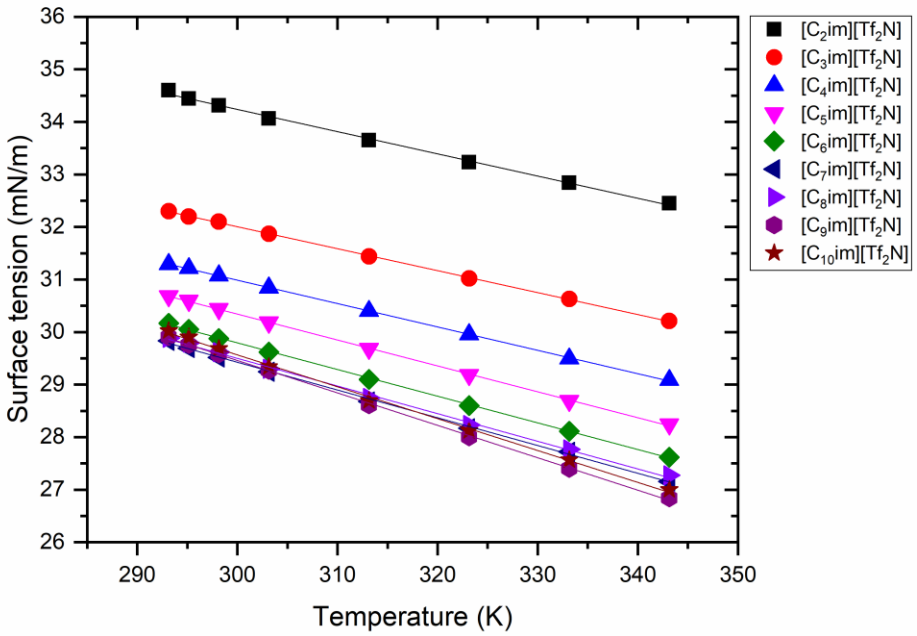

Figure S14. Surface tension of $[C_n im][Tf_2N]$ ILs as a function of temperature. The solid lines are linear fits of the data.

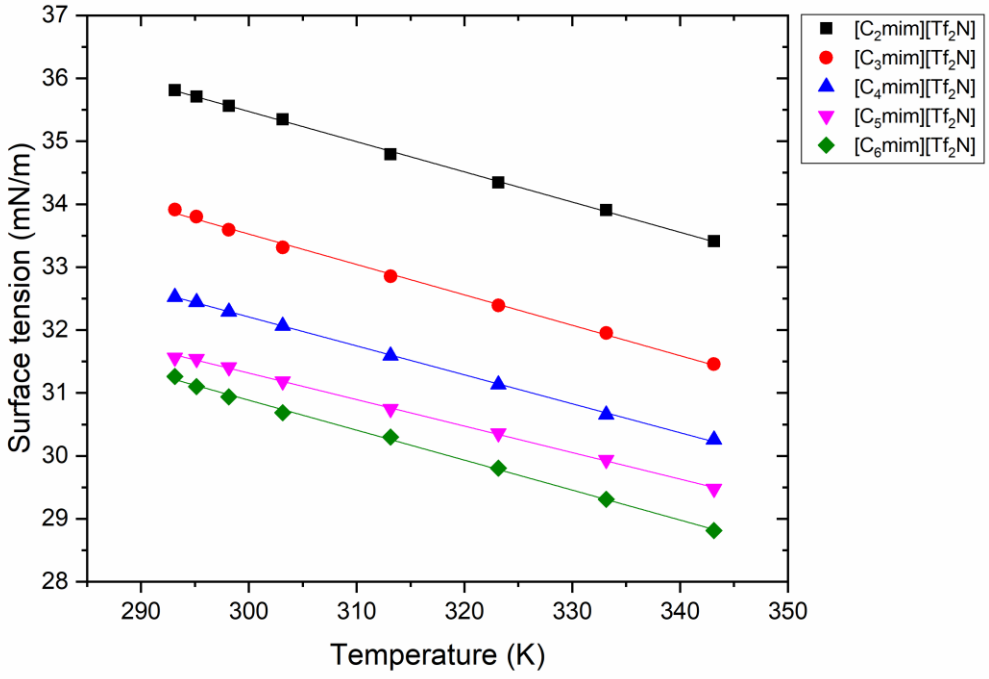

Figure S15. Surface tension of $[C_n mim][Tf_2N]$ ILs as a function of temperature. The solid lines are linear fits of the data.

