Mixing divalent ionic liquids: Effects of charge and side-chains

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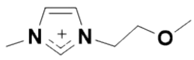
Ionic liquid structures and nomenclature

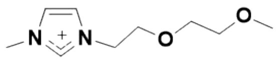
The *bis*(trifluoromethanesulfonyl)imide anion $[NTf_2]^-$ was the ionic liquid anion of choice in this work. All imidazolium $[NTf_2]^-$ salts with the cations depicted below are room temperature ionic liquids, except $[C_{10}C_1C_1C_1biim][NTf_2]_2$ and $[(C_4im)_2C_1][NTf_2]_2$.

$[C_2C_1im]^+$

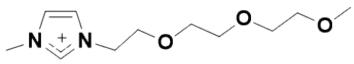
$[(C_3O)C_1im]^+$



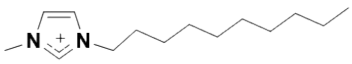
$[(C_5O_2)C_1im]^+$



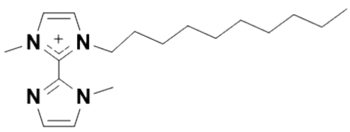
$[(C_7O_3)C_1im]^+$



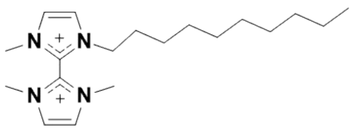
$[C_{10}C_1im]^+$



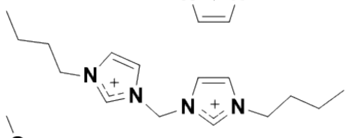
$[C_{10}C_1C_1biim]^+$



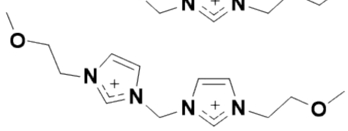
$[C_{10}C_1C_1C_1biim]^{2+}$



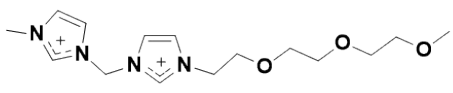
$[(C_4im)_2C_1]^{2+}$



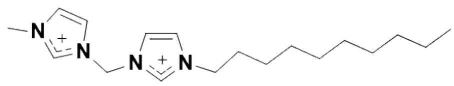
$[((C_3O)im)_2C_1]^{2+}$



$[(C_7O_3)imC_1imC_1]^{2+}$

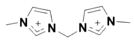
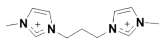


$[C_{10}imC_1imC_1]^{2+}$



Literature comparison

Table S1
Structures, abbreviations and melting points of divalent imidazolium cation $[NTf_2]^-$ ILs selected from literature

Structure	Chg	Abbreviation	m.p.
	2+	$[(C_1im)_2C_1]^{2+}$	solid [1,2] 90−94°C[3]
	2+	$[(C_1im)_2C_3]^{2+}$	48−52 °C[4] <25 °C[5]
	2+	$[(C_1im)_2C_4]^{2+}$	54−56 °C[3]

Synthetic procedures

Syntheses were carried out under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. The liquid alkylimidazoles were dried over KOH and distilled at reduced pressure prior to use. NMR spectra (Bruker Av-400) were referenced against the solvent residue signal (DMSO-d_6 = 2.50 ppm, $CDCl_3$ = 7.26 ppm). Melting points (*OptiMelt* MPA100) were read visually at a heating rate of 2 °C·min^{-1}.

For quaternisations, haloethers were preferred over alkyl sulfonates because the first could easily be purified *via* vacuum distillation. Alkyl sulfonates were found to be thermally unstable at distillation conditions[6] and therefore irreversibly contaminate the final ILs. Reaction of crude alkylsulfonates with 1-methylimidazole at our reaction conditions led to formation of unidentified sideproducts in small quantities, as judged from NMR analysis.

Ionic liquids $[C_2C_1im][NTf_2]$[7] and $[C_{10}C_1im][NTf_2]$[8] were synthesized *via* the corresponding Br^- salts as described before, and ILs with satisfactory analytical data were obtained.

$[(C_3O)C_1im][NTf_2]$, ***N-(2-Methoxyethyl)-N'-methylimidazolium bis(Trifluoromethanesulfonyl)-imide.*** *N*-Methylimidazole (69.89 g, 852 mmol, 1.00 eq) was added dropwise to a solution of 2-chloroethylmethyl ether (121.71 g, 1287 mmol, 1.51 eq) in acetonitrile (30 mL) with stirring. The solution was stirred for 5 h at room temperature and then for a further 110 h at 80 ºC. No residual *N*-methylimidazole could be detected (NMR) in the reaction mixture after this time. The volatiles were removed *via* rotary evaporation and the residue diluted with water (~250 mL). Powdered charcoal was added to the solution and it was stirred at 80 ºC for 1 h, following a gradual cooling to room temperature and to 0 ºC. The suspension was filtered through a glass fibre membrane; a nearly colourless solution (343.56 g) was obtained, which contained *N*-(2-methoxyethyl)-*N*'-methylimidazolium chloride (151.54 g, 44.1% w/w).

To an aqueous solution containing *N*-(2-methoxyethyl)-*N*'-methylimidazolium chloride (60.71 g, 343.9 mmol) a solution of lithium *bis*(trifluoromethanesulfonyl)imide (98.72 g, 343.9 mmol) in water (50 mL) was added. The mixture was extracted with dichloromethane (100 mL) and the organic phase washed with water (3 x 20 mL) until chloride-free by the silver nitrate test. The solution was filtered through the hydrophobic filter paper, evaporated *via* rotary evaporation and dried with stirring at 0.1 mbar, 60 ºC for 24 h. A colourless liquid was obtained.

δ_H (400 MHz; DMSO-d_6) 3.27 (3 H, s, CH_3), 3.65-3.70 (2 H, m, CH_2), 3.86 (3 H, s, NCH_3), 4.32-4.37 (2 H, m, CH_2), 7.68 (1 H, t, $^3J_{HH}$ 1.7 Hz, =CH), 7.72 (1 H, t, $^3J_{HH}$ 1.7 Hz, =CH), 9.05 (1 H, bs, CH) ppm
δ_C (101 MHz; DMSO-d_6) 35.7, 48.7, 58.0, 69.6, 119.5 (q, $^1J_{13C-19F}$ 323 Hz), 122.6, 123.5, 136.8 ppm
δ_F (377 MHz; DMSO-d_6) -79.2 ppm
ATR-FTIR, ν (neat): 3160 (arom. $H^{4/5}$ stretch, w), 3123 (arom. H^2 stretch, w), 3103 (w), 2942 (w), 2900 (w), 2840 (w), 2824 (w), 1576 (m), 1567 (m), 1347 (s), 1330 (asym. S=O stretch, s), 1227 (sym. CF_3 str., s), 1177 (vs), 1133 (sym. S=O stretch, vs), 1083 (m), 1050 (vs), 1013 (s), 836 (s), 788 (s), 763 (s), 740 (s), 704 (w), 653 (s), 610 (vs) cm^{-1}
m/z (ES+): 141 (100%, $[(C_3O)C_1im]^+$)
m/z (ES-): 280 (100%, $[NTf_2]^-$)

$[(C_5O_2)C_1im][NTf_2]$, ***1-(2-(2-Methoxyethoxy)ethyl)-3-methylimidazolium bis(Trifluoromethhane-sulfonyl)imide***. A solution of *N*-methylimidazole (25.28 g, 307.9 mmol, 1 eq) and 1-chloro-2-(2-methoxyethoxy)ethane[9] (49.58 g, 357.8 mmol, 1.16 eq) in acetonitrile (100 mL) was stirred in an oil bath (80 ºC) for 8 days. The volatiles were removed *via* rotary evaporation and the residue dissolved in water (50 mL). The solution was transferred into a separatory funnel and a solution of lithium *bis*(trifluoromethanesulfonyl)imide (87.01 g, 303.1 mmol) in a minimal amount of water was added.

The mixture was extracted with dichloromethane (3x30 mL) and the organic phase washed with water until chloride-free. Dichloromethane was evaporated and the remaining ionic liquid dried at 60 ºC. Powdered charcoal was carefully stirred into the coloured ionic liquid, and the drying continued. The mixture was cooled to room temperature and filtered at reduced pressure through a glass fibre membrane and 0.2 μm PTFE filter providing a colourless liquid (65.87 g, 45%).

δ_H (400 MHz; DMSO-d_6) 3.22 (3 H, s, OCH_3), 3.40-3.44 (2 H, m, CH_2), 3.53-3.56 (2 H, m, CH_2), 3.76 (2 H, t, $^3J_{HH}$ 4.9 Hz, CH_2), 3.86 (3 H, s, N-CH_3), 4.34 (2 H, t, $^3J_{HH}$ 4.9 Hz, N-CH_2), 7.67 (1 H, t, $^3J_{HH}$ 1.7 Hz, =CH), 7.71 (1 H, t, $^3J_{HH}$ 1.7 Hz, =CH), 9.05 (1 H, s, CH) ppm
δ_C (101 MHz; DMSO-d_6) 35.7, 48.9, 58.0, 68.2, 69.4, 71.1, 119.6 (q, $^1J_{13C-19F}$ 321 Hz), 122.7, 123.4, 136.9 ppm
δ_F (377 MHz; DMSO-d_6) -78.9 ppm
m/*z* (ES^+): 185 (100%, $[RC_1im]^+$)
m/*z* (ES^-): 280 (100%, $[NTf_2]^-$)
ATR-FTIR, ν (neat): 3160 (arom. $H^{4/5}$ stretch, m), 3122 (arom. H^2 stretch, m), 2885 (aliph. C-H stretch, m), 1576 (m), 1567 (m), 1454 (m), 1349 (s), 1330 (asym. S=O stretch, vs), 1227 (sym. CF_3 str., m), 1178 (vs), 1132 (sym. S=O stretch, s), 1103 (s), 1052 (vs), 925 (m), 844 (m), 789 (m), 762 (m), 740 (s), 704 (m), 653 (s) cm^{-1}
Elemental Analysis (expected): C, 28.52 (28.39); H, 3.59 (3.68); N, 9.10 (9.03) %

2-(2-(2-Methoxyethoxy)ethoxy)ethyl Mesylate. Triethylamine (98.86 g, 977 mmol) and triethylene glycol monomethylether (150.00 g, 914 mmol) was dissolved in dichloromethane (500 mL) and cooled to +5 ºC by stirring in an ice-water bath. Under nitrogen, methanesulfonyl chloride (104.68 g, 914 mmol) from a dropping funnel was added to the cooled solution over 1 h. The white suspension which formed was further stirred at room temperature for 16 h. Water (300 mL) was added to the mixture. The organic phase was separated and extracted twice more with water (2x150 mL) following the drying over anhydrous sodium sulphate. Dichloromethane was removed *via* rotary evaporation and the yellowish liquid (184.06 g, 83%) was dried over anhydrous potassium carbonate and converted to the corresponding alkylbromide withouth purification (due to thermal decomposition the mesylate could not be purified by distillation).

δ_H (400 MHz; $CDCl_3$) 2.95 (3 H, s, S-CH_3), 3.23 (3 H, s, O-CH_3), 3.38-3.43 (2 H, m, CH_2), 3.47-3.57 (6 H, m, CH_2), 3.61-3.65 (2 H, m, CH_2), 4.22-4.26 (2 H, m, CH_2) ppm
δ_C (101 MHz; $CDCl_3$) 37.6, 58.9, 68.9, 69.4, 70.4 (2 C), 70.5, 71.8 ppm

2-(2-(2-Methoxyethoxy)ethoxy)ethyl Bromide. To a stirred solution of 2-(2-(2-methoxyethoxy)ethoxy)ethyl mesylate (184.0 g, 759 mmol, 1.0 eq) in dimethylformamide (250 mL) lithium bromide (99.0 g, 1139 mmol, 1.5 eq) was slowly added under a flow of nitrogen. The rate of addition was adjusted so the temperature of the mixture didn't rise above 50 ºC. Dissolution and reappearance of a white solid was observed. The mixture was stirred for 48 h at room temperature, diluted with 0.5 L of ethyl acetate and after stirring for 12 more hours filtered using a sintered filter. The organic phase was washed with water (4 x 100 mL), aqueous lithium chloride (3 x 100 mL of a 5% solution), water (100 mL) and brine (100 mL). The organic phase was died over anhydrous sodium sulphate, and ethyl acetate removed *via* rotary evaporation. The slightly yellow liquid, which contained no more traces of dimethylformamide, was dried over anhydrous potassium carbonate and distilled at reduced pressure to afford a colourless liquid (102.2 g, 59.3%).

δ_H (400 MHz; $CDCl_3$) 3.35 (3 H, s, O-CH_3), 3.44 (2 H, t, $^3J_{HH}$ 6.3 Hz, CH_2), 3.50-3.55 (2 H, m, CH_2), 3.60-3.68 (6 H, m, CH_2), 3.78 (2 H, t, $^3J_{HH}$ 6.3 Hz, CH_2) ppm
δ_C (101 MHz; $CDCl_3$) 30.4, 59.1, 70.6, 70.7 (2 C), 71.24, 72.0 ppm

[$(C_7O_3)C_1$im][NTf_2], ***1-(2-(2-(2-Methoxyethoxy)ethyl)ethyl)-3-methylimidazolium bis(Trifluoromethhanesulfonyl)imide.*** To a stirred solution of 1-methylimidazole (30.76 g, 375 mmol, 1.0 eq) in acetonitrile (120 mL) 2-(2-(2-methoxyethoxy)ethoxy)ethyl bromide (102.20 g, 450 mmol, 1.2 eq) was slowly added dropwise over 10 minutes.The mixture was stirred at 60 °C for 48 h. The volatiles were removed *via* rotary evaporation and the residue washed by vigorously stirring with ethyl acetate for 10 min (4x100 mL) to remove the residual trace of 1-methylimidazole. The viscous oil that remained was dissolved in water (100 mL) and aqueous solution of lithium *bis*(trifluoromethanesulfonyl)imide (107.70 g, 375 mmol, 1.0 eq) in a minimal amount of water was added. The mixture was extracted with dichloromethane (100 mL) and the organic phase washed with water until chloride-free (3x50 mL). Dichloromethane was evaporated and the remaining ionic liquid dried at 60 ºC. Powdered charcoal was carefully stirred into the coloured ionic liquid, and the drying continued for 12 h. The mixture was cooled to room temperature and filtered at reduced pressure through a glass fibre membrane and 20 μm PTFE filter providing a colourless liquid (146.76 g, 77%).

δ_H (400 MHz; DMSO-d_6) 3.24 (3 H, s, O-CH_3), 3.40-3.45 (2 H, m, CH_2), 3.47-3.53 (4 H, m, CH_2), 3.54-3.58 (2 H, m, CH_2), 3.77 (2 H, t, $^3J_{HH}$ 4.9 Hz, CH_2), 3.86 (3 H, s, NCH_3), 4.34 (2 H, t, $^3J_{HH}$ 4.9 Hz, CH_2), 7.67-7.70 (1 H, m, =CH), 7.72-7.72 (1 H, m, =CH), 9.04 (1 H, bs, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 35.7, 48.7, 58.0, 68.1, 69.5 (2 C), 71.3, 119.5 (q, $^1J_{13C-19F}$ 323 Hz), 122.7, 123.3, 136.9 ppm
δ_F (377 MHz; DMSO-d_6) -78.9 ppm
m/*z* (ES^+): 229 (100%, [RC_1im]$^+$), 185 (40%), 125 (40%)
m/*z* (ES^-): 280 (100%, [NTf_2]$^-$)
ATR-FTIR, ν (neat): 3157 (arom. $H^{4/5}$ stretch, m), 3120 (arom. H^2 stretch, m), 2883 (aliph. C-H stretch, m), 1575 (m), 1567 (m), 1451 (m), 1348 (s), 1331 (asym. S=O stretch, vs), 1227 (sym. CF_3 str., m), 1179 (vs), 1133 (sym. S=O stretch, s), 1109 (m), 1053 (vs), 934 (m), 849 (m), 789 (m), 762 (m), 739 (s), 704 (m), 653 (s) cm^{-1}
Elemental Analysis (expected): C, 30.69 (30.65); H, 4.09 (4.16); N, 8.09 (8.25) %

Na[im], ***Sodium imidazolide.*** In a 500 mL round bottomed flask imidazole (59.60 g, 875 mmol, 1.00 eq) was mixed with sodium hydroxide pellets (36.05 g, 901 mmol, 1.03 eq) and water (ca. 3 mL) to form a wet mass. Toluene (250 mL) was added, and the mixture was efficiently and vigorously stirred under reflux (bath temperature 150-160 ºC) using a Dean-Stark trap and a condenser. Most of the water was collected in the receiver within the next 4 h, and a partial crystallization of the mixture had occurred. The semi-solid mixture was crushed into powder with a spatula, and the reaction continued for 20 more hours. The crushing was repeated and after 1 more hour of refluxing the toluene was removed *via* rotary evaporation. Drying (0.1 mbar, 100 ºC) afforded off-white crystals in a quantitative yield. The product is soluble in dimethylsulfoxide and dimethylformamide, and can be stored under nitrogen for extended period of time. The procedure can be scaled up without difficulty to at least 100 g of imidazole starting material, and provides a material in a physical form that is easy to handle.

δ_H (400 MHz; DMSO-d_6) 6.68-6.76 (2 H, m, =CH), 7.10-7.19 (1 H, m, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 125.2, 143.7 ppm
ATR-FTIR, ν: 3083 (w), 2972 (w), 1460 (s), 1247 (m), 1229 (s), 1137 (m), 1111 (w), 1087 (s), 942 (w), 921 (s), 849 (m), 833 (s), 749 (vs), 683 (vs) cm^{-1}

1-(2-Methoxyethyl)imidazole. Sodium imidazolide (147.27 g, 1.64 mol, 1.00 eq) was suspended in acetonitrile (600 mL) and 2-chloroethyl methyl ether (146.84 g, 1.55 mol, 0.95 eq) was added dropwise over 1 h. The mixture was stirred at room temperature for 3 h and then heated under reflux for 13 h. After cooling to room temperature the suspension was filtered over a sintered filter, the solids washed with acetonitrile (2 x 70 mL) and the filtrate concentrated by rotary evaporation. The remaining dark, viscous oil was stirred with potassium hydroxide overnight and distilled at reduced pressure (101 °C, 0.7 mbar) providing a colourless liquid with a characteristic peanut butter odour (172.55 g, 88%).

δ_H (400 MHz; $CDCl_3$) 3.31 (3 H, s, OCH_3), 3.60 (2 H, t, $^3J_{HH}$ 5.1 Hz, CH_2), 4.07 (2 H, t, $^3J_{HH}$ 5.1 Hz, CH_2), 6.95 (1 H, s, =CH), 7.02 (1 H, s, =N-C*H*=), 7.54 (1 H, s, NCHN) ppm
δ_C (101 MHz; $CDCl_3$) 47.1, 59.1, 71.8, 119.5, 129.0, 137.5 ppm

$[((C_3O)im)_2C_1]Br_2$, *Methylene bis(3-(2-methoxyethyl)imidazolium dibromide*. Dibromomethane (61.13 g, 352 mmol, 1.0 eq) was added to a solution of 1-(2-methoxyethyl)imidazole (110.91 g, 879 mmol, 2.5 eq) in acetonitrile (200 mL). The mixture was stirred at 90 °C for 96 h. The volatiles were removed *via* rotary evaporation, the residue crushed and washed with ethyl acetate (2x100 mL). The dark crystalline material was dissolved in water (300 mL) and stirred overnight with powdered charcoal at 70 °C. The mixture was cooled to room temperature, filtered through a glass fibre membrane and a cellulose syringe-filter, and evaporated to dryness. Toluene was added and azeotropically distilled off to remove water from the material (2x100 mL). Recrystallization from ethanol with dropwise addition of ethyl acetate was done; the product was allowed to crystallize at -20 °C, filtered *via* canula and washed with cold absolute ethanol (3x70 mL), ethyl acetate (70 mL) and dried at reduced pressure (100 °C, 0.1 mbar). Snow white crystals (113.86 g, 76%, m.p. 162.0-164.0 °C).

δ_H (400 MHz; DMSO-d_6) 3.27 (6 H, s, OCH_3), 3.72 (4 H, t, $^3J_{HH}$ 4.8 Hz, CH_2), 4.44 (4 H, t, $^3J_{HH}$ 4.8 Hz, CH_2), 6.84 (2 H, s, NCH_2N), 7.89-7.92 (2 H, m, =CH), 8.17-8.21 (2 H, m, =CH), 9.71 (2 H, s, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 49.2, 57.9, 58.1, 69.2, 121.9, 123.5, 137.9 ppm

$[((C_3O)im)_2C_1][NTf_2]_2$, *Methylene bis(3-(2-methoxyethyl)imidazolium bis(trifluoromethhane-sulfonyl)imide*. Methylene *bis(*3-(2-methoxyethyl)imidazolium dibromide (83.79 g, 197 mmol, 1 eq) was dissolved in water (100 mL) and a solution of lithium *bis(*trifluoromethanesulfonyl)imide (112.89 g, 395 mmol, 2.0 eq) in a minimal amount of water was added. The mixture was extracted with ethyl acetate (3x50 mL) and the organic phase washed with water until halide-free. Ethyl acetate was evaporated and the remaining ionic liquid dried at reduced pressure (70 ºC, 0.1 mbar) to afford an almost colourless viscous liquid (137.70 g, 85%).

δ_H (400 MHz; DMSO-d_6) 3.29 (6 H, s, OCH_3), 3.70 (4 H, t, $^3J_{HH}$ 4.8 Hz, CH_2), 4.42 (4 H, t, $^3J_{HH}$ 4.8 Hz, CH_2), 6.64 (2 H, s, NCH_2N), 7.81-7.84 (2 H, m, =CH), 7.96-7.99 (2 H, m, =CH), 9.39-9.41 (2 H, s, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 49.2, 58.1, 58.4, 69.3, 119.5 (q, $^1J_{13C-19F}$ 322 Hz), 122.0, 123.7, 137.9 ppm
δ_F (377 MHz; DMSO-d_6) -78.8 ppm
ATR-FTIR, ν (neat): 3156 (arom. $H^{4/5}$ stretch, m), 3115 (m), 2943 (m), 2901 (m), 2843 (w), 1578 (m), 1567 (m), 1550 (m), 1454 (m), 1346 (s), 1327 (asym. S=O stretch, s), 1227 (sym. CF_3 str., m), 1178 (vs), 1131 (sym. S=O stretch, vs), 1085 (s), 1051 (vs), 1013 (s), 969 (m), 941 (w), 838 (m), 790 (s), 771 (s), 764 (s), 740 (s), 654 (s) cm^{-1}
m/*z* (ES^+): 207 (100%, $[(RimC_1im]^+)$, 133 (65%, $[(Rim)_2C_1]^{2+}/2$), 265 (40%, $[(Rim)_2C_1]^{2+}–H^+$)
m/*z* ($ES^–$): 280 (100%, $[NTf_2]^–$)
Elemental Analysis (expected): C, 24.58 (24.70); H, 2.69 (2.68); N, 10.15 (10.17) %

$[(C_4im)_2C_1]Br_2$, *1,1'-Dibutyl-3,3'-methylidene-bis-imidazolium dibromide* was prepared as described before,[10] m.p. 180.4-185.5 ºC (lit.[10] 178.6 ºC). White crystalline material with satisfying analytical data was obtained.

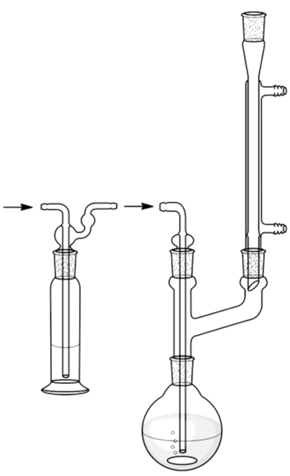
δ_H (400 MHz; DMSO-d_6) 0.90 (6 H, t, $^3J_{HH}$ 7.2 Hz, CCH_3), 1.28 (4 H, sextet, $^3J_{HH}$ 7.5 Hz, $C\underline{H_2}CH_3$), 1.79 (4 H, quintet, $^3J_{HH}$ 7.4 Hz, $NCH_2C\underline{H_2}$), 4.24 (4 H, t, $^3J_{HH}$ 7.2 Hz, NCH_2), 6.75 (2 H, s, NCH_2N), 7.92-7.95 (2 H, m, =CH), 8.12-8.16 (2 H, m, =CH), 9.69 (2 H, bs, N-CH=N) ppm
m/*z* (ES^+): 207 (100%, $[(RimC_1im])$, 133 (65%, $[(Rim)_2C_1]^{2+}/2$), 265 (40%, $[(Rim)_2C_1]^{2+}–H^+$)
ATR-FTIR, ν: 3494 (w), 3436 (w), 3129 (w), 3050 (s), 2962 (s), 2937 (m), 2872 (m), 1680 (w), 1628 (w), 1579 (m), 1546 (s), 1465 (m), 1435 (s), 13734369 (m), 1332 (m), 1303 (m), 1257 (w), 1227 (w),

1170 (vs), 1124 (m), 1053 (m), 1027 (w), 981 (w), 946 (w), 900 (m), 871 (m), 787 (s), 761 (s), 678 (w), 658 (w) cm^{-1}

[$(C_4im)_2C_1$][NTf_2]$_2$, ***1,1'-Dibutyl-3,3'-methylidene-bis-imidazolium bis(trifluoromethhanesulfonyl)imide*** was prepared *via* aqueous metathesis between the corresponding bromide and lithium *bis(*trifluoromethanesulfonyl)imide as described for [$((C_3O)im)_2C_1$][NTf_2]$_2$. White crystalline material with satisfying analytical data was obtained, m.p. 58.6-59.3 ^{o}C.

δ_H (400 MHz; DMSO-d_6) 0.91 (6 H, t, $^3J_{HH}$ 7.3 Hz, CCH_3), 1.30 (4 H, sextet, $^3J_{HH}$ 7.5 Hz, $C\underline{H_2}CH_3$), 1.79 (4 H, quintet, $^3J_{HH}$ 7.3 Hz, $NCH_2C\underline{H_2}$), 4.22 (4 H, t, $^3J_{HH}$ 7.2 Hz, NCH_2), 6.59 (2 H, s, NCH_2N), 7.86-7.89 (2 H, m, =CH), 7.95-7.98 (2 H, m, =CH), 9.39 (2 H, bs, N-CH=N) ppm
δ_C (101 MHz; DMSO-d_6) 13.2, 18.8, 31.1, 49.1, 58.4, 119.5 (q, $^1J_{13C-19F}$ 322 Hz), 122.3, 123.2, 137.5 ppm
δ_F (377 MHz; DMSO-d_6) -78.8 ppm
ATR-FTIR, ν: 3165 (w), 3153 (w), 3138 (w), 3060 (w), 2971 (w), 2943 (w), 2883 (w), 1580 (w), 1551 (m), 1460 (w), 1346 (s), 1327 (s), 1227 (m), 1178 (vs), 1163 (vs), 1133 (vs), 1052 (vs), 948 (w), 909 (w), 848 (m), 789 (s), 768 (s), 754 (s), 739 (s), 697 (w), 652 (w) cm^{-1}
Elemental Analysis (expected): C, 27.53 (27.74); H, 3.02 (3.19); N, 10.11 (10.22) %

1,1'-Dimethyl-2,2'-biimidazole. A literature procedure[11] was adapted for a multi-gram scale. To a stirred suspension of copper(I) chloride (7.22 g, 73 mmol, 0.095 eq) and 2-hydroxypyridine sodium salt (17.20 g, 148 mmol, 0.19 eq, **Note 1**) in xylenes (330 mL, **Note 2**) 1-methylimidazole (63.24 g, 770 mmol, 1.00 eq) was added dropwise. The mixture was heated under reflux while dry air was bubbled through (**Note 3**). After all the 1-methylimidazole had been consumed (**Note 4**) the volatiles were removed *via* rotary evaporation and the black residue dried (80 ºC, 10 mbar) followed by a sublimation (110 ºC, 0.1 mbar, ~12 h, **Note 5**). Large snow-white crystals were obtained (52.56 g, 84%).



Note 1: Equimolar amounts of 2-hydroxypyridine and methanolic sodium methoxide were mixed, evaporated and dried (70 ºC, 0.1 mbar) to afford 2-hydroxypyridine sodium salt, which was used without further purification.
Note 2: The reaction was also attempted in toluene - at the boiling point of this solvent no conversion was observed.
Note 3: An aquarium pump was used; the air was first passed through a wash bottle containing concentrated sulfuric acid. The gas flow was adjusted so the boiling xylenes weren't excessively lost from the mixture. The gas inlet tube was at least 5 mm in diameter to avoid getting blocked. See the figure for a schematic setup.
Note 4: Stirring and refluxing was stopped from time to time, and the clear solvent phase analysed by ^{1}H NMR in $CDCl_3$. The methyl signal of the product appeared at 4.05 ppm while that of 1-methylimidazole at 3.60 ppm. When the refluxing, stirring and aeration was efficient, 8 hours of reaction time were sufficient to achieve a complete consumption of 1-methylimidazole.
Note 5: A large glass vessel with air-cooled surfaces is sufficient for sublimation.

δ_H (400 MHz; $CDCl_3$) 3.96 (6 H, s, CH_3), 6.89 (2 H, s, =CH), 7.04 (2 H, s, =CH) ppm
δ_C (101 MHz; $CDCl_3$) 35.3, 122.6, 127.8, 138.6 ppm
m/*z* (ES$^+$): 161 (100%, M$^+$), 107 (20%)

[$C_{10}C_1C_1$biim]Br, ***1-Decyl-1',3-dimethyl-2,2'-biimidazolium bromide***. To neat 1-bromodecane (150 mL, 723 mmol, 3.5 eq) crystalline 1,1'-dimethyl-2,2'-biimidazole (33.84 g, 209 mmol, 1.0 eq) was added, and the mixture stirred at 120 ºC for 6 h. The biimidazole initially dissolved providing a clear solution, soon after which fine crystals started to form. After stirring at 120 ºC the mixture was cooled to room temperature, diluted with ethyl acetate (60 mL) and cooled at -20 ºC for 0.5 h. The crystals were filtered *via* suction filtration, washed on the filter with ethyl acetate (3x50 mL) and ether (50 mL), air-dried and recrystallized from boiling ethyl acetate with dropwise addition of propanol-2. The solution was allowed to crystallize until the mixture reached room temperature, and further cooled at -20 ºC for 0.5 h. The product was collected *via* suction filtration and washed with ethyl acetate (3x50 mL) and ether (50 mL), and dried in air. Snow-white flaky crystals (50.05 g, 63%, m.p. 204.0-205.0 °C).

δ_H (400 MHz; DMSO-d_6) 0.83 (3 H, t, $^3J_{HH}$ 6.9, C-CH_3), 1.04-1.29 (14 H, m, $(CH_2)_7$), 1.65 (2 H, m, CH_2), 3.71 (3 H, s, NCH_3), 3.75 (3 H, s, NCH_3) 4.04 (2 H, m, NCH_2), 7.33 (1 H, m, =CH), 7.73 (1 H, m, =CH), 8.11 (1 H, d, $^3J_{HH}$ 2.2 Hz, =CH), 8.19 (1 H, d, $^3J_{HH}$ 2.2 Hz, =CH) ppm
δ_C (101 MHz; DMSO-d_6) 13.9, 22.1, 25.2, 28.1, 28.6, 28.7, 28.8, 29.1, 31.3, 33.8, 35.8, 48.7, 123.5, 125.1, 126.2, 128.3, 130.9, 134.5 ppm
ATR-FTIR, ν: 3478 (w), 3419 (w), 3071 (m), 3044 (m), 2994 (m), 2953 (m), 2919 (s), 2851 (m), 1800 (w), 1709 (w), 1603 (m), 1520 (s), 1468 (vs), 1419 (s), 1404 (m), 1380 (w), 1360 (w), 1329 (w), 1310 (w), 1278 (s), 1240 (s), 1202 (m), 1143 (m), 1098 (w), 1078 (m), 1059 (w), 1030 (m), 918 (m), 862 (w), 810 (s), 780 (vs), 761 (s), 731 (vs), 722 (s), 705 (s), 667 (w) cm^{-1}
m/*z* (ES^+): 303 (100%, $[(C_{10}C_1C_1biim]^+$)
m/*z* (ES^-): 81 (100%, $^{81}Br^-$), 79 (95%, $^{79}Br^-$)
Elemental Analysis (expected): C, 56.22 (56.39); H, 8.17 (8.15); N, 14.48 (14.61) %

$[C_{10}C_1C_1biim][NTf_2]$, ***1-Decyl-1',3-dimethyl-2,2'-biimidazolium bis(trifluoromethhanesulfonyl)imide***. To a solution of $[C_{10}C_1C_1biim]Br$, 1-decyl-1',3-dimethyl-2,2'-biimidazolium bromide (20.91 g, 55 mmol, 1 eq) in water (80 mL) a solution of lithium *bis(*trifluoromethanesulfonyl)imide (15.66 g, 55 mmol, 1 eq) in a minimal amount of water was added. The mixture was extracted with dichloromethane (2x50 mL) and the organic phase washed with water until halide-free. The dichloromethane solution was filtered through the hydrophobic filter paper, treated with powdered charcoal, filtered *via* gravity and then through a 0.2 μm PTFE filter, and evaporated *via* rotary evaporation. Drying at reduced pressure (70 ºC, 0.1 mbar) afforded an almost colourless viscous liquid (27.30 g, 86%).