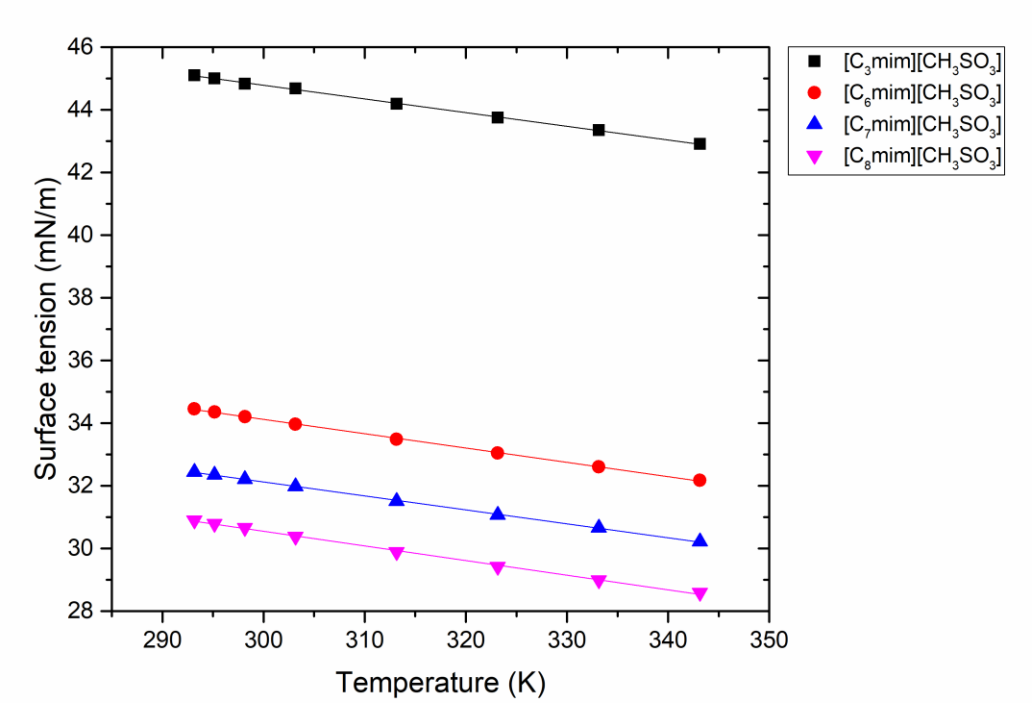

Figure S16. Surface tension of $[C_n mim][CH_3SO_3]$ ILs as a function of temperature. The solid lines are linear fits of the data.

Table S4. Surface tension (mN/m) of the four series of $[C_n mim][CH_3SO_3]$, $[C_n mim][CF_3SO_3]$, $[C_n mim][Tf_2N]$, and $[C_n im][Tf_2N]$ ionic liquids at various temperatures (K).

ILs \ T (K)	Water Content (ppm)	Surface Tension (mN/m)							
		293.15	295.15	298.15	303.15	313.15	323.15	333.15	343.15
$[C_2mim][Tf_2N]$	125	35.8	35.7	35.6	35.3	34.8	34.3	33.9	33.4
$[C_3mim][Tf_2N]$	165	33.9	33.8	33.6	33.3	32.9	32.4	32.0	31.5
$[C_4mim][Tf_2N]$	140	32.5	32.4	32.3	32.1	31.6	31.1	30.7	30.3
$[C_5mim][Tf_2N]$	84	31.6	31.5	31.4	31.2	30.7	30.4	29.9	29.5
$[C_6mim][Tf_2N]$	162	31.3	31.1	30.9	30.7	30.3	29.8	29.3	28.8
$[C_2im][Tf_2N]$	260	34.6	34.4	34.3	34.1	33.7	33.2	32.8	32.5
$[C_3im][Tf_2N]$	272	32.3	32.2	32.1	31.9	31.4	31.0	30.6	30.2
$[C_4im][Tf_2N]$	150	31.3	31.2	31.1	30.8	30.4	30.0	29.5	29.1
$[C_5im][Tf_2N]$	114	30.7	30.6	30.4	30.2	29.7	29.2	28.7	28.2
$[C_6im][Tf_2N]$	132	30.2	30.1	29.9	29.6	29.1	28.6	28.1	27.6
$[C_7im][Tf_2N]$	74	29.8	29.7	29.5	29.2	28.7	28.2	27.7	27.2
$[C_8im][Tf_2N]$	160	29.9	29.8	29.6	29.3	28.7	28.2	27.8	27.3
$[C_9im][Tf_2N]$	317	29.9	29.8	29.6	29.3	28.6	28.0	27.4	26.8
$[C_{10}im][Tf_2N]$	63	30.0	29.9	29.7	29.3	28.7	28.1	27.6	27.0
$[C_2mim][CF_3SO_3]$	370	39.9	39.8	39.7	39.5	39.1	38.7	38.4	38.1
$[C_3mim][CF_3SO_3]$	148	36.9	36.9	36.8	36.6	36.3	35.9	35.6	35.2
$[C_4mim][CF_3SO_3]$	128	34.5	34.5	34.4	34.2	33.7	33.5	33.2	32.8
$[C_6mim][CF_3SO_3]$	326	31.8	31.7	31.6	31.3	30.9	30.5	30.0	29.6
$[C_7mim][CF_3SO_3]$	227	31.3	31.1	31.0	30.7	30.3	29.8	29.4	29.0
$[C_8mim][CF_3SO_3]$	240	30.5	30.4	30.3	30.0	29.4	28.9	28.4	27.9
$[C_9mim][CF_3SO_3]$	206	30.4	30.3	30.1	29.8	29.3	28.8	28.3	27.8
$[C_{10}mim][CF_3SO_3]$	240	29.7	29.7	29.5	29.2	28.7	28.2	27.7	27.2
$[C_3mim][CH_3SO_3]$	320	45.1	45.0	44.8	44.7	44.2	43.8	43.4	42.9
$[C_6mim][CH_3SO_3]$	488	34.5	34.4	34.2	34.0	33.5	33.0	32.6	32.2
$[C_7mim][CH_3SO_3]$	550	32.4	32.4	32.2	32.0	31.5	31.1	30.7	30.2
$[C_8mim][CH_3SO_3]$	379	30.9	30.8	30.7	30.4	29.9	29.4	29.0	28.6

[a]The instrument uncertainty is ±0.3 mN/m. The uncertainty based on the standard deviation of the five measurements is much smaller.