δ_H (400 MHz; DMSO-d_6) 0.81-0.90 (3 H, s, CCH_3), 1.08-1.32 (14 H, m, $(CH_2)_7$), 1.63-1.74 (2 H, m, CH_2), 3.71 (3 H, s, NCH_3), 3.76 (3 H, s, $^+NCH_3$), 4.05 (2 H, t, $^3J_{HH}$ 4.8 Hz, NCH_2), 7.33 (1 H, bs, =CH), 7.65 (1 H, bs, =CH), 8.00 (1 H, d, $^3J_{HH}$ 4.8 Hz, =CH), 8.07 (1 H, d, $^3J_{HH}$ 2.1 Hz, =CH) ppm
δ_C (101 MHz; DMSO-d_6) 13.7, 22.0, 25.2, 28.1, 28.58, 28.64, 28.8, 29.1, 31.2, 33.5, 35.6, 48.8, 119.5 (q, $^1J_{13C-19F}$ 324 Hz), 123.4, 125.0, 126.0, 128.2, 130.9, 134.7 ppm
δ_F (377 MHz; DMSO-d_6) -78.9 ppm
ATR-FTIR, ν (neat): 3148 (arom. $H^{4/5}$ stretch, w), 2928 (m), 2857 (m), 1605 (w), 1520 (m), 1466 (m), 1420 (w), 1348 (s), 1331 (asym. S=O stretch, s), 1281 (m), 1227 (sym. CF_3 str., s), 1179 (vs), 1134 (sym. S=O stretch, s), 1054 (vs), 918 (m), 786 (m), 762 (m), 740 (m), 726 (m), 653 (m) cm^{-1}
m/*z* (ES^+): 303 (100%, $[C_{10}C_1C_1biim]^+$)
m/*z* (ES^-): 280 (100%, $[NTf_2]^-$)
Elemental Analysis (expected): C, 41.08 (41.16); H, 5.20 (5.35); N, 11.92 (12.00) %

$[C_{10}C_1C_1C_1biim][NTf_2]_2$, ***1-Decyl-1',3,3'-trimethyl-2,2'-biimidazolium bis(trifluoromethanesulfonyl)imide.*** 1-Decyl-1',3-dimethyl-2,2'-biimidazolium bromide (22.13 g, 58 mmol, 1 eq) was stirred with dimethylsulfate (60 mL, 11 eq) for 21 h at 130 ºC under nitrogen. Ethyl acetate (300 mL) and water (100 mL) was added to a cooled mixture; it was slowly stirred until two clear layers separated. The ethyl acetate layer was cannulated off and residue washed twice more with ethyl acetate (2x50 mL). Powdered charcoal was added to the aqueous phase, and after it was stirred for 1 h the mixture was filtered through a glass fibre membrane. Aqueous lithium *bis(*trifluoromethanesulfonyl)imide (33.14 g, 116 mmol, 2 eq) was added to the clear filtrate. The mixture was extracted with ethyl acetate (3x20 mL) and the organic phase washed with water until bromide-free. Ethyl acetate was evaporated and the remaining ionic liquid dried at reduced pressure (90 °C, 0.1 mbar) to afford an almost colourless material (38.00 g, 75% in two steps, m.p. 60.0-63.0 °C).

δ_H (400 MHz; DMSO-d_6) 0.85 (3 H, m, C-CH_3), 1.13-1.31 (14 H, m, $(CH_2)_7$), 1.68-1.80 (2 H, m, CH_2), 3.83 (3 H, s, NCH_3), 3.85 (6 H, s, $^+NCH_3$) 4.10 (2 H, t, $^3J_{HH}$ 7.3 Hz, NCH_2), 8.28 (2 H, s, CH=CH), 8.34 (1 H, d, $^3J_{HH}$ 2.0 Hz, -CH=C), 8.39 (1 H, $^3J_{HH}$ 2.2 Hz, -CH=C), 8.19 (1 H, d, $^3J_{HH}$ 2.1 Hz, -CH=C) ppm
δ_C (101 MHz; DMSO-d_6) 13.9, 22.1, 25.4, 28.5, 28.7, 28.8, 28.9, 29.1, 31.3, 36.38, 36.41, 49.3, 119.5 (q, $^1J_{13C-19F}$ 321 Hz), 124.1, 124.6, 126.3, 128.2, 128.8 ppm
δ_F (377 MHz; DMSO-d_6) -78.7 ppm
ATR-FTIR, ν: 3143 (arom. $H^{4/5}$ stretch, m), 2930 (m), 2860 (w), 1566 (w), 1532 (w), 1515 (w), 1459 (w), 1343 (s), 1328 (asym. S=O stretch, s), 1232 (sym. CF_3 str., s), 1182 (vs), 1134 (sym. S=O stretch, vs), 1051 (vs), 789 (m), 758 (m), 740 (m), 653 (m) cm^{-1}
m/z (ES^+): 157 (100%), 159 (60%, $[C_{10}C_1C_1C_1biim]^{2+}/2$), 317 (60%, $[C_{10}C_1C_1C_1biim]^{2+}-H^+$)
m/z (ES^-): 280 (100%, $[NTf_2]^-$)
Elemental Analysis (expected): C, 31.38 (31.44); H, 3.88 (3.90); N, 9.64 (9.56) %

bis(Imidazol-1-yl)methane. Imidazole (43.0 g, 632 mmol, 1 eq), potassium hydroxide (86.0 g, 1536 mmol, 2.4 eq), and a small amount of water (<5 mL) were mixed together to provide a viscous syrupy liquid. Tetrabutylammonium bromide (4.2 g, 13 mmol, 0.021 eq) and dichloromethane (250 mL) was added, and the mixture vigorously stirred and heated under reflux for 24 h. The volatiles were removed *via* rotary evaporation and the remaining solid dried (80 °C, 0.1 mbar). The residue was crushed and vigorously stirred with ether (400 mL) to extract any remaining liquid contaminants and water. The suspension was filtered over a sintered filter, dried (80 °C, 10 mbar) and transferred into a wide-mouth glass vessel with air-cooled walls. Sublimation was performed by heating the vessel (140 to 180 °C, 0.1 mbar, 24 h). Snow-white crystals (36.0 g, 77%) were collected.

δ_H (400 MHz; $CDCl_3$) 6.00 (2 H, s, CH_2), 6.98 (2 H, bs, =CH), 7.11 (2 H, bs, =CH), 7.64 (2 H, bs, NCHN) ppm
δ_C (101 MHz; $CDCl_3$) 56.4, 118.2, 131.3, 136.7 ppm

[C_1imC_1im]I, ***1-(Imidazol-1-ylmehyl)-3-methylimidazolium iodide*** was prepared according to a reported procedure.[12]

1-((3-Decylimidazolium-1-ylmehyl)-3-methylimidazolium iodide/bromide. 1-(imidazol-1-ylmehyl)-3-methylimidazolium iodide[12] (5.06 g, 17.4 mmol, 1.0 eq) and bromodecane (10.81 g, 48.9 mmol, 2.8 eq) were added to acetonitrile (50 mL) in a glass pressure ampoule (170 mL), and the mixture stirred at 80 °C for 37 h. The mixture was cooled to room temperature and diluted with ethyl acetate (25 mL). The white precipitate was collected by suction filtration and thoroughly washed with cold acetonitrile (5x5 mL) to completely remove traces of bromodecane. Drying in air afforded an off-white solid (7.08 g), which provided an elemental analysis not matching a stoichiometric ratio of anions.

δ_H (400 MHz; DMSO-d_6) 0.79-0.88 (3 H, m, C-CH_3), 1.16-1.33 (14 H, m, $(CH_2)_7$), 1.73-1.85 (2 H, m, CH_2), 3.91 (3 H, s, NCH_3), 4.22 (2 H, t, $^3J_{HH}$ 7.3 Hz, NCH_2), 6.78 (2 H, s, NCH_2N), 7.84 (1 H, bs, -CH=C), 7.94 (1 H, bs, -CH=C), 8.14 (2 H, bs, -CH=C), 9.60 (1 H, bs, NCHN), 9.69 (1 H, bs, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 14.0, 22.1, 25.5, 28.4, 28.7, 28.8, 28.9, 29.1, 31.3, 36.3, 49.3, 57.9, 121.9, 122.1, 123.0, 124.3, 137.4, 138.1 ppm
ATR-FTIR, ν: 3127 (w), 3053 (s), 2959 (s), 2920 (s), 2851 (w), 1661 (w), 1582 (m), 1545 (s), 1467 (m), 1428 (s), 1379 (w), 1328 (m), 1295 (w), 1172 (vs), 861 (m), 761 (vs), 654 (m) cm^{-1}
m/z (ES^+): 193 (100%), 194 (40%), 303 (30% $[C_{10}imC_1imC_1]^{2+}-H^+$)

m/z (ES^-): 127 (100%, I^-), 81 (35%, $^{81}Br^-$), 79 (35%, $^{79}Br^-$)

$[C_{10}imC_1imC_1][NTf_2]_2$, ***1-((3-decylimidazolium-1-ylmehyl)-3-methylimidazolium bis(trifluoro-methanesulfonyl)imide.*** To a solution of 1-((3-decylimidazolium-1-ylmehyl)-3-methylimidazolium iodide/bromide. (6.96 g, 15.0 mmol assuming dibromide, 1 eq) in water (80 mL) a spoonful of powdered charcoal was added. The mixture was stirred at 60 ºC for 1 h, cooled to room temperature, following a filtration *via* gravity and cellulose syringe filter. A solution of lithium *bis(*trifluoromethanesulfonyl)imide (15.66 g, 55 mmol, 1 eq) in a minimal amount of water was added to the filtrate. The mixture was extracted with dichloromethane (2x80 mL) and the organic phase washed with water until halide-free. The dichloromethane solution was evaporated *via* rotary evaporation. Drying at reduced pressure (70 ºC, 0.1 mbar) afforded an almost colourless, very viscous liquid (10.53 g, 81% in two steps).

δ_H (400 MHz; DMSO-d_6) 0.81-0,87 (3 H, m, C-CH_3), 1.17-1.34 (14 H, m, $(CH_2)_7$), 1.71-1.85 (2 H, m, CH_2), 3.90 (3 H, s, NCH_3), 4.20 (2 H, t, $^3J_{HH}$ 7.4 Hz, NCH_2), 6.60 (2 H, s, NCH_2N), 7.76-7.79 (1 H, m, -CH=C), 7.86-7.88 (1 H, m, -CH=C), 7.92-7.97 (2 H, bs, -CH=C), 9.32 (1 H, bs, NCHN), 9.38 (1 H, bs, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 13.9, 22.1, 25.5, 28.4, 28.7, 28.8, 28.9, 29.2, 31.3, 36.2, 49.3, 58.3, 119.5 (q, $^1J_{13C-19F}$ 322 Hz), 122.0, 122.2, 123.2, 124.5, 137.4, 138.1 ppm
δ_F (377 MHz; DMSO-d_6) -78.9 ppm
ATR-FTIR, ν: 3149 (w), 3117 (w), 2929 (w), 2859 (w), 1568 (w), 1460 (w), 1346 (s), 1328 (s), 1225 (m), 1176 (ws), 1131 (ws), 1052 (ws), 850 (w), 790 (m), 772 (m), 764 (m), 740 (s), 861 (m), 654 (w) cm^{-1}
m/z (ES^+): 193 (100%), 115 (40%), 103 (40%), 83 (40%), 173 (35%), 194 (35%), 303 (30%, $[C_{10}imC_1imC_1]^{2+}$-H^+)
m/z (ES^-): 280 (100%, $[NTf_2]^-$)
Elemental Analysis (expected): C, 30.49 (30.56); H, 3.63 (3.73); N, 9.61 (9.72) %

$[(C_7O_3)imC_1imC_1][NTf_2]_2$. 1-(imidazol-1-ylmehyl)-3-methylimidazolium iodide[12] (5.30 g, 18.3 mmol, 1.0 eq) and 2-(2-(2-methoxyethoxy)ethoxy)ethyl chloride[9] (14.65 g, 80.2 mmol, 4.4 eq) were added to acetonitrile (40 mL) in a glass pressure ampoule (170 mL). The ampoule was flushed with nitrogen, sealed and the mixture stirred at 100 ºC for 72 h, and then for further 7x24 h at 120 ºC. The contents were diluted with ether (60 mL) and the clear solvent layer was cannulated off. The residue was washed with ethyl acetate (5 x 60 mL) and ether (60 mL). The residue was taken up in water (80 mL) and stirred with a spoonful of powdered charcoal at 60 ºC for 1.5 h. The solution was filtered and passed through a cellulose syringe filter providing a colourless solution. Aqueous lithium *bis(*trifluoromethanesulfonyl)imide (10.55 g, 36.7 mmol, 2 eq) in a minimal amount of water was added to the filtrate with stirring. The mixture was extracted with ethyl acetate (3 x 10 mL) and the organic phase washed with water until halide-free (3 x 15 mL). The solution was filtered through the hydrophobic filter paper, evaporated *via* rotary evaporation and dried (0.1 mbar, 60 ºC, 24 h) to afford a nearly colourless liquid (13.75 g, 86% in two steps).

δ_H (400 MHz; DMSO-d_6) 3.24 (3 H, s, OCH_3), 3.40-3.44 (2 H, m, OCH_2), 3.47-3.53 (4 H, m, OCH_2), 3.55-3.59 (2 H, m, OCH_2), 3.77-3.81 (2 H, m, OCH_2), 3.90 (3 H, s, NCH_3), 4.38-4.44 (2 H, m, NCH_2 C), 6.65 (2 H, s, NCH_2N), 7.76-7.79 (1 H, m, -CH=C), 7.82-7.85 (1 H, m, -CH=C), 7.92-7.97 (2 H, m, -CH=C), 9.31-9.34 (1 H, bs, NCHN), 9.36-9.39 (1 H, bs, NCHN) ppm
δ_C (101 MHz; DMSO-d_6) 36.2, 49.3, 58.0, 58.3, 67.9, 69.5 (2 C), 69.6, 71.2, 119.5 (q, $^1J_{13C-19F}$ 322 Hz), 121.9 (2 C), 123.7, 124.5, 137.8, 138.1 ppm
δ_F (377 MHz; DMSO-d_6) -78.9 ppm
ATR-FTIR (neat): 3151 (w), 3116 (w), 2926 (w), 2883 (w), 1587 (w), 1569 (w), 1552 (w), 1454 (w),

1346 (s), 1328 (s), 1227 (m), 1173 (vs), 1131 (vs), 1050 (vs), 848 (w), 790 (m), 771 (m), 764 (m), 740 (s), 653 (w) cm^{-1}
m/*z* (ES^+): 155 (100%, $[(C_7O_3)imC_1imC_1]^{2+}/2$), 309 (40%, $[(C_7O_3)imC_1imC_1]^{2+}-H^+$)
m/*z* (ES^-): 280 (100%, $[NTf_2]^-$)
Elemental Analysis (expected): C, 26.06 (26.21); H, 2.94 (3.01); N, 9.50 (9.61) %

Thermal stability of monocationic and dicationic ionic liquids

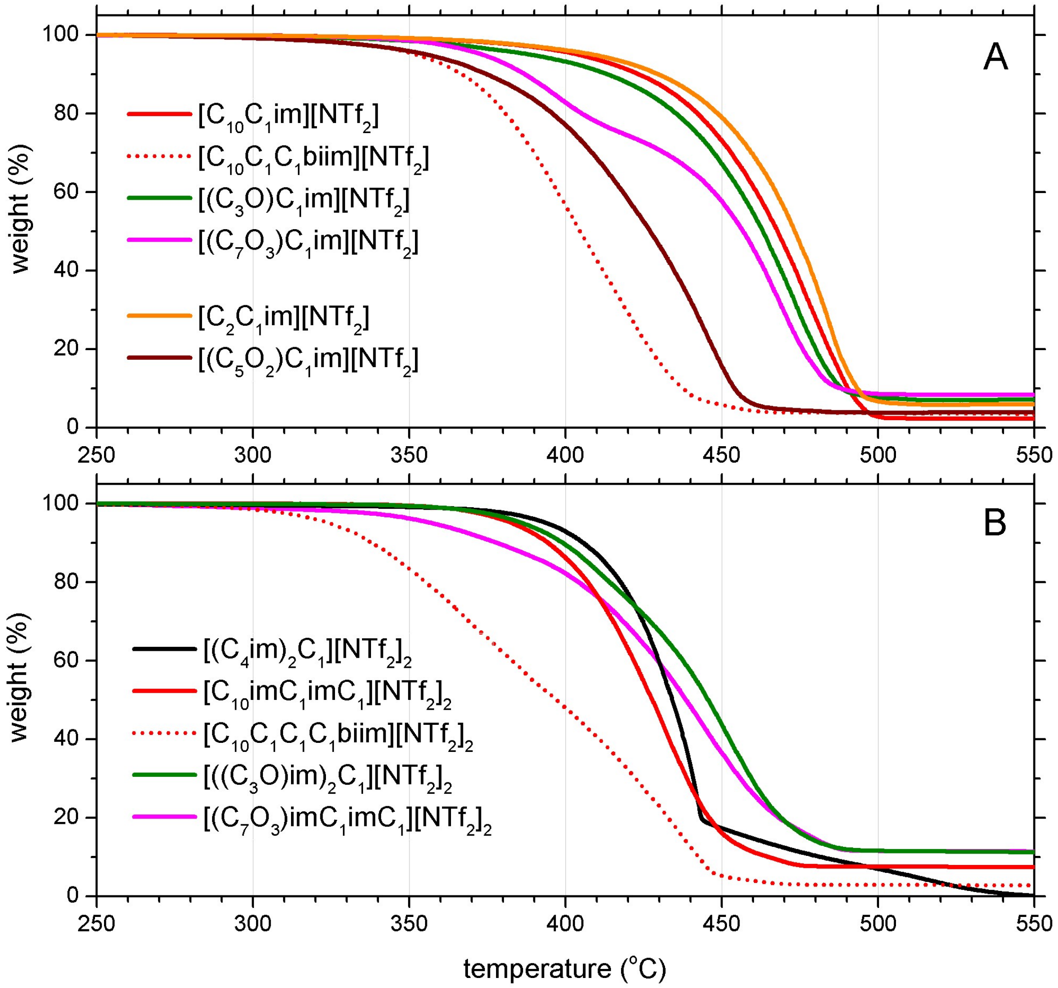


Figure S1

Thermal degradation curves of **monocationic** (**A**) and **dicationic** (**B**) ionic liquids, measured by temperature ramped TGA. A *PerkinElmer Pyris 1 TGA* instrument and Pt sample pans were used; heating rate 10 ºC min^{-1}, and nitrogen carrier gas flow 20 mL min^{-1}. IL samples (5-15 mg) were isothermally dried at 70 ºC in nitrogen flow for 1 h following a temperature ramp to 600 ºC.

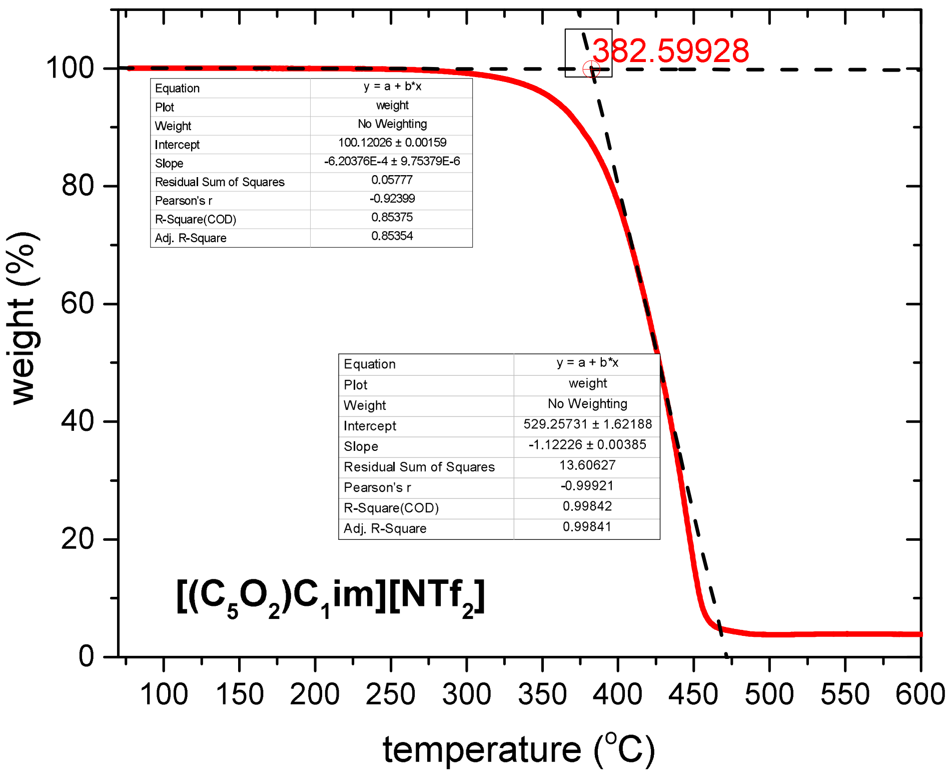


Figure S2
Typical example of the T_{onset} calculation from the intersection of the tangents of the baseline and the first weight loss.

Table S2
T_{onset} and corresponding $T_{0.01/10}$ values

No	IL	Cation charge	T_{onset}, °C [a]	$T_{0.01/10}$, °C [b]
1	$[C_{10}C_1im][NTf_2]$	1+	441	361
2	$[C_{10}C_1C_1biim][NTf_2]$	1+	368	311
3	$[(C_3O)C_1im][NTf_2]$	1+	435	357
4	$[(C_7O_3)C_1im][NTf_2]$	1+	369	303
5	$[C_2C_1im][NTf_2]$	1+	450	367
6	$[(C_5O_2)C_1im][NTf_2]$	1+	383	321
7	$[(C_4im)_2C_1][NTf_2]_2$	2+	411	341
8	$[C_{10}imC_1imC_1][NTf_2]_2$	2+	400	333
9	$[C_{10}C_1C_1C_1biim][NTf_2]_2$	2+	329	284
10	$[(C_3Oim)_2C_1][NTf_2]_2$	2+	387	324
11	$[(C_7O_3)imC_1imC_1][NTf_2]_2$	2+	341	292

[a] heating rate 10 °C min^{-1}; [b] estimated *via* relation $T_{0.01/10} = 0.6902T_{onset} + 56.829$ from ref.[13]

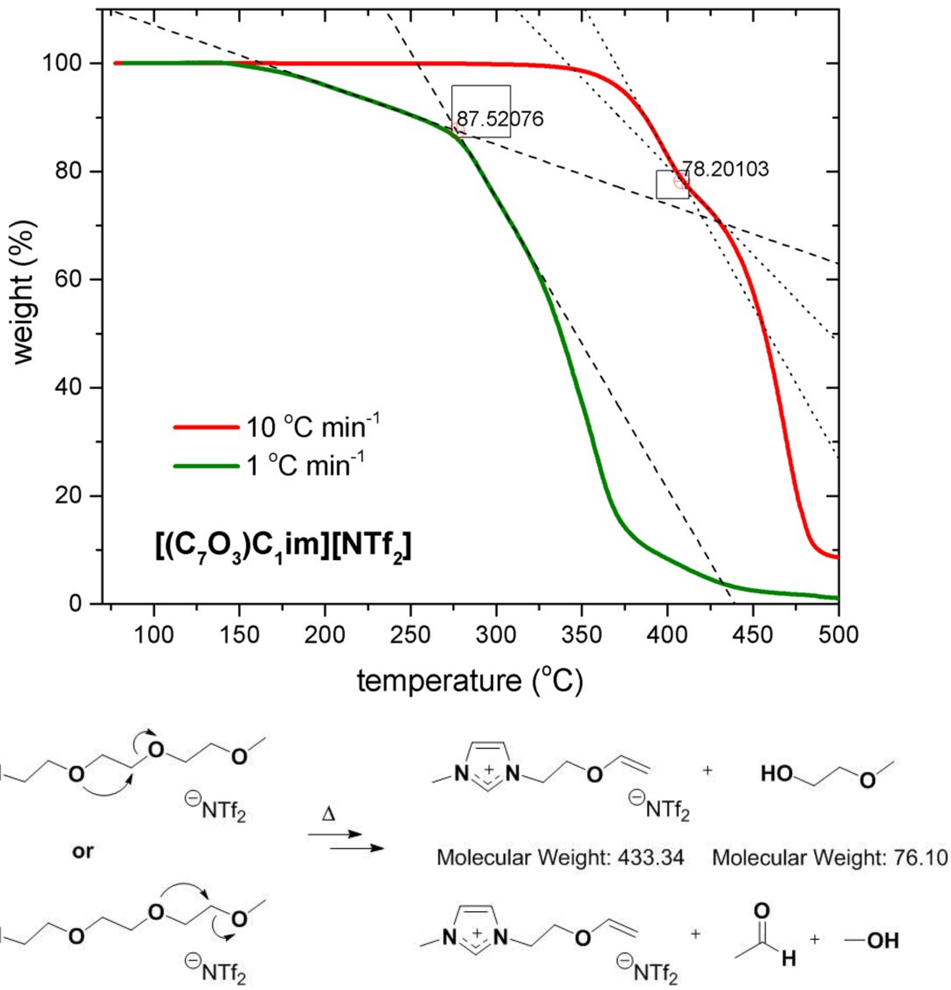


Figure S3

Thermal degradation curves of $[(C_7O_3)C_1im][NTf_2]$ at different heating rates. The green curve (1 ºC min^{-1}) shows the first distinct weigth loss (approx. 12.5%) what is comparable with the expected for a loss of ethylene glycol monomethylether / acetaldehyde and methanol (14.9%)

Densities and excess molar volumes

Table S3

Pure ionic liquid density data (ρ) and the derived molar volumes (V_m). Also listed are the molar volumes as calculated from the group contribution method using literature parameters (V_m^{GCM}) and a separately fitted parameter for the divalent cation group $[(C_0imC_1)_2]^{2+}$ (V_m^{GCM*}). All parameters and groups are listed in Table S5 and Table S6.

no IL	IL	M_w g·mol^{-1}	T K	ρ g·cm^{-3}	V_m cm^{-3}·mol^{-1}	V_m^{GCM} cm^{-3}·mol^{-1}	V_m^{GCM*} cm^{-3}·mol^{-1}
1	$[C_2C_1im][NTf_2]$	391.301	293.152	1.523736	256.8037	257.4570	
			298.151	1.518770	257.6434	258.0400	
			303.149	1.513710	258.5046	258.6533	
			313.147	1.503658	260.2327	259.9711	
			323.149	1.493669	261.9730	261.4104	
			333.149	1.483754	263.7236	262.9711	
			353.149	1.464155	267.2538	266.4568	
2	$[C_{10}C_1im]$ $[NTf_2]$	503.517	298.151	1.278697	393.7735	393.7760	
			303.148	1.274368	395.1111	394.4457	
			313.147	1.265748	397.8016	395.8785	
			313.149	1.265749	397.8035	395.8785	
			313.150	1.265744	397.8032	395.8785	
			313.151	1.265743	397.8019	395.8785	
			323.149	1.257192	400.5092	397.4359	
			333.149	1.248693	403.2352	399.1178	
			353.149	1.231848	408.7493	402.8555	
3	$[(C_3O)C_1im][NTf_2]$	421.327	298.151	1.505373	279.8821	279.5780	
			303.149	1.500272	280.8337	280.2082	
			313.149	1.490137	282.7438	281.5632	
			323.149	1.480075	284.6660	283.0441	
			333.147	1.47009	286.5995	284.6510	
			353.148	1.450327	290.5048	288.2427	
4	$[(C_5O_2)C_1im][NTf_2]$	465.380	298.148	1.458482	319.0786	318.0830	
			298.151	1.458512	319.0834	318.0830	
			298.151	1.458490	319.0852	318.0830	
			303.149	1.453560	320.1657	318.7372	
			303.149	1.453548	320.1683	318.7372	
			313.147	1.443723	322.3472	320.1437	
			313.147	1.443710	322.3501	320.1437	
			323.149	1.433967	324.5402	321.6811	
			333.148	1.424282	326.7450	323.3494	
			333.149	1.424291	326.7471	323.3494	
			353.149	1.405159	331.1938	327.0784	
			353.149	1.405149	331.1962	327.0784	

no IL	IL	M_w g·mol-1	T K	ρ g·cm-3	V_m cm-3·mol-1	V_m^{GCM} cm-3·mol-1	V_m^{GCM*} cm-3·mol-1
5	$[(C_7O_3)C_1im][NTf_2]$	509.433	298.150	1.426309	357.1687	356.5880	
			298.150	1.426230	357.1885	356.5880	
			303.148	1.421400	358.3819	357.2661	
			303.149	1.421481	358.4023	357.2661	
			313.149	1.411893	360.8156	358.7242	
			313.149	1.411877	360.8225	358.7242	
			313.149	1.411812	360.8197	358.7242	
			313.151	1.411866	360.8363	358.7242	
			323.149	1.402387	363.2614	360.3181	
			323.149	1.402309	363.2816	360.3181	
			333.148	1.392959	365.7200	362.0477	
			333.149	1.392882	365.7402	362.0477	
			353.147	1.374304	370.6844	365.9141	
			353.149	1.374240	370.7016	365.9141	
6	$[C_{10}imC_1imC_1][NTf_2]2$	864.748	298.150	1.462698	591.2043	617.8820	591.200292
			298.151	1.462689	591.2006	617.8820	591.200292
			303.149	1.458131	593.0588	619.1509	593.055379
			303.151	1.458115	593.0523	619.1509	593.055379
			313.147	1.449061	596.7644	621.8728	596.772305
			323.149	1.440071	600.4898	624.8399	600.498233
			333.149	1.431113	604.2486	628.0522	604.233162
			353.149	1.413614	611.7285	635.2126	611.730024
			353.149	1.413616	611.7277	635.2126	611.730024
7	$[(C_7O_3)imC_1imC_1][NTf_2]_2$	870.664	293.151	1.608784	541.1938	579.4807	552.153802
			298.149	1.603837	542.9552	580.6940	554.012292
			298.150	1.603565	542.8631	580.6940	554.012292
			303.149	1.598904	544.5380	581.9714	555.875827
			313.149	1.589141	547.8834	584.7185	559.618033
			323.148	1.579504	551.2262	587.7221	563.380422
			333.149	1.569924	554.5899	590.9820	567.162992
			353.148	1.551307	561.2455	598.2713	574.788678
9	$[((C_3O)im)_2C_1][NTf_2]_2$	826.611	293.151	1.602748	515.7461	540.9984	513.671526
			298.149	1.597723	517.3682	542.1890	515.507292
			303.148	1.592722	518.9926	543.4424	517.34688
			311.151	1.584828	521.5777	545.5788	520.298171
			313.147	1.582790	522.2493	546.1380	521.037522
			313.147	1.582910	522.2097	546.1380	521.037522
			313.149	1.582860	522.2262	546.1380	521.037522
			323.149	1.572917	525.5274	549.0851	524.743452
			323.149	1.573059	525.4800	549.0851	524.743452
			323.149	1.572991	525.5027	549.0851	524.743452

no IL	IL	M_w g·mol-1	T K	ρ g·cm-3	V_m cm-3·mol-1	V_m^{GCM} cm-3·mol-1	V_m^{GCM*} cm-3·mol-1
			333.148	1.563390	528.7772	552.2837	528.464669
			333.149	1.563250	528.7299	552.2837	528.464669
			333.149	1.563320	528.7536	552.2837	528.464669
			353.149	1.544064	535.3476	559.4356	535.952965
			353.149	1.544207	535.2981	559.4356	535.952965
			353.149	1.544133	535.3237	559.4356	535.952965
10	$[C_{10}C_1C_1C_1biim][NTf_2]_2$	878.775	338.151	1.420820	618.4985	646.7764	623.130076
			338.152	1.420837	618.4911	646.7764	623.130076
			343.151	1.416627	620.3291	648.5437	625.010988
			343.151	1.416645	620.3213	648.5437	625.010988
			353.151	1.408457	623.9337	652.2625	628.779856
			353.152	1.408443	623.9275	652.2625	628.779856
			363.151	1.400321	627.5597	656.2269	632.558115
			363.151	1.400305	627.5525	656.2269	632.558115
11	$[C_{10}C_1C_1biim][NTf_2]$	583.607	313.147	1.276920	457.0427	462.6992	
			313.147	1.276916	457.0442	462.6992	
			333.147	1.259882	463.2221	466.7411	
			333.148	1.259886	463.2235	466.7411	
			353.148	1.243073	469.4873	471.7237	
			353.148	1.243066	469.4900	471.7237	