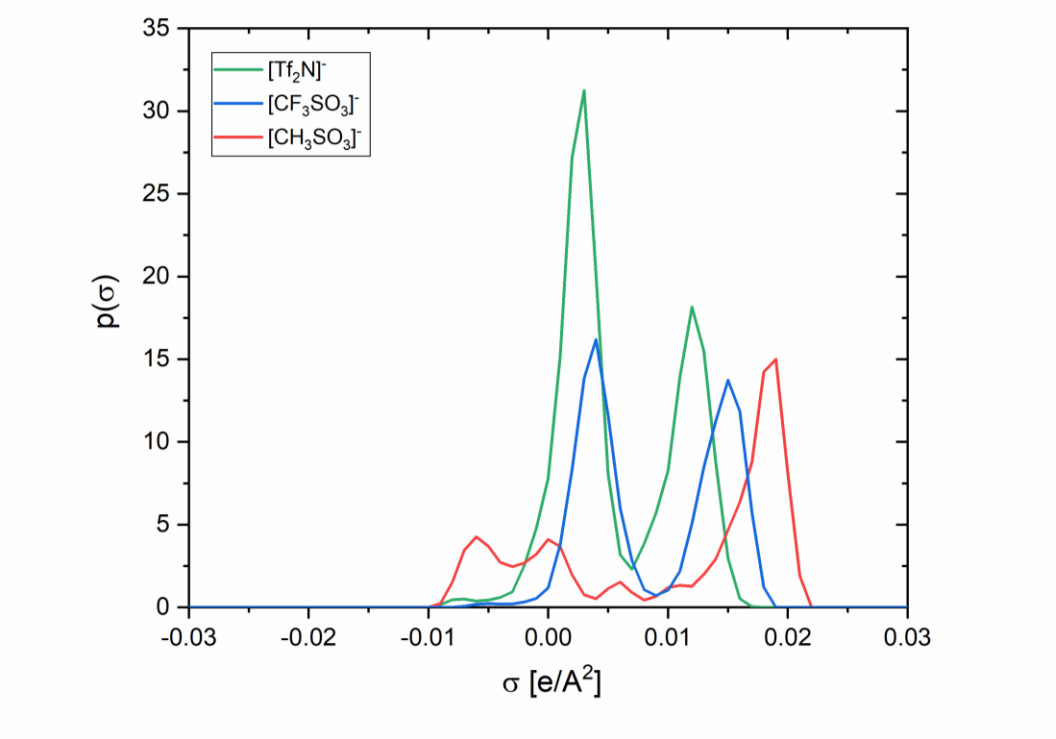

Figure S17. Sigma profiles of $[CH_3SO_3]^-$, $[CF_3SO_3]^-$ and $[Tf_2N]^-$ anions.

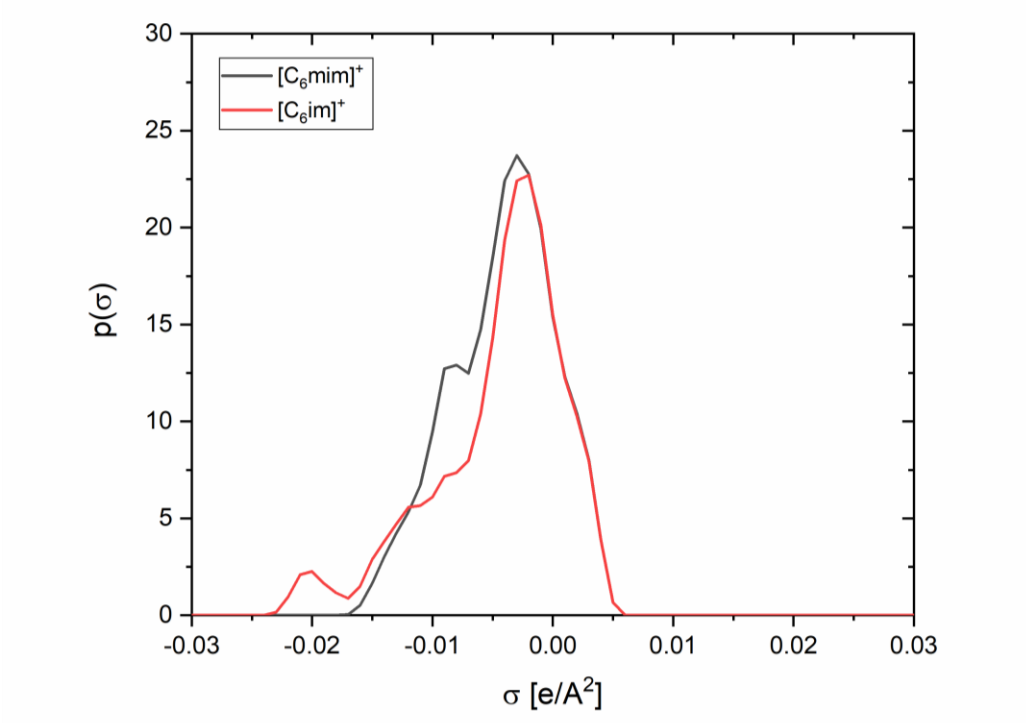

Figure S18. Sigma profiles of $[C_6mim]^+$ and $[C_6im]^+$ cations.