Table S4

Fitting parameters of the second order polynomial ($V_m = p_0 + p_1T + p_2T^2$) used for the interpolation of the pure ionic liquid (IL) molar volumes (V_m) studied at atmospheric pressure as a function of temperature (T) within temperature range T_{range}. IL numbers correspond to table 1 of the manuscript, AAD is the absolute average deviation $\sum\left|V_m - V_m^{fit}\right|/n$.

no IL	IL	$Trange$ K	p_0 cm3·mol-1	p_1 cm3·mol-1·K-1	$p_2 \cdot 10^3$ cm3·mol-1·K-2	AAD $\cdot 10^6$ cm3·mol-1
1	$[C_2C1im][NTf_2]$	293.15–353.15	211.977	0.135079	60.7384	3.90362
2	$[C_{10}C_1im][NTf_2]$	298.15–353.15	322.531	0.210832	94.3142	1.02245
3	$[(C_3O)C_1im][NTf_2]$	298.15–353.15	228.590	0.154222	59.7489	0.356482
4	$[(C_5O_2)C_1im][NTf_2]$	298.15–353.15	260.061	0.179155	63.0686	1.51649
5	$[(C_7O_3)C_1im][NTf_2]$	298.15–353.15	291.131	0.201120	68.4430	8.86676
6	$[C_{10}imC_1imC_1][NTf_2]_2$	298.15–353.15	484.668	0.343837	45.1881	5.15451
7	$[(C_7O_3)imC_1imC_1][NTf_2]_2$	293.15–353.15	443.061	0.335603	-2.64144	21.5239
9	$[((C_3O)im)_2C_1][NTf_2]_2$	293.15–353.15	425.024	0.295557	47.4879	14.1575
10	$[C_{10}C_1C_1C_1biim][NTf_2]_2$	338.15–363.15	491.882	0.385899	-33.8766	6.75149
11	$[C_{10}C_1C_1biim][NTf_2]$	313.15–353.15	371.566	0.239113	108.084	0.924364

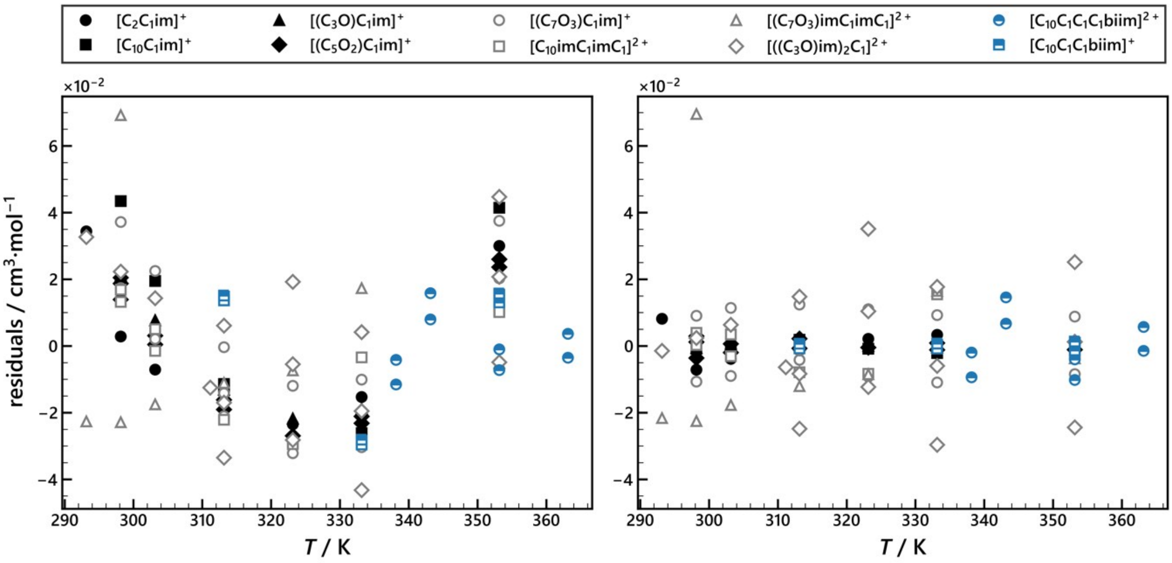


Figure S4
Residual plots of the temperature (T) versus density (ρ) fits using a first order ($\rho = p_0 + p_1 T$, left) or second order ($\rho = p_0 + p_1 T + p_2 T^2$, right) polynomial.

Table S5
Group contribution parameters used to calculate the molar volume using equation.

Group j	C_0	C_1	C_2	Ref
	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-2}$	
CH_2	16.967	0.001399	0.000001946	[14]
O	4.571	0.001869	0.00002058	[15]
$[NTf_2]^-$	157.597	0.104348374	5.05171E-05	[14]
$[C_0imC_1]^+$	66.509	0.012485755	0.000552882	[14]
$[(C_0imC_1)_2]^{2+}$	106.336	0.14810570577647800	-7.54867746938373E-05	This work

Table S6

Number of groups (n_j) taken into account for the calculation of the molar volume of the studied ILs using the group contribution method (eq. 1 main text). For the divalent ILs, either two imidazolium groups (C_0C_1im) or one divalent cation group ($[(C_0imC_1)_2]^{2+}$) were taken into account.

no IL	IL	n_j				
	$j =$	C_0imC_1	$[(C_0imC_1)_2]^{2+}$	CH_2	O	NTf_2
1	$[C_2C_1im][NTf_2]$	1	0	2	0	1
2	$[C_{10}C_1im][NTf_2]$	1	0	10	0	1
3	$[(C_3O)C_1im][NTf_2]$	1	0	3	1	1
4	$[(C_5O_2)C_1im][NTf_2]$	1	0	5	2	1
5	$[(C_7O_3)C_1im][NTf_2]$	1	0	7	3	1
6	$[C_{10}imC_1imC_1][NTf_2]_2$	2 ¦ 0	0 ¦ 1	10	0	2
7	$[(C_7O_3)imC_1imC_1][NTf_2]_2$	2 ¦ 0	0 ¦ 1	7	3	2
9	$[((C_3O)im)_2C_1][NTf_2]_2$	2 ¦ 0	0 ¦ 1	5	2	2
10	$[C_{10}C_1C_1biim][NTf_2]_2$	2 ¦ 0	0 ¦ 1	11	0	2
11	$[C_{10}C_1C_1biim][NTf_2]$	2	0	10	0	1

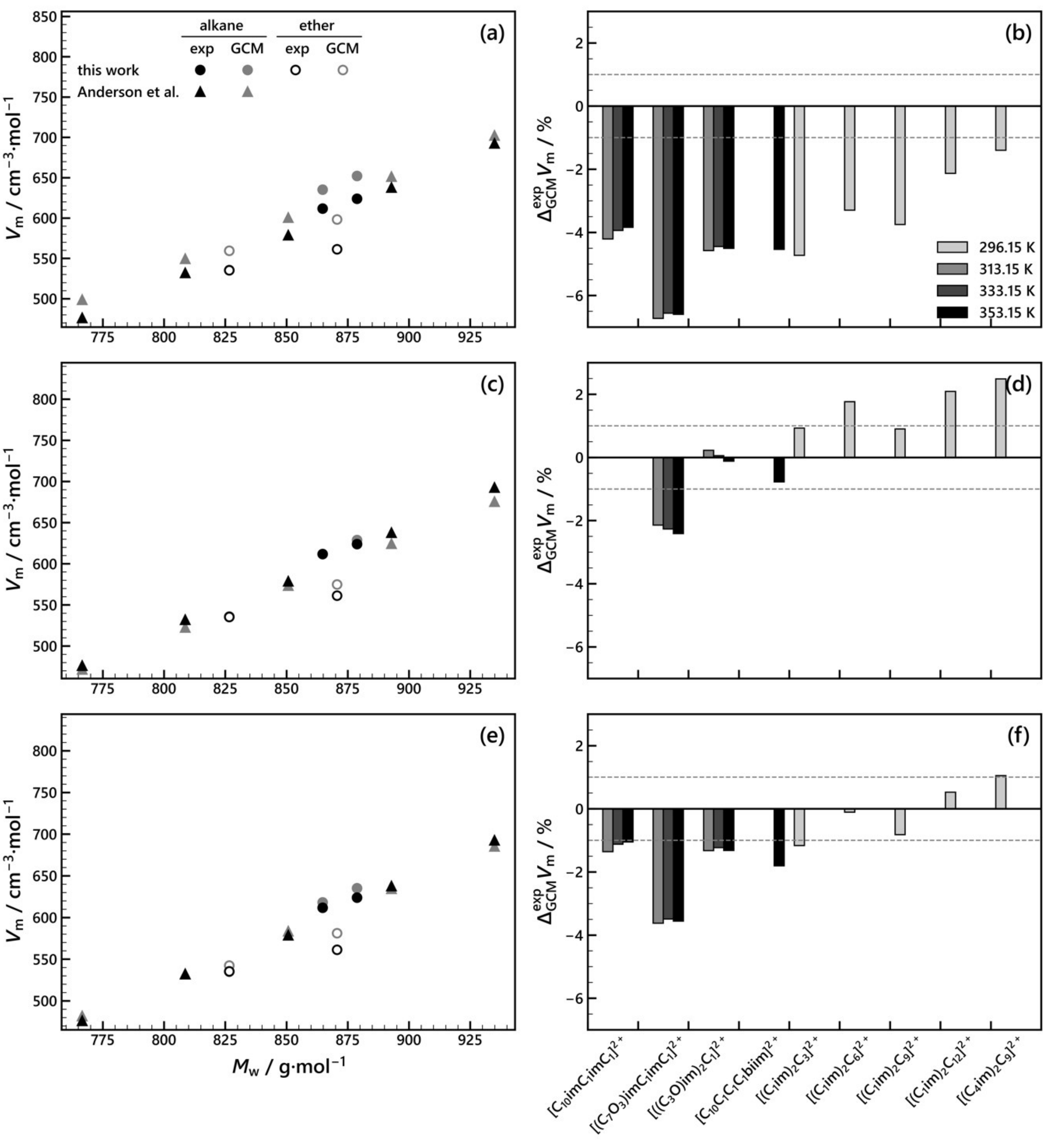


Figure S5
(a), (c), and (e): Molar volume (V_m) as function of molar mass (M_w) of divalent imidazolium bistriflimide ionic liquids at 353.15 K (this work) or 296.15 K (Anderson et al.[5]) calculated from the experimental density data (exp) and described/predicted using the group contribution method (GCM). The nature of the imidazolium side-chain (aliphatic/ether) is also distinguished. (b), (d), and (f): Relative difference between the experimental and calculated molar volume using the GCM ($\Delta^{exp}_{GCM} V_m$) at different temperatures. The top panels–(a) and (b)–show the GCM calculations based on Table S6 by representing the divalent cations with two C_0C_1im groups. For the middle panels–(c) and (d)– new GCM parameters were taken into account for the doubly charged diimidazolium head-group based on $[C_{10}imC_1imC_1][NTf_2]_2$. The bottom panels–(e) and (f)–are calculated using $n_{CH_2} - 1$ as compared to the top panels.

Table S7

Excess molar volumes ($V_m^E = V_m^{id} - V_m$) of the studied binary ionic liquid (IL) mixtures at various mole fractions (x_{IL2}) temperatures (T), where $V_m^{id} = (1 - x_{IL2})V_{m,IL1} + x_{IL2}V_{m,IL2}$ with $V_{m,ILi}$ being the molar volume of pure IL i determined from the temperature interpolation presented in Table S4 and $V_m = \left[(1 - x_{IL2})M_{w,IL1} + x_{IL2}M_{w,IL2}\right]/\rho$ where ρ is the experimental density of the mixture.

IL1	IL2	x_{IL2}	T	ρ	$V_{m,IL1}$	$V_{m,IL2}$	V_m^{id}	V_m	V_m^E
			K	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}
$[((C_3O)im)_2C_1][NTf_2]_2$	$[C_{10}C_1im][NTf_2]$	0.2189	298.151	1.538482	517.4290	393.8154	490.3754	491.3284	0.9530
			303.150	1.533575	519.0115	395.1309	491.8994	492.9005	1.0011
			313.147	1.523733	522.2052	397.7883	494.9758	496.0842	1.1084
			313.151	1.523798	522.2065	397.7893	494.9770	496.0630	1.0860
			323.149	1.514202	525.4402	400.4829	498.0925	499.2068	1.1143
		0.4973	298.151	1.45733	517.4290	393.8154	455.9570	456.9583	1.0013
			298.151	1.457337	517.4290	393.8154	455.9570	456.9561	0.9991
			303.150	1.45261	519.0115	395.1309	457.4067	458.4431	1.0364
			303.152	1.452596	519.0121	395.1315	457.4073	458.4475	1.0402
			313.147	1.443229	522.2052	397.7883	460.3337	461.4230	1.0893
			313.149	1.443116	522.2059	397.7888	460.3343	461.4591	1.1248
			313.151	1.443213	522.2065	397.7893	460.3349	461.4281	1.0932
			323.149	1.433827	525.4402	400.4829	463.3000	464.4487	1.1487
			333.149	1.424552	528.7148	403.2138	466.3042	467.4726	1.1684
			353.149	1.40621	535.3880	408.7888	472.4313	473.5701	1.1388
		0.7006	293.151	1.395617	515.8559	392.5084	429.4332	430.0873	0.6541
			298.151	1.391044	517.4290	393.8154	430.8199	431.5012	0.6813
			303.148	1.386463	519.0108	395.1304	432.2148	432.9269	0.7121
			313.147	1.37731	522.2052	397.7883	435.0332	435.8039	0.7707
			323.149	1.3682	525.4402	400.4829	437.8896	438.7057	0.8161
			333.149	1.359175	528.7148	403.2138	440.7833	441.6187	0.8355
$[((C_3O)im)_2C_1][NTf_2]_2$	$[(C_7O_3)C1im][NTf2]$	0.2008	298.150	1.57277	517.4287	357.2181	485.2531	485.0748	-0.1783
			303.150	1.567778	519.0115	358.4061	486.7565	486.6193	-0.1372
			313.150	1.557834	522.2062	360.8059	489.7916	489.7255	-0.0661
			323.148	1.548123	525.4398	363.2375	492.8642	492.7974	-0.0668
			333.149	1.538435	528.7148	365.7029	495.9766	495.9007	-0.0758
			353.149	1.519251	535.3880	370.7350	502.3202	502.1626	-0.1576
		0.5099	298.150	1.526658	517.4287	357.2181	435.7430	435.5220	-0.2210
			298.150	1.526626	517.4287	357.2181	435.7430	435.5311	-0.2119
			298.152	1.526637	517.4293	357.2186	435.7436	435.5280	-0.2155
			298.152	1.526612	517.4293	357.2186	435.7436	435.5351	-0.2084
			303.147	1.521701	519.0105	358.4054	437.1236	436.9408	-0.1829
			303.149	1.521737	519.0111	358.4058	437.1242	436.9304	-0.1938
			313.149	1.511976	522.2059	360.8056	439.9136	439.7511	-0.1625
			313.149	1.511938	522.2059	360.8056	439.9136	439.7622	-0.1514

IL1	IL2	x_{IL2}	T K	ρ g·cm^{-3}	$V_{m,IL1}$ cm^3·mol^{-1}	$V_{m,IL2}$ cm^3·mol^{-1}	V_m^{id} cm^3·mol^{-1}	V_m cm^3·mol^{-1}	V_m^E cm^3·mol^{-1}
			323.148	1.502222	525.4398	363.2375	442.7386	442.6065	-0.1322
			333.149	1.492542	528.7148	365.7029	445.6008	445.4770	-0.1238
			353.149	1.473464	535.3880	370.7350	451.4373	451.2449	-0.1923
		0.7966	298.149	1.473073	517.4284	357.2179	389.8014	389.6213	-0.1802
			303.151	1.468143	519.0118	358.4063	391.0702	390.9296	-0.1406
			313.147	1.458425	522.2052	360.8051	393.6306	393.5345	-0.0961
			333.149	1.43922	528.7148	365.7029	398.8562	398.7858	-0.0704
			353.149	1.420337	535.3880	370.7350	404.2221	404.0876	-0.1345
[((C$_3$O)im)$_2$C$_1$][NTf$_2$]$_2$	[(C$_5$O$_2$)C$_1$im][NTf$_2$]	0.2010	308.151	1.569249	520.6042	321.2436	480.5257	480.4788	-0.0470
			323.149	1.55449	525.4402	324.5045	485.0450	485.0406	-0.0044
			323.150	1.554488	525.4405	324.5047	485.0453	485.0413	-0.0040
			323.150	1.554487	525.4405	324.5047	485.0453	485.0416	-0.0037
			323.150	1.554485	525.4405	324.5047	485.0453	485.0422	-0.0031
			333.149	1.544755	528.7148	326.7157	488.1058	488.0973	-0.0085
			353.149	1.525508	535.3880	331.2298	494.3450	494.2556	-0.0894
		0.4994	313.149	1.530315	522.2059	322.3230	422.3762	422.2644	-0.1118
			313.149	1.53023	522.2059	322.3230	422.3762	422.2878	-0.0884
			323.148	1.520368	525.4398	324.5043	425.0844	425.0270	-0.0574
			323.149	1.520451	525.4402	324.5045	425.0847	425.0038	-0.0809
			333.147	1.510593	528.7141	326.7153	427.8276	427.7774	-0.0503
			333.148	1.510675	528.7145	326.7155	427.8279	427.7541	-0.0738
			353.149	1.491423	535.3880	331.2298	433.4231	433.2758	-0.1473
		0.7994	303.151	1.494062	519.0118	320.1710	360.0513	359.9783	-0.0730
			313.149	1.484163	522.2059	322.3230	362.4123	362.3793	-0.0330
			333.149	1.464618	528.7148	326.7157	367.2295	367.2152	-0.0143
			343.148	1.454973	532.0301	328.9571	369.6862	369.6494	-0.0368
			353.149	1.445404	535.3880	331.2298	372.1766	372.0966	-0.0800
[((C$_3$O)im)$_2$C$_1$][NTf$_2$]$_2$	[(C$_3$O)C$_1$im][NTf$_2$]	0.2042	313.151	1.571488	522.2065	282.7283	473.2938	473.3304	0.0365
			323.149	1.561689	525.4402	284.6401	476.2575	476.3003	0.0428
			333.149	1.551937	528.7148	286.5784	479.2592	479.2933	0.0341
			353.149	1.53264	535.3880	290.5351	485.3775	485.3279	-0.0496
		0.4980	293.151	1.570207	515.8559	278.9800	397.8967	397.9018	0.0051
			298.151	1.565418	517.4290	279.9077	399.1485	399.1191	-0.0294
			298.152	1.565192	517.4293	279.9079	399.1487	399.1767	0.0280
			303.149	1.560193	519.0111	280.8413	400.4076	400.4557	0.0481
			303.150	1.560414	519.0115	280.8415	400.4079	400.3990	-0.0089
			313.149	1.5502	522.2059	282.7279	402.9510	403.0372	0.0862
			323.148	1.540217	525.4398	284.6399	405.5266	405.6495	0.1228
			333.149	1.530301	528.7148	286.5784	408.1360	408.2780	0.1420
		0.5965	298.153	1.55662	517.4297	279.9081	375.7445	375.7199	-0.0246
			303.149	1.551613	519.0111	280.8413	376.9393	376.9323	-0.0070

IL1	IL2	x_{IL2}	T K	ρ g·cm^{-3}	$V_{m,IL1}$ cm^3·mol^{-1}	$V_{m,IL2}$ cm^3·mol^{-1}	V_m^{id} cm^3·mol^{-1}	V_m cm^3·mol^{-1}	V_m^E cm^3·mol^{-1}
			313.149	1.541581	522.2059	282.7279	379.3537	379.3852	0.0315
			323.149	1.531606	525.4402	284.6401	381.7994	381.8561	0.0567
			333.149	1.52174	528.7148	286.5784	384.2768	384.3318	0.0550
			353.149	1.502275	535.3880	290.5351	389.3296	389.3116	-0.0180
$[(C_7O_3)imC_1imC_1][NTf_2]_2$	$[C_{10}C_1im][NTf_2]$	0.4996	298.149	1.464811	542.9109	393.8149	468.4182	469.1572	0.7390
			298.151	1.464921	542.9116	393.8154	468.4188	469.1220	0.7032
			303.148	1.460124	544.5378	395.1304	469.8895	470.6632	0.7737
			303.152	1.460229	544.5391	395.1315	469.8907	470.6294	0.7387
			313.147	1.450853	547.8211	397.7883	472.8603	473.6708	0.8104
			323.149	1.441647	551.1454	400.4829	475.8700	476.6955	0.8255
			333.149	1.432463	554.5095	403.2138	478.9177	479.7517	0.8340
			353.149	1.414297	561.3625	408.7888	485.1322	485.9139	0.7817
$[C_{10}imC_1imC_1][NTf_2]_2$	$[C_{10}C_1im][NTf_2]$	0.4993	298.152	1.389828	591.2529	393.8157	492.6672	492.4175	-0.2497
			303.149	1.385332	593.0612	395.1307	494.2292	494.0156	-0.2136
			313.149	1.376387	596.7134	397.7888	497.3850	497.2262	-0.1588
			323.149	1.367573	600.4109	400.4829	500.5815	500.4308	-0.1507
			333.149	1.358785	604.1545	403.2138	503.8194	503.6674	-0.1520
			353.149	1.341358	611.7835	408.7888	510.4228	510.2110	-0.2117
$[(C_3O)C_1im][NTf_2]$	$[C_2C_1im][NTf_2]$	0.2500	303.149	1.503135	280.8413	258.5055	275.2577	275.3052	0.0476
			313.149	1.49302	282.7279	260.2150	277.1001	277.1704	0.0703
			323.149	1.482975	284.6401	261.9474	278.9673	279.0478	0.0805
			333.148	1.473004	286.5782	263.7027	280.8597	280.9367	0.0771
			353.148	1.453278	290.5349	267.2853	284.7229	284.7500	0.0271
		0.3993	313.149	1.494939	282.7279	260.2150	273.7382	273.8153	0.0771
		0.7492	303.148	1.51005	280.8411	258.5053	264.1061	264.1172	0.0111
			313.147	1.499953	282.7276	260.2147	265.8599	265.8951	0.0352
			323.149	1.48992	284.6401	261.9474	267.6376	267.6856	0.0479
			333.149	1.479962	286.5784	263.7029	269.4390	269.4867	0.0477
			353.149	1.460316	290.5351	267.2855	273.1154	273.1122	-0.0032
$[(C_3O)C_1im][NTf_2]$	$[C_{10}C_1im][NTf_2]$	0.2535	298.149	1.430744	279.9073	393.8149	308.7881	309.0461	0.2580
			303.149	1.425896	280.8413	395.1307	309.8188	310.0969	0.2781
			313.149	1.416261	282.7279	397.7888	311.9011	312.2065	0.3054
			323.149	1.406699	284.6401	400.4829	314.0116	314.3287	0.3172
			333.149	1.3972	286.5784	403.2138	316.1508	316.4657	0.3150
			353.149	1.378391	290.5351	408.7888	320.5178	320.7841	0.2663
		0.4995	293.151	1.375744	278.9800	392.5084	335.6873	336.0951	0.4078
			298.149	1.371226	279.9073	393.8149	336.8040	337.2025	0.3985
			303.149	1.366594	280.8413	395.1307	337.9287	338.3454	0.4167
			313.149	1.357356	282.7279	397.7888	340.2007	340.6481	0.4474
			323.148	1.348168	284.6399	400.4827	342.5032	342.9697	0.4665

IL1	IL2	x_{IL2}	T K	ρ g·cm^{-3}	$V_{m,IL1}$ cm^3·mol^{-1}	$V_{m,IL2}$ cm^3·mol^{-1}	V_m^{id} cm^3·mol^{-1}	V_m cm^3·mol^{-1}	V_m^E cm^3·mol^{-1}
			333.149	1.338997	286.5784	403.2138	344.8376	345.3188	0.4812
			353.499	1.320786	290.6054	408.8877	349.6873	350.0800	0.3928
		0.7491	293.151	1.325254	278.9800	392.5084	364.0267	364.3810	0.3543
			298.149	1.321072	279.9073	393.8149	365.2381	365.5345	0.2964
			303.149	1.316604	280.8413	395.1307	366.4581	366.7750	0.3169
			313.149	1.307683	282.7279	397.7888	368.9227	369.2771	0.3544
			323.149	1.298795	284.6401	400.4829	371.4207	371.8042	0.3835
			333.148	1.289919	286.5782	403.2135	373.9524	374.3626	0.4102
			353.147	1.272162	290.5347	408.7882	379.1212	379.5880	0.4668
$[(C_7O_3)C_1im][NTf_2]$	$[C_{10}C_1im][NTf_2]$	0.5003	298.151	1.348145	357.2184	393.8154	375.5279	375.6816	0.1537
			313.149	1.334516	360.8056	397.7888	379.3083	379.5183	0.2100
			323.149	1.325513	363.2378	400.4829	381.8715	382.0960	0.2245
			333.149	1.31658	365.7029	403.2138	384.4696	384.6885	0.2189
			353.149	1.298887	370.7350	408.7888	389.7733	389.9286	0.1553
$[C_{10}C_1C_1biim][NTf_2]$	$[C_{10}C_1im][NTf_2]$	0.2037	298.149	1.287657	452.5575	393.8149	440.5902	440.5604	-0.0298
			303.148	1.283391	454.0469	395.1304	442.0442	442.0248	-0.0193
			313.149	1.274828	457.0562	397.7888	444.9820	444.9939	0.0119
			333.149	1.25777	463.1956	403.2138	450.9758	451.0290	0.0531
			353.149	1.240952	469.5021	408.7888	457.1333	457.1415	0.0082
		0.5070	298.151	1.284666	452.5581	393.8154	422.7741	422.6775	-0.0966
			298.152	1.284636	452.5584	393.8157	422.7744	422.6874	-0.0870
			303.148	1.280381	454.0469	395.1304	424.1748	424.0921	-0.0827
			303.149	1.280332	454.0472	395.1307	424.1751	424.1083	-0.0668
			313.149	1.271772	457.0562	397.7888	427.0062	426.9629	-0.0433
			313.149	1.271718	457.0562	397.7888	427.0062	426.9810	-0.0252
			313.152	1.271708	457.0571	397.7896	427.0071	426.9844	-0.0227
			333.149	1.254713	463.1956	403.2138	432.7834	432.7679	-0.0155
			333.149	1.254658	463.1956	403.2138	432.7834	432.7868	0.0034
			353.149	1.237892	469.5021	408.7888	438.7190	438.6485	-0.0705
			353.149	1.237836	469.5021	408.7888	438.7190	438.6683	-0.0507

Table S8

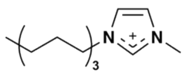
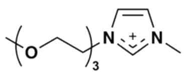
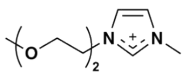
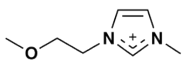
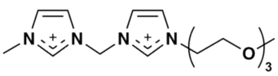
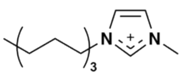
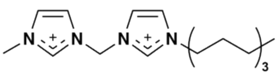
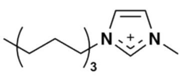
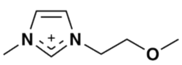
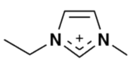
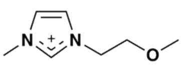
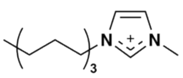
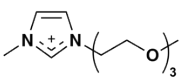
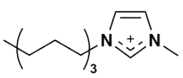
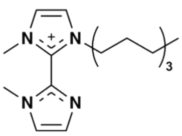
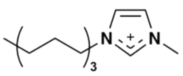
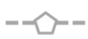
Fitting parameters of the zero order Redlich–Kister polynomial $V_m^E = (1 - x_{IL2})x_{IL2}A_0$ for the excess molar volumes ($V_m^E = V_m^{id} - V_m$) of the studied binary ionic liquid (IL) mixtures at various temperatures (T). For each fit the maximum excess molar volume ($V_m^{E,max}$) at equimolar composition of the mixture is given as well as the absolute average deviation $AAD = \sum |V_m - V_m^{fit}|/n$, where n is the amount of data points available for the fit.