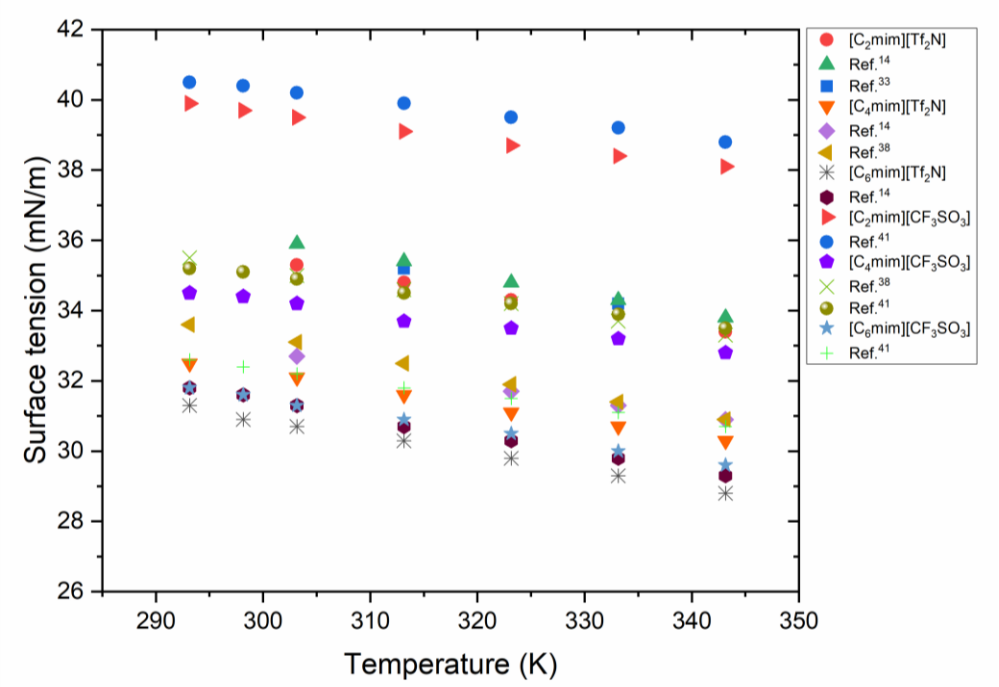

Figure S19. Comparison between the experimental data of surface tension (mN/m) of ILs in this work and the literature data (the reference numbers in the figure are the reference numbers in the main text).

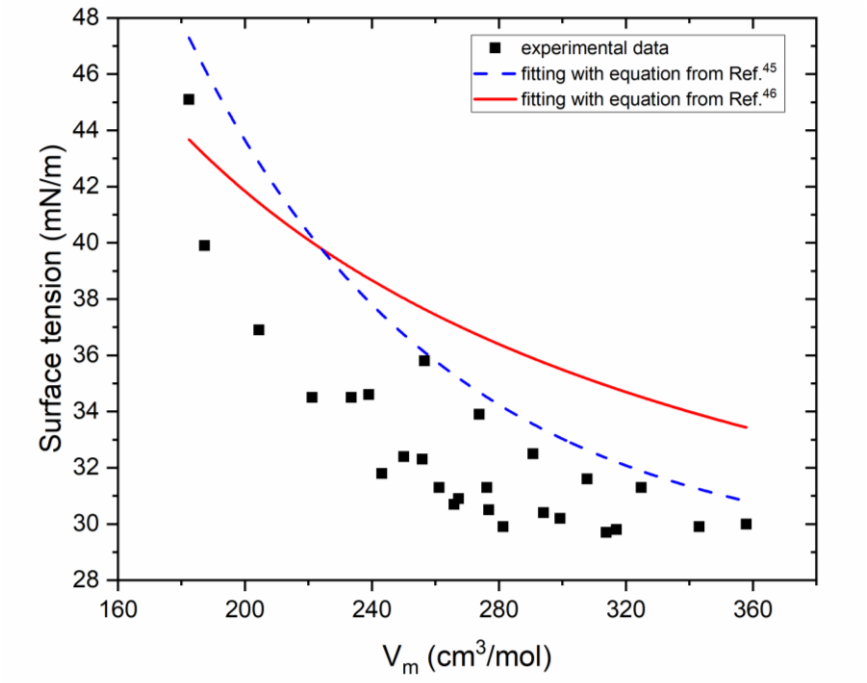

Figure S20. Surface tension of the four series of $[C_nmim][CH_3SO_3]$, $[C_nmim][CF_3SO_3]$, $[C_nmim][Tf_2N]$, and $[C_nim][Tf_2N]$ ionic liquids vs. their molar volume at 293.15 K, fitted by equations from the literature (the reference numbers in the figure are the reference numbers in the main text).

Table S5. Molar volume (V_m) of the four series of $[C_n mim][CH_3SO_3]$, $[C_n mim][CF_3SO_3]$, $[C_n mim][Tf_2N]$, and $[C_n im][Tf_2N]$ ionic liquids at 293.15 K.

ILs	V_m (cm^3/mol)
$[C_2mim][Tf_2N]$	256.6
$[C_3mim][Tf_2N]$	273.8
$[C_4mim][Tf_2N]$	290.8
$[C_5mim][Tf_2N]$	307.7
$[C_6mim][Tf_2N]$	324.9
$[C_2im][Tf_2N]$	239.1
$[C_3im][Tf_2N]$	255.9
$[C_4im][Tf_2N]$	276.3
$[C_5im][Tf_2N]$	265.9
$[C_6im][Tf_2N]$	299.3
$[C_7im][Tf_2N]$	317.0
$[C_8im][Tf_2N]$	281.3
$[C_9im][Tf_2N]$	343.1
$[C_{10}im][Tf_2N]$	357.9
$[C_2mim][CF_3SO_3]$	187.3
$[C_3mim][CF_3SO_3]$	204.5
$[C_4mim][CF_3SO_3]$	221.2
$[C_6mim][CF_3SO_3]$	243.2
$[C_7mim][CF_3SO_3]$	261.2
$[C_8mim][CF_3SO_3]$	276.8
$[C_9mim][CF_3SO_3]$	294.0
$[C_{10}mim][CF_3SO_3]$	313.8
$[C_3mim][CH_3SO_3]$	182.4
$[C_6mim][CH_3SO_3]$	233.5
$[C_7mim][CH_3SO_3]$	250.0
$[C_8mim][CH_3SO_3]$	267.3

Table S6. Calculated surface tension (mN/m) of the three series of $[C_n mim][CH_3SO_3]$, $[C_n mim][CF_3SO_3]$ and $[C_n mim][Tf_2N]$ ionic liquids at different temperatures (K) and comparison with the experimental values in Table S4. Calculated values are using a group contribution method.[47]

ILs	293.15 K			295.15 K		
	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)
$[C_2mim][Tf_2N]$	36.3	35.8	1.4	36.2	35.7	1.4
$[C_3mim][Tf_2N]$	34.3	33.9	1.1	34.2	33.8	1.1
$[C_4mim][Tf_2N]$	32.7	32.5	0.7	32.6	32.4	0.7
$[C_5mim][Tf_2N]$	31.6	31.6	0.1	31.5	31.5	0.1
$[C_6mim][Tf_2N]$	30.7	31.3	1.9	30.6	31.1	1.5
$[C_2mim][CF_3SO_3]$	43.3	39.9	8.6	43.2	39.8	8.4
$[C_3mim][CF_3SO_3]$	39.7	36.9	7.7	39.6	36.9	7.3
$[C_4mim][CF_3SO_3]$	36.8	34.5	6.6	36.6	34.5	6.2
$[C_6mim][CF_3SO_3]$	32.5	31.8	2.1	32.4	31.7	2.1
$[C_7mim][CF_3SO_3]$	31.0	31.3	0.9	30.9	31.1	0.6
$[C_8mim][CF_3SO_3]$	29.9	30.5	1.9	29.8	30.4	1.9
$[C_9mim][CF_3SO_3]$	29.1	30.4	4.2	29.0	30.3	4.1
$[C_{10}mim][CF_3SO_3]$	28.6	29.7	3.8	28.5	29.7	4.1
$[C_3mim][CH_3SO_3]$	36.0	45.1	20.1	35.9	45.0	20.2
$[C_6mim][CH_3SO_3]$	30.7	34.5	11.1	30.6	34.4	11.1
$[C_7mim][CH_3SO_3]$	29.7	32.4	8.4	29.6	32.4	8.7
$[C_8mim][CH_3SO_3]$	28.9	30.9	6.3	28.9	30.8	6.3
ILs	298.15 K			303.15 K		
	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)
$[C_2mim][Tf_2N]$	36.1	35.6	1.3	35.8	35.3	1.5
$[C_3mim][Tf_2N]$	34.1	33.6	1.4	33.8	33.3	1.6
$[C_4mim][Tf_2N]$	32.5	32.3	0.7	32.3	32.1	0.7
$[C_5mim][Tf_2N]$	31.4	31.4	0.1	31.2	31.2	0.1
$[C_6mim][Tf_2N]$	30.5	30.9	1.3	30.3	30.7	1.2
$[C_2mim][CF_3SO_3]$	42.9	39.7	8.2	42.6	39.5	7.7
$[C_3mim][CF_3SO_3]$	39.4	36.8	7.0	39.0	36.6	6.7
$[C_4mim][CF_3SO_3]$	36.5	34.4	6.0	36.1	34.2	5.7
$[C_6mim][CF_3SO_3]$	32.2	31.6	1.9	32.0	31.3	2.1
$[C_7mim][CF_3SO_3]$	30.8	31.0	0.7	30.5	30.7	0.5
$[C_8mim][CF_3SO_3]$	29.7	30.3	2.0	29.5	30.0	1.8
$[C_9mim][CF_3SO_3]$	28.9	30.1	3.9	28.7	29.8	3.7
$[C_{10}mim][CF_3SO_3]$	28.4	29.5	3.9	28.1	29.2	3.6
$[C_3mim][CH_3SO_3]$	35.7	44.8	20.3	35.4	44.7	20.7
$[C_6mim][CH_3SO_3]$	30.4	34.2	11.0	30.2	34.0	11.2