IL1	IL2	T	A_0	$V_m^{E,max}$	AAD	n
		K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	
$[((C_3O)im)_2C_1][NTf_2]_2$	$[C_{10}C_1im][NTf_2]$	293.15	3.11856598	0.7796415	3.82E-09	1
		298.15	4.06582098	1.01645524	0.46183812	4
		303.15	4.23610596	1.05902649	0.49457735	4
		313.15	4.7031643	1.17579107	1.0220068	6
		323.15	4.78076843	1.19519211	0.53006999	3
		333.15	4.38855204	1.09713801	0.15631878	2
		353.15	4.55552607	1.13888152	6.02E-08	1
$[((C_3O)im)_2C_1][NTf_2]_2$	$[(C_7O_3)C1im][NTf2]$	298.15	-0.9009609	-0.2252402	0.11171262	6
		303.15	-0.7853187	-0.1963297	0.04038508	4
		313.15	-0.5913764	-0.1478441	0.04744294	4
		323.15	-0.4958596	-0.1239649	0.02107541	2
		333.15	-0.476178	-0.1190445	0.01216703	3
		353.15	-0.8311708	-0.2077927	0.03973124	3
$[((C_3O)im)_2C_1][NTf_2]_2$	$[(C_5O_2)C_1im][NTf_2]$	303.15	-0.4553373	-0.1138343	1.2E-09	1
		308.15	-0.2923584	-0.0730896	1.19E-09	1
		313.15	-0.3672198	-0.0918049	0.04933503	3
		323.15	-0.1621996	-0.0405499	0.14609591	6
		333.15	-0.196444	-0.049111	0.06611453	4
		343.15	-0.229416	-0.057354	1.18E-09	1
		353.15	-0.5614844	-0.1403711	0.01768732	3
$[((C_3O)im)_2C_1][NTf_2]_2$	$[(C_3O)C_1im][NTf_2]$	293.15	0.02030328	0.00507582	1.86E-09	1
		298.15	-0.0343072	-0.0085768	0.07375361	3
		303.15	0.04444816	0.01111204	0.07462862	3
		313.15	0.23883171	0.05970793	0.05474256	3
		323.15	0.3494937	0.08737342	0.07684875	3
		333.15	0.36958536	0.09239634	0.10949457	3
		353.15	-0.1471114	-0.0367778	0.04309287	2
$[(C_7O_3)imC_1imC_1][NTf_2]_2$	$[C_{10}C_1im][NTf_2]$	298.15	2.88436667	0.72109167	0.0358155	2
		303.15	3.02479929	0.75619982	0.03502473	2
		313.15	3.24166717	0.81041679	1.45E-08	1
		323.15	3.30193815	0.82548454	0.000000024	1
		333.15	3.3360064	0.8340016	2.54E-08	1
		353.15	3.1268536	0.7817134	2.28E-08	1
$[C_{10}imC_1imC_1][NTf_2]_2$	$[C_{10}C_1im][NTf_2]$	298.15	-0.9987282	-0.2496821	3.86E-09	1

IL1	IL2	T K	A_0 cm³·mol⁻¹	$V_m^{E,max}$ cm³·mol⁻¹	AAD cm³·mol⁻¹	n
		303.15	-0.854237	-0.2135593	1.65E-09	1
		313.15	-0.6353443	-0.1588361	2.16E-09	1
		323.15	-0.6027613	-0.1506903	1.96E-09	1
		333.15	-0.6081524	-0.1520381	4.49E-09	1
		353.15	-0.8469533	-0.2117383	3.21E-09	1
$[(C_3O)C_1im][NTf_2]$	$[C_2C_1im][NTf_2]$	303.15	0.15618655	0.03904664	0.03657039	2
		313.15	0.29920842	0.07480211	0.040576	3
		323.15	0.34220345	0.08555086	0.03272668	2
		333.15	0.3324388	0.0831097	0.02947992	2
		353.15	0.06360448	0.01590112	0.03039754	2
$[(C_3O)C_1im][NTf_2]$	$[C_{10}C_1im][NTf_2]$	293.15	1.72298416	0.43074604	0.05342065	2
		298.15	1.52764824	0.38191206	0.0569037	3
		303.15	1.61895929	0.40473982	0.05294908	3
		313.15	1.76799438	0.44199859	0.05681298	3
		323.15	1.86120491	0.46530123	0.0700144	3
		333.15	1.92298074	0.48074519	0.09817516	3
		353.15	1.94166192	0.48541548	0.20312558	3
$[(C_7O_3)C_1im][NTf_2]$	$[C_{10}C_1im][NTf_2]$	298.15	0.61479185	0.15369796	2.18E-09	1
		313.15	0.83990581	0.20997645	3.52E-09	1
		323.15	0.89794852	0.22448713	7.02E-10	1
		333.15	0.87568437	0.21892109	3.18E-09	1
		353.15	0.62127749	0.15531937	1.44E-09	1
$[C_{10}C_1C_1biim][NTf_2]$	$[C_{10}C_1im][NTf_2]$	298.15	-0.3353225	-0.0838306	0.04064084	3
		303.15	-0.2677862	-0.0669466	0.04007477	3
		313.15	-0.0976546	-0.0244137	0.04917819	4
		333.15	0.03701483	0.00925371	0.07772158	3
		353.15	-0.1914961	-0.047874	0.06474839	3

Table S9

Partial molar excess enthalpy at infinite dilution ($H_i^{E,\infty}$), the (excess) enthalpy of mixing at equimolar compostion ($H_{x_2=0.5}^{E}$), and the maximum excess molar volume ($V_m^{E,max}$) at equimolar composition of the mixture for the studied binary mixtures of ILs with common $[NTF_2]^-$ anions. The symbols, colours, and line styles correspond to Fig. 5 of the main text.

IL_1	IL_2	Sym	$H_1^{E,\infty}$ kJ·mol^{-1}	$H_2^{E,\infty}$ kJ·mol^{-1}	$H_{x_2=0.5}^{E}$ kJ·mol^{-1}	$V_m^{E,max}$ cm^3·mol^{-1}
			3.41	5.44	0.97	1.15
			-3.47	-3.84	-0.95	-0.17
			-0.90	-1.03	-0.24	-0.12
			0.18	0.24	0.05	0.04
			4.05	6.33	1.27	0.77
			0.94	0.64	0.20	-0.19
			0.15	0.17	0.04	0.05
			2.29	4.00	0.69	0.42
			1.29	2.16	0.47	0.19
			0.43	0.31	0.08	-0.02

Viscosities

Table S10
Pure ionic liquid viscosity (η) data at atmospheric pressure and temperature (T). IL numbers correspond to table 1 of the manuscript.

no	IL	T K	η mPa·s
1	$[C_2C_1im][NTf_2]$	293.15	38.174
		298.15	31.795
		303.15	26.777
		313.15	19.725
		323.15	15.115
		333.15	12.014
		353.15	7.846
2	$[C_{10}C1im][NTf2]$	298.15	112.5
		303.15	87.308
		313.15	55.395
		313.15	57.423
		313.15	56.423
		313.15	55.959
		323.15	37.575
		333.15	26.582
		353.15	15.016
3	$[(C_3O)C_1im][NTf_2]$	298.151	45.088
		303.149	36.567
		313.149	25.261
		323.149	18.425
		333.147	14.088
		353.148	8.8267
4	$[(C_5O_2)C_1im][NTf_2]$	298.15	56.173
		303.15	44.762
		313.15	30.101
		333.15	15.939
		353.15	9.7042
5	$[(C_7O_3)C_1im][NTf_2]$	298.15	83.517
		303.15	64.45
		313.15	41.146
		313.15	41.026
		313.15	40.782
		323.15	28.051
		333.15	20.166
		353.15	11.864
6	$[C_{10}imC_1imC_1][NTf_2]_2$	323.15	1201.9
		333.15	614.8
		353.15	207.12
7	$[(C_7O_3)imC_1imC_1][NTf_2]_2$	333.15	713.48
		353.15	222.46
9	$[((C_3O)im)_2C1][NTf_2]_2$	311.15	1367.7
		313.15	1211.5
		313.15	1150.8
		323.15	573.8
		323.15	551.66
		333.15	306.1
		333.15	294.28
		343.15	178.76
		353.15	112.43
		353.15	108.52
11	$[C_{10}C_1C_1biim][NTf_2]$	298.15	770
		313.15	268.3
		333.15	148.4

Table S11

Fitting parameters of the Vogel–Fülcher–Tammann–Hesse equation, $\ln \eta = A + B/(T - T_0)$, used for the interpolation of the pure ionic liquid (IL) viscosities (η) studied at atmospheric pressure as a function of temperature (T) within temperature range T_{range}. IL numbers correspond to table 1 of the manuscript, AAD is the absolute average deviation $\sum|\eta - \eta_{fit}|/n$.

No	IL	$Trange$ K	A	B K	T_0 K	AAD mPa·s
1	$[C_2C_1im][NTf_2]$	293.15–353.15	-1.7389	779.51	148.19	0.0728
2	$[C_{10}C_1im][NTf_2]$	298.15–353.15	-2.2328	935.82	163.63	0.4045
3	$[(C_3O)C_1im][NTf_2]$	298.15–353.15	-1.3979	629.68	177.16	0.0588
4	$[(C_5O_2)C_1im][NTf_2]$	298.15–353.15	-1.5200	660.18	179.13	0.0531
5	$[(C_7O_3)C_1im][NTf_2]$	298.15–353.15	-1.2186	587.39	194.06	0.0623
6	$[C_{10}imC_1imC_1][NTf_2]_2$	323.15–353.15	-11.5716	5399.6	33.539	14.269
7	$[(C_7O_3)imC_1imC_1][NTf_2]_2$	333.15–353.15	-12.1379	5632.2	32.093	0.0001
9	$[((C_3O)im)_2C_1][NTf_2]_2$	313.15–353.15	-1.9117	1005.1	201.22	11.296
11	$[C_{10}C_1C_1biim][NTf_2]$	298.15–333.15	3.8014	72.486	272.67	0.0004

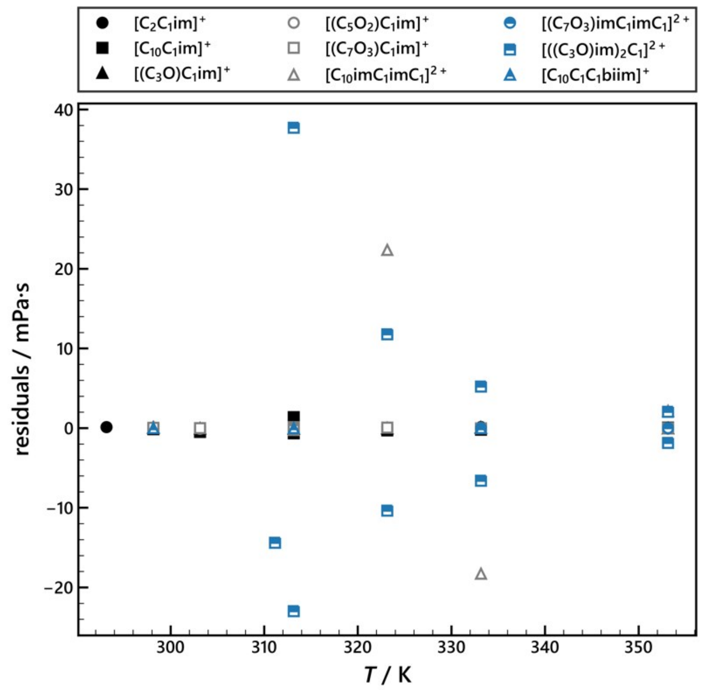


Figure S6

Residual plot of the temperature (T) versus dynamic viscosity (η) fit for the studied ionic liquids using the Vogel–Fülcher–Tammann–Hesse equation $\ln \eta = A + B/(T - T_0)$.

Calorimetric data for mixing of ionic liquids

Table S12
Stochiometric data and heat effect of the calorimetry experiments for the different mixtures at 313.15 K. The subscripts c and d mean cell (or container) and dispenser (or syringe) respectively.

$[(C_3O)C_1im]_{(1-x)}[C_2C_1im]_x[NTf_2]$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mmol	Q / mJ
0.0000E+00	3.07876E-03	1.76136E-02	0.00000E+00	2.869
1.7614E-05	3.07876E-03	1.76136E-02	0.00000E+00	2.799
3.5227E-05	3.07876E-03	1.76136E-02	0.00000E+00	2.751
5.2841E-05	3.07876E-03	1.76136E-02	0.00000E+00	2.764
7.0454E-05	3.07876E-03	1.76136E-02	0.00000E+00	2.705
8.8068E-05	3.07876E-03	1.76136E-02	0.00000E+00	2.655
1.0568E-04	3.07876E-03	1.76136E-02	0.00000E+00	2.642
1.2330E-04	3.07876E-03	1.76136E-02	0.00000E+00	2.598
1.4091E-04	3.07876E-03	1.76136E-02	0.00000E+00	2.561
7.5444E-04	2.25426E-03	0.00000E+00	3.06662E-02	0.316
7.5444E-04	2.28493E-03	0.00000E+00	3.06662E-02	0.320
7.5444E-04	2.31559E-03	0.00000E+00	3.06662E-02	0.320
7.5444E-04	2.34626E-03	0.00000E+00	3.06662E-02	0.314
7.5444E-04	2.37692E-03	0.00000E+00	3.06662E-02	0.371
7.5444E-04	2.40759E-03	0.00000E+00	3.06662E-02	0.355
7.5444E-04	2.43826E-03	0.00000E+00	3.06662E-02	0.286
7.5444E-04	2.46892E-03	0.00000E+00	3.06662E-02	0.293
7.5444E-04	2.49959E-03	2.82241E-02	0.00000E+00	2.272
7.8266E-04	2.49959E-03	2.82241E-02	0.00000E+00	2.212
8.1089E-04	2.49959E-03	2.82241E-02	0.00000E+00	2.177
8.3911E-04	2.49959E-03	2.82241E-02	0.00000E+00	2.125
8.6734E-04	2.49959E-03	2.82241E-02	0.00000E+00	2.099
8.9556E-04	2.49959E-03	2.82241E-02	0.00000E+00	2.083
2.8287E-03	1.91952E-05	0.00000E+00	3.06662E-02	4.430
2.8287E-03	4.98614E-05	0.00000E+00	3.06662E-02	4.388
2.8287E-03	8.05276E-05	0.00000E+00	3.06662E-02	4.379

2.8287E-03	1.11194E-04	0.00000E+00	3.06662E-02	4.303
2.8287E-03	1.41860E-04	0.00000E+00	3.06662E-02	4.170
2.8287E-03	1.72526E-04	0.00000E+00	3.06662E-02	4.122
2.8287E-03	2.03192E-04	0.00000E+00	3.06662E-02	4.118
2.8287E-03	2.33859E-04	0.00000E+00	3.06662E-02	4.079
2.8287E-03	2.64525E-04	0.00000E+00	3.06662E-02	3.926
2.8287E-03	2.95191E-04	0.00000E+00	3.06662E-02	3.796
1.7567E-03	1.16778E-03	3.53368E-02	0.00000E+00	0.548
1.7920E-03	1.16778E-03	3.53368E-02	0.00000E+00	0.638
1.8274E-03	1.16778E-03	3.53368E-02	0.00000E+00	0.527
1.8627E-03	1.16778E-03	3.53368E-02	0.00000E+00	0.509
1.8980E-03	1.16778E-03	3.53368E-02	0.00000E+00	0.587
1.9334E-03	1.16778E-03	0.00000E+00	3.83942E-02	2.436
1.9334E-03	1.20617E-03	0.00000E+00	3.83942E-02	2.411
1.9334E-03	1.24457E-03	0.00000E+00	3.83942E-02	2.393

$[(C_3O)C_1im]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mmol	Q / mJ
1.91260E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.883
1.93027E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.918
1.94793E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.978
1.96560E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.764
1.98326E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.730
2.00093E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.663
2.01859E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.539
2.03626E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.464
2.05392E-03	6.49650E-04	1.76656E-02	0.00000E+00	5.381
0.00000E+00	2.01020E-03	1.76656E-02	0.00000E+00	39.16
1.76656E-05	2.01020E-03	1.76656E-02	0.00000E+00	38.87
3.53312E-05	2.01020E-03	1.76656E-02	0.00000E+00	38.56
5.29969E-05	2.01020E-03	1.76656E-02	0.00000E+00	38.05
7.06625E-05	2.01020E-03	1.76656E-02	0.00000E+00	37.59
8.83281E-05	2.01020E-03	1.76656E-02	0.00000E+00	37.26
1.05994E-04	2.01020E-03	1.76656E-02	0.00000E+00	36.68
1.23659E-04	2.01020E-03	1.76656E-02	0.00000E+00	36.46
1.41325E-04	2.01020E-03	1.76656E-02	0.00000E+00	36.04
1.58991E-04	2.01020E-03	1.76656E-02	0.00000E+00	35.65
1.76656E-04	2.01020E-03	1.76656E-02	0.00000E+00	35.43
1.94322E-04	2.01020E-03	1.76656E-02	0.00000E+00	34.90
2.82850E-03	1.50226E-04	0.00000E+00	7.52865E-03	25.46
2.82850E-03	1.57755E-04	0.00000E+00	7.52865E-03	25.10
2.82850E-03	1.65283E-04	0.00000E+00	7.52865E-03	24.81
2.82850E-03	1.72812E-04	0.00000E+00	7.52865E-03	24.58
4.77504E-04	1.55116E-03	0.00000E+00	2.51148E-02	2.581
4.77504E-04	1.57627E-03	0.00000E+00	2.51148E-02	2.550
4.77504E-04	1.60139E-03	0.00000E+00	2.51148E-02	2.226
4.77504E-04	1.62650E-03	0.00000E+00	2.51148E-02	2.164
1.19397E-03	1.19158E-03	0.00000E+00	2.00596E-02	9.775
1.19397E-03	1.21164E-03	0.00000E+00	2.00596E-02	9.519
1.19397E-03	1.23170E-03	0.00000E+00	2.00596E-02	9.377
1.19397E-03	1.25176E-03	0.00000E+00	2.00596E-02	9.122
1.19397E-03	1.27182E-03	0.00000E+00	2.00596E-02	9.031
1.19397E-03	1.29188E-03	0.00000E+00	2.00596E-02	8.947
1.19397E-03	1.31194E-03	0.00000E+00	2.00596E-02	8.457
1.19397E-03	1.33200E-03	0.00000E+00	2.00596E-02	8.288
1.19397E-03	1.35206E-03	2.82225E-02	0.00000E+00	27.28
1.22219E-03	1.35206E-03	2.82225E-02	0.00000E+00	26.93
1.25042E-03	1.35206E-03	2.82225E-02	0.00000E+00	26.40
1.27864E-03	1.35206E-03	2.82225E-02	0.00000E+00	26.04
1.30686E-03	1.35206E-03	2.82225E-02	0.00000E+00	25.69
1.33508E-03	1.35206E-03	2.82225E-02	0.00000E+00	25.41
1.81933E-03	5.50327E-04	0.00000E+00	1.25561E-02	19.73
1.81933E-03	5.62883E-04	0.00000E+00	1.25561E-02	19.55
1.81933E-03	5.75439E-04	0.00000E+00	1.25561E-02	19.03
1.81933E-03	5.87995E-04	0.00000E+00	1.25561E-02	18.84
1.81933E-03	6.00552E-04	0.00000E+00	1.25561E-02	18.62
1.81933E-03	6.13108E-04	0.00000E+00	1.25561E-02	18.14
1.81933E-03	6.25664E-04	0.00000E+00	1.25561E-02	17.97