$[C_7mim][CH_3SO_3]$	29.4	32.2	8.6	29.2	32.0	8.7
$[C_8mim][CH_3SO_3]$	28.7	30.7	6.4	28.5	30.4	6.2
ILs	313.15 K			323.15 K		
	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)
$[C_2mim][Tf_2N]$	35.4	34.8	1.6	34.9	34.3	1.8
$[C_3mim][Tf_2N]$	33.4	32.9	1.5	33.0	32.4	1.8
$[C_4mim][Tf_2N]$	31.9	31.6	1.0	31.5	31.1	1.3
$[C_5mim][Tf_2N]$	30.8	30.7	0.3	30.4	30.4	0.0
$[C_6mim][Tf_2N]$	29.9	30.3	1.2	29.6	29.8	0.8
$[C_2mim][CF_3SO_3]$	41.8	39.1	6.9	41.1	38.7	6.1
$[C_3mim][CF_3SO_3]$	38.4	36.3	5.7	37.7	35.9	5.0
$[C_4mim][CF_3SO_3]$	35.5	33.7	5.5	34.9	33.5	4.3
$[C_6mim][CF_3SO_3]$	31.4	30.9	1.7	30.9	30.5	1.4
$[C_7mim][CF_3SO_3]$	30.0	30.3	0.8	29.6	29.8	0.8
$[C_8mim][CF_3SO_3]$	29.0	29.4	1.3	28.6	28.9	1.2
$[C_9mim][CF_3SO_3]$	28.3	29.3	3.5	27.8	28.8	3.4
$[C_{10}mim][CF_3SO_3]$	27.7	28.7	3.4	27.3	28.2	3.2
$[C_3mim][CH_3SO_3]$	34.8	44.2	21.2	34.3	43.8	21.8
$[C_6mim][CH_3SO_3]$	29.7	33.5	11.3	29.3	33.0	11.4
$[C_7mim][CH_3SO_3]$	28.8	31.5	8.7	28.3	31.1	8.9
$[C_8mim][CH_3SO_3]$	28.1	29.9	6.1	27.7	29.4	5.9
ILs	333.15 K			343.15 K		
	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)	γ_{calc} (mN/m)	γ_{exp} (mN/m)	AAD (%)
$[C_2mim][Tf_2N]$	34.4	33.9	1.6	34.0	33.4	1.7
$[C_3mim][Tf_2N]$	32.5	32.0	1.7	32.1	31.5	2.0
$[C_4mim][Tf_2N]$	31.1	30.7	1.3	30.7	30.3	1.3
$[C_5mim][Tf_2N]$	30.0	29.9	0.3	29.6	29.5	0.4
$[C_6mim][Tf_2N]$	29.2	29.3	0.3	28.8	28.8	0.1
$[C_2mim][CF_3SO_3]$	40.3	38.4	5.0	39.6	38.1	3.8
$[C_3mim][CF_3SO_3]$	37.0	35.6	4.0	36.4	35.2	3.3
$[C_4mim][CF_3SO_3]$	34.3	33.2	3.4	33.7	32.8	2.8
$[C_6mim][CF_3SO_3]$	30.4	30.0	1.3	29.9	29.6	1.0
$[C_7mim][CF_3SO_3]$	29.1	29.4	1.1	28.6	29.0	1.4
$[C_8mim][CF_3SO_3]$	28.1	28.4	1.1	27.6	27.9	0.9
$[C_9mim][CF_3SO_3]$	27.4	28.3	3.2	27.0	27.8	3.0
$[C_{10}mim][CF_3SO_3]$	26.9	27.7	2.9	26.5	27.2	2.7
$[C_3mim][CH_3SO_3]$	33.7	43.4	22.4	33.1	42.9	22.9
$[C_6mim][CH_3SO_3]$	28.8	32.6	11.7	28.3	32.2	12.1
$[C_7mim][CH_3SO_3]$	27.9	30.7	9.2	27.4	30.2	9.1
$[C_8mim][CH_3SO_3]$	27.2	29.0	6.1	26.8	28.6	6.3

[a]The average absolute deviation (AAD) is defines as

$$\text{AAD (\%)} = \left|\frac{(\gamma_{calc} - \gamma_{exp})}{\gamma_{exp}}\right|$$

Table S7. Contact angles of $[C_4mim][Tf_2N]$ at 293.15 K on the substrates.

	Contact Angle (°)		
Water content (ppm)	PTFE	Glassy carbon	Platinum[a]
140	92.7 ± 2.4	22.1 ± 1.9	< 10.0
470	90.5 ± 1.6	27.0 ± 1.5	< 10.0
1053	89.3 ± 1.2	29.7 ± 2.3	< 10.0
1496	87.4 ± 0.4	24.3 ± 2.6	< 10.0
1915	89.2 ± 2.1	25.6 ± 1.4	< 10.0
2641	92.3 ± 2.4	25.2 ± 1.2	< 10.0
4020	91.7 ± 1.2	27.7 ± 1.3	< 10.0

[a]The instrumental uncertainty is ±0.3°. The contact angles on platinum were too small for the instrument to detect and measure. Considering the uncertainty, a contact angle value less than 10.0° on platinum is decided.

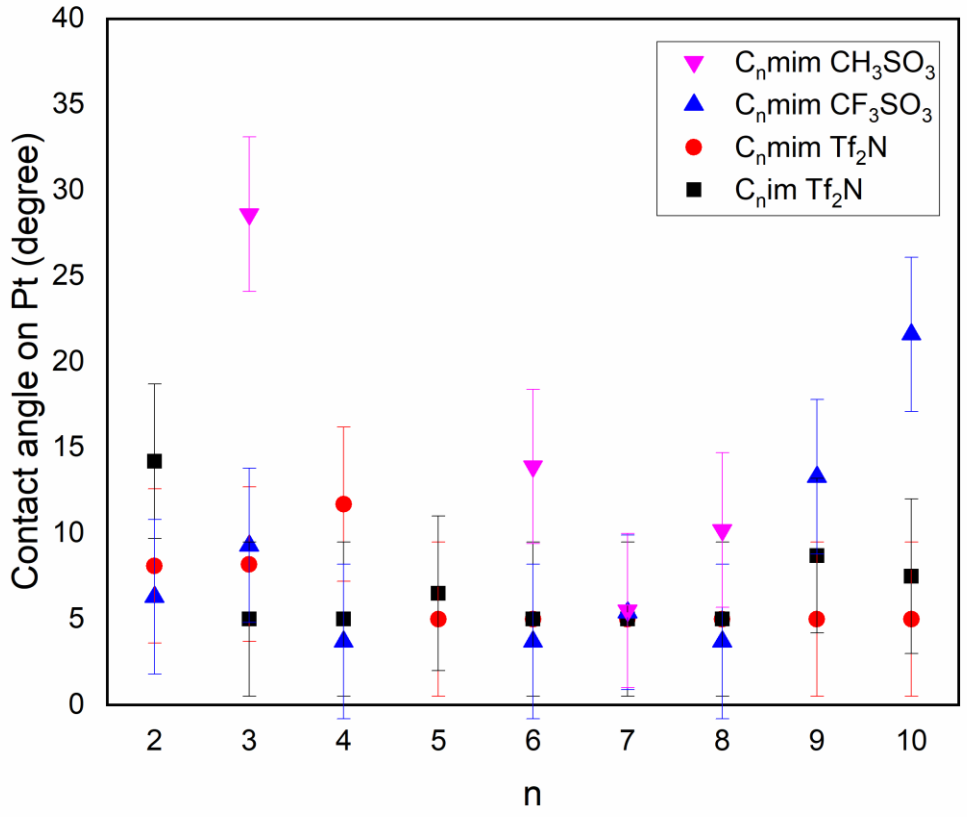

Figure S21. Contact angles of the four series of $[C_n mim][CH_3SO_3]$, $[C_n mim][CF_3SO_3]$, $[C_n mim][Tf_2N]$, and $[C_n im][Tf_2N]$ ILs on platinum at 293.15 K as a function of alkyl chain length.

Table S8. Contact angle of the four series of $[C_n mim][CH_3SO_3]$, $[C_n mim][CF_3SO_3]$, $[C_n mim][Tf_2N]$, and $[C_n im][Tf_2N]$ ILs on PTFE, glassy carbon and platinum substrates at 293.15 K.

Substrates / ILs	Water Content (ppm)	Contact Angle (°)		
		PTFE	Glassy carbon	Platinum[a]
$[C_2mim][Tf_2N]$	111	102.5 ± 2.0	40.5 ± 3.2	8.1 ± 5.0
$[C_3mim][Tf_2N]$	47	99.3 ± 1.9	33.6 ± 2.2	8.2 ± 5.0
$[C_4mim][Tf_2N]$	83	92.8 ± 3.0	26.8 ± 1.3	11.7 ± 5.0
$[C_5mim][Tf_2N]$	148	90.8 ± 1.1	20.5 ± 1.2	< 10.0
$[C_6mim][Tf_2N]$	47	91.4 ± 1.4	20.5 ± 1.4	< 10.0
$[C_7mim][Tf_2N]$	240	88.0 ± 1.6	24.2 ± 2.6	< 10.0
$[C_8mim][Tf_2N]$	120	85.7 ± 0.8	25.6 ± 1.2	< 10.0
$[C_9mim][Tf_2N]$	252	88.9 ± 1.4	20.2 ± 3.0	< 10.0
$[C_{10}mim][Tf_2N]$	121	88.7 ± 1.1	14.5 ± 1.4	< 10.0
$[C_2im][Tf_2N]$	402	99.2 ± 3.5	23.7 ± 2.2	14.2 ± 5.0
$[C_3im][Tf_2N]$	425	89.3 ± 2.6	22.9 ± 1.1	< 10.0
$[C_4im][Tf_2N]$	323	87.6 ± 1.8	20.9 ± 2.1	< 10.0
$[C_5im][Tf_2N]$	331	83.1 ± 0.9	16.4 ± 2.6	6.5 ± 5.0
$[C_6im][Tf_2N]$	204	71.2 ± 0.9	15.1 ± 2.0	< 10.0
$[C_7im][Tf_2N]$	104	73.3 ± 1.2	13.1 ± 1.2	< 10.0
$[C_8im][Tf_2N]$	203	72.6 ± 1.9	12.9 ± 1.5	< 10.0
$[C_9im][Tf_2N]$	317	72.8 ± 1.6	12.2 ± 2.7	8.7 ± 5.0
$[C_{10}im][Tf_2N]$	86	71.8 ± 2.1	10.7 ± 1.1	7.5 ± 5.0
$[C_2mim][CF_3SO_3]$	220	115.3 ± 1.8	61.9 ± 0.9	6.3 ± 5.0
$[C_3mim][CF_3SO_3]$	340	107.3 ± 0.9	54.1 ± 0.6	9.3 ± 5.0
$[C_4mim][CF_3SO_3]$	680	100.8 ± 3.4	42.6 ± 3.3	3.7 ± 5.0
$[C_6mim][CF_3SO_3]$	572	96.1 ± 1.9	32.1 ± 0.7	3.7 ± 5.0
$[C_7mim][CF_3SO_3]$	427	91.7 ± 1.8	21.2 ± 1.1	5.4 ± 5.0
$[C_8mim][CF_3SO_3]$	219	91.3 ± 2.3	20.8 ± 2.2	3.7 ± 5.0
$[C_9mim][CF_3SO_3]$	89	86.6 ± 2.5	15.8 ± 1.4	13.3 ± 5.0
$[C_{10}mim][CF_3SO_3]$	278	85.3 ± 1.6	10.0 ± 0.3	21.6 ± 5.0
$[C_3mim][CH_3SO_3]$	1400	128.1 ± 2.5	47.8 ± 3.9	28.6 ± 5.0
$[C_6mim][CH_3SO_3]$	1700	106.0 ± 1.6	26.9 ± 2.9	13.9 ± 5.0
$[C_7mim][CH_3SO_3]$	580	103.7 ± 2.4	17.1 ± 0.6	5.5 ± 5.0
$[C_8mim][CH_3SO_3]$	621	98.9 ± 3.2	17.6 ± 2.5	10.2 ± 5.0

[a]The instrumental uncertainty is ±0.3°. For some experiments, the contact angles on platinum were too small for the instrument to detect and measure. Considering the uncertainty, a contact angle value less than 10.0° on platinum is decided.

Table S9. Dispersive and non-dispersive components of the IL surface energy at 293.15 K, where γ_l is the total surface tension, γ_l^D is the dispersive part of the surface energy, γ_l^{ND} is the non-dispersive part of the surface energy and γ_l^{ND}/γ_l is the fraction of the surface energy that is non-dispersive.

ILs	γ_l (mJ/m^2)	γ_l^D (mJ/m^2)	γ_l^{ND} (mJ/m^2)	γ_l^{ND}/γ_l
[C_2mim][Tf_2N]	35.8	9.0	26.8	0.75
[C_3mim][Tf_2N]	33.9	9.4	24.5	0.72
[C_4mim][Tf_2N]	32.5	11.5	21.0	0.65
[C_5mim][Tf_2N]	31.6	11.8	19.8	0.63
[C_6mim][Tf_2N]	31.3	11.3	20.0	0.64
[C_2im][Tf_2N]	34.6	9.9	24.7	0.71
[C_3im][Tf_2N]	32.3	13.2	19.1	0.59
[C_4im][Tf_2N]	31.3	13.8	18.1	0.56
[C_5im][Tf_2N]	30.7	14.9	15.8	0.51
[C_6im][Tf_2N]	30.2	21.3	8.9	0.29
[C_7im][Tf_2N]	29.8	19.4	10.4	0.35
[C_8im][Tf_2N]	29.9	20.0	9.9	0.33
[C_9im][Tf_2N]	29.9	20.0	9.9	0.33
[C_{10}im][Tf_2N]	30.0	20.6	9.4	0.31
[C_2mim][CF_3SO_3]	39.9	4.8	35.1	0.88
[C_3mim][CF_3SO_3]	36.9	6.8	30.2	0.82
[C_4mim][CF_3SO_3]	34.5	8.4	26.2	0.76
[C_6mim][CF_3SO_3]	31.8	8.8	23.0	0.72
[C_7mim][CF_3SO_3]	31.3	10.4	20.9	0.67
[C_8mim][CF_3SO_3]	30.5	10.0	20.5	0.67
[C_9mim][CF_3SO_3]	30.4	12.1	18.3	0.60
[C_{10}mim][CF_3SO_3]	29.7	12.1	17.6	0.59
[C_3mim][CH_3SO_3]	45.1	2.0	43.1	0.96
[C_6mim][CH_3SO_3]	34.5	4.5	30.0	0.87
[C_7mim][CH_3SO_3]	32.4	6.4	26.0	0.80
[C_8mim][CH_3SO_3]	30.9	8.6	22.3	0.72

[a]The overall relative uncertainty is ±5%.