$[(C_3Oim)_2C_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mmol	Q / mJ
1.54050E-03	1.25568E-05	0.00000E+00	1.25568E-02	64.99
1.54050E-03	2.51136E-05	0.00000E+00	1.25568E-02	64.29
1.54050E-03	3.76704E-05	0.00000E+00	1.25568E-02	62.35
1.54050E-03	5.02271E-05	0.00000E+00	1.25568E-02	60.89
1.54050E-03	6.27839E-05	0.00000E+00	1.25568E-02	58.69
1.54050E-03	7.53408E-05	5.48241E-03	1.28289E-02	44.73
1.54598E-03	8.81697E-05	5.48241E-03	1.28289E-02	0.00
1.55146E-03	1.00999E-04	5.48241E-03	1.28289E-02	41.49
1.55695E-03	1.13828E-04	5.48241E-03	1.28289E-02	40.30
0.00000E+00	2.01771E-03	3.43166E-03	8.03012E-03	2.000
3.43166E-06	2.02574E-03	3.43166E-03	8.03012E-03	1.904
6.86331E-06	2.03377E-03	3.43166E-03	8.03012E-03	1.930
1.02950E-05	2.04180E-03	3.43166E-03	8.03012E-03	1.859
1.37266E-05	2.04983E-03	3.43166E-03	8.03012E-03	2.004
5.51193E-04	1.29007E-03	0.00000E+00	1.25568E-02	2.909
5.51193E-04	1.30263E-03	0.00000E+00	1.25568E-02	2.857
5.51193E-04	1.31518E-03	0.00000E+00	1.25568E-02	2.848
5.51193E-04	1.32774E-03	0.00000E+00	1.25568E-02	2.653
5.51193E-04	1.34030E-03	0.00000E+00	1.25568E-02	2.792
5.47192E-04	1.35285E-03	0.00000E+00	2.00607E-02	4.232
5.47192E-04	1.37291E-03	0.00000E+00	2.00607E-02	4.106
5.47192E-04	1.39297E-03	0.00000E+00	2.00607E-02	3.944
5.47192E-04	1.41303E-03	0.00000E+00	2.00607E-02	3.679
5.47192E-04	1.43310E-03	5.48241E-03	1.28289E-02	-0.325
5.52674E-04	1.44593E-03	5.48241E-03	1.28289E-02	-0.318
5.58157E-04	1.45876E-03	5.48241E-03	1.28289E-02	-0.318
1.71556E-05	2.05786E-03	3.43166E-03	8.03012E-03	2.721
2.05873E-05	2.06589E-03	3.43166E-03	8.03012E-03	2.835
2.40189E-05	2.07392E-03	3.43166E-03	8.03012E-03	2.770
2.74506E-05	2.08195E-03	3.43166E-03	8.03012E-03	2.831

1.26742E-03	3.55099E-04	0.00000E+00	2.00607E-02	46.22
1.26742E-03	3.75160E-04	0.00000E+00	2.00607E-02	44.44
1.26742E-03	3.95220E-04	0.00000E+00	2.00607E-02	42.89
8.72362E-04	8.62962E-04	1.57319E-02	4.40881E-03	5.146
8.88094E-04	8.67371E-04	1.57319E-02	4.40881E-03	5.028
9.03826E-04	8.71780E-04	1.57319E-02	4.40881E-03	4.793
1.26742E-03	4.15281E-04	1.08848E-02	1.07679E-02	4.850
1.27830E-03	4.26049E-04	1.08848E-02	1.07679E-02	4.617
1.28919E-03	4.36817E-04	1.08848E-02	1.07679E-02	4.646
9.19659E-04	9.16335E-04	0.00000E+00	2.00607E-02	16.23
9.19659E-04	9.36396E-04	0.00000E+00	2.00607E-02	15.81
9.19659E-04	9.56456E-04	0.00000E+00	2.00607E-02	14.26

$[(C_3Oim)_2C_1]_{(1-x)}[(C_3O)C_1im]_x[NTf_2]_{(2-x)}$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mmol	Q / mJ
0.00000E+00	1.53783E-03	1.76668E-02	0.00000E+00	3.116
1.76668E-05	1.53783E-03	1.76668E-02	0.00000E+00	3.061
3.53336E-05	1.53783E-03	1.76668E-02	0.00000E+00	3.020
5.30004E-05	1.53783E-03	1.76668E-02	0.00000E+00	2.936
7.06673E-05	1.53783E-03	9.86047E-03	9.93967E-03	0.715
8.05278E-05	1.54777E-03	9.86047E-03	9.93967E-03	0.711
9.03882E-05	1.55771E-03	9.86047E-03	9.93967E-03	0.695
1.00249E-04	1.56765E-03	9.86047E-03	9.93967E-03	0.674
1.15979E-03	1.02693E-03	2.82245E-02	0.00000E+00	1.526
1.18801E-03	1.02693E-03	2.82245E-02	0.00000E+00	1.449
1.21624E-03	1.02693E-03	2.82245E-02	0.00000E+00	1.387
1.27431E-03	8.61942E-04	2.82245E-02	0.00000E+00	1.140
1.30253E-03	8.61942E-04	2.82245E-02	0.00000E+00	1.106
1.33076E-03	8.61942E-04	2.82245E-02	0.00000E+00	1.081
1.35898E-03	8.61942E-04	2.82245E-02	0.00000E+00	1.062
1.38721E-03	8.61942E-04	3.53372E-02	0.00000E+00	1.339
1.42255E-03	8.61942E-04	3.53372E-02	0.00000E+00	1.314
1.45788E-03	8.61942E-04	3.53372E-02	0.00000E+00	1.305
3.94738E-04	1.39529E-03	3.53372E-02	0.00000E+00	4.399
4.30075E-04	1.39529E-03	3.53372E-02	0.00000E+00	4.261
4.65412E-04	1.39529E-03	3.53372E-02	0.00000E+00	4.123
5.00750E-04	1.39529E-03	3.53372E-02	0.00000E+00	3.998

$[(C_3Oim)_2C_1]_{(1-x)}[(C_7O_3)C_1im]_x[NTf_2]_{(2-x)}$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mmol	Q / mJ
1.38438E-05	1.35225E-03	1.38437E-02	0.00000E+00	-46.42
2.76875E-05	1.35225E-03	1.38437E-02	0.00000E+00	-45.60
4.15313E-05	1.35225E-03	1.38437E-02	0.00000E+00	-45.25
5.53750E-05	1.35225E-03	1.38437E-02	0.00000E+00	-44.22
6.92188E-05	1.35225E-03	1.38437E-02	0.00000E+00	-43.95
8.30625E-05	1.35225E-03	1.38437E-02	0.00000E+00	-43.18
0.00000E+00	1.35091E-03	5.20120E-03	4.99924E-03	-12.20
5.20120E-06	1.35591E-03	5.20120E-03	4.99924E-03	-8.603
1.04024E-05	1.36091E-03	5.20120E-03	4.99924E-03	-8.607
1.56036E-05	1.36591E-03	5.20120E-03	4.99924E-03	-8.472
2.08048E-05	1.37091E-03	5.20120E-03	4.99924E-03	-8.323
1.94655E-03	0.00000E+00	5.20120E-03	4.99924E-03	-9.717
1.95175E-03	4.99924E-06	5.20120E-03	4.99924E-03	-9.707
1.95695E-03	9.99847E-06	5.20120E-03	4.99924E-03	-9.570
1.96215E-03	1.49977E-05	5.20120E-03	4.99924E-03	-9.501
1.96735E-03	1.99969E-05	5.20120E-03	4.99924E-03	-9.422
8.14258E-04	7.82750E-04	1.38437E-02	0.00000E+00	-12.74
8.28102E-04	7.82750E-04	1.38437E-02	0.00000E+00	-12.55
8.41945E-04	7.82750E-04	1.38437E-02	0.00000E+00	-12.51
8.55789E-04	7.82750E-04	1.38437E-02	0.00000E+00	-12.32
8.69633E-04	7.82750E-04	1.38437E-02	0.00000E+00	-12.00
2.87780E-04	1.14515E-03	1.38437E-02	0.00000E+00	-33.29
3.01624E-04	1.14515E-03	1.38437E-02	0.00000E+00	-33.01
3.15467E-04	1.14515E-03	1.38437E-02	0.00000E+00	-32.62
3.29311E-04	1.14515E-03	1.38437E-02	0.00000E+00	-31.85
3.43155E-04	1.14515E-03	1.38437E-02	0.00000E+00	-31.55
1.41894E-03	3.62260E-04	1.93896E-02	0.00000E+00	-2.718
1.43833E-03	3.62260E-04	1.93896E-02	0.00000E+00	-2.661
1.45772E-03	3.62260E-04	1.93896E-02	0.00000E+00	-2.590
1.47711E-03	3.62260E-04	1.93896E-02	0.00000E+00	-2.521

1.49650E-03	3.62260E-04	1.93896E-02	0.00000E+00	-2.371

$[(C_3Oim)_2C_1]_{(1-x)}[(C_5O_2)C_1im]_x[NTf_2]_{(2-x)}$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mmol	Q / mJ
0.00000E+00	1.34664E-03	1.54966E-02	0.00000E+00	-13.38
1.54966E-05	1.34664E-03	1.54966E-02	0.00000E+00	-13.55
3.09932E-05	1.34664E-03	1.54966E-02	0.00000E+00	-13.00
4.64898E-05	1.34664E-03	1.54966E-02	0.00000E+00	-12.99
6.19864E-05	1.34664E-03	1.54966E-02	0.00000E+00	-12.68
0.00000E+00	1.36245E-03	5.90678E-03	5.92098E-03	-2.519
5.90678E-06	1.36837E-03	5.90678E-03	5.92098E-03	-2.486
1.18136E-05	1.37429E-03	5.90678E-03	5.92098E-03	-2.459
1.77204E-05	1.38021E-03	5.90678E-03	5.92098E-03	-2.404
2.36271E-05	1.38613E-03	5.90678E-03	5.92098E-03	-2.373
2.95364E-05	1.39205E-03	9.43666E-03	9.45934E-03	-3.839
3.89731E-05	1.40151E-03	9.43666E-03	9.45934E-03	-3.577
4.84097E-05	1.41097E-03	9.43666E-03	9.45934E-03	-3.550
5.78464E-05	1.42043E-03	9.43666E-03	9.45934E-03	-3.468
2.18125E-03	0.00000E+00	8.27304E-03	8.29292E-03	-4.843
2.18952E-03	8.29292E-06	8.27304E-03	8.29292E-03	-4.663
2.19780E-03	1.65858E-05	8.27304E-03	8.29292E-03	-4.512
2.20607E-03	2.48788E-05	8.27304E-03	8.29292E-03	-4.412
8.29070E-04	8.30927E-04	2.47573E-02	0.00000E+00	-5.981
8.53827E-04	8.30927E-04	2.47573E-02	0.00000E+00	-5.765
8.78585E-04	8.30927E-04	2.47573E-02	0.00000E+00	-5.652
9.03342E-04	8.30927E-04	2.47573E-02	0.00000E+00	-5.561
9.28099E-04	8.30927E-04	2.47573E-02	0.00000E+00	-5.387
2.92125E-04	1.16098E-03	2.17045E-02	0.00000E+00	-12.80
3.13830E-04	1.16098E-03	2.17045E-02	0.00000E+00	-12.42
3.35534E-04	1.16098E-03	2.17045E-02	0.00000E+00	-12.07
3.57239E-04	1.16098E-03	2.17045E-02	0.00000E+00	-11.95
3.78943E-04	1.16098E-03	2.17045E-02	0.00000E+00	-11.48

1.55317E-03	3.96754E-04	9.43666E-03	9.45934E-03	-1.977
1.56261E-03	4.06213E-04	9.43666E-03	9.45934E-03	-1.966
1.57204E-03	4.15673E-04	9.43666E-03	9.45934E-03	-1.926
1.58148E-03	4.25132E-04	9.43666E-03	9.45934E-03	-1.887

$[C_{10}imC_1imC_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mail	Q / mJ
0.00000E+00	1.76247E-03	6.97378E-03	6.95428E-03	3.948
6.97378E-06	1.76942E-03	6.97378E-03	6.95428E-03	3.779
1.39476E-05	1.77638E-03	6.97378E-03	6.95428E-03	3.587
2.09213E-05	1.78333E-03	6.97378E-03	6.95428E-03	3.521
2.78951E-05	1.79029E-03	6.97378E-03	6.95428E-03	3.455
1.16414E-03	0.00000E+00	0.00000E+00	1.25568E-02	7.997
1.16414E-03	1.25568E-05	0.00000E+00	1.25568E-02	7.971
1.16414E-03	2.51136E-05	0.00000E+00	1.25568E-02	7.771
1.16414E-03	3.76703E-05	0.00000E+00	1.25568E-02	7.696
1.16414E-03	5.02271E-05	0.00000E+00	1.25568E-02	7.754
6.98325E-04	7.14034E-04	0.00000E+00	1.75870E-02	4.075
6.98325E-04	7.31621E-04	0.00000E+00	1.75870E-02	3.827
6.98325E-04	7.49208E-04	0.00000E+00	1.75870E-02	3.913
6.98325E-04	7.66795E-04	0.00000E+00	1.75870E-02	3.731
0.00000E+00	1.76247E-03	6.97378E-03	6.95428E-03	3.948
6.97378E-06	1.76942E-03	6.97378E-03	6.95428E-03	3.779
1.39476E-05	1.77638E-03	6.97378E-03	6.95428E-03	3.587
2.09213E-05	1.78333E-03	6.97378E-03	6.95428E-03	3.521
2.78951E-05	1.79029E-03	6.97378E-03	6.95428E-03	3.455
1.16414E-03	0.00000E+00	0.00000E+00	1.25568E-02	7.997
1.16414E-03	1.25568E-05	0.00000E+00	1.25568E-02	7.971
1.16414E-03	2.51136E-05	0.00000E+00	1.25568E-02	7.771
1.16414E-03	3.76703E-05	0.00000E+00	1.25568E-02	7.696

$[C_{10}C_1C_1biim]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$

n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mail	Q / mJ
8.16148E-04	8.59466E-04	0.00000E+00	2.00607E-02	1.844
8.16148E-04	8.79527E-04	0.00000E+00	2.00607E-02	1.846
8.16148E-04	8.99587E-04	0.00000E+00	2.00607E-02	1.737
8.16148E-04	9.19648E-04	0.00000E+00	2.00607E-02	1.860

1.53591E-03	1.75871E-05	0.00000E+00	1.75870E-02	5.190
1.53591E-03	3.51741E-05	0.00000E+00	1.75870E-02	5.053
1.53591E-03	5.27612E-05	0.00000E+00	1.75870E-02	4.922
1.53591E-03	7.03482E-05	0.00000E+00	1.75870E-02	4.864
1.25530E-03	3.41226E-04	0.00000E+00	2.00607E-02	3.930
1.25530E-03	3.61287E-04	0.00000E+00	2.00607E-02	3.843
1.25530E-03	3.81347E-04	0.00000E+00	2.00607E-02	3.745
1.25530E-03	4.01408E-04	0.00000E+00	2.00607E-02	3.589

$[(C_7O_3)C_1im]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$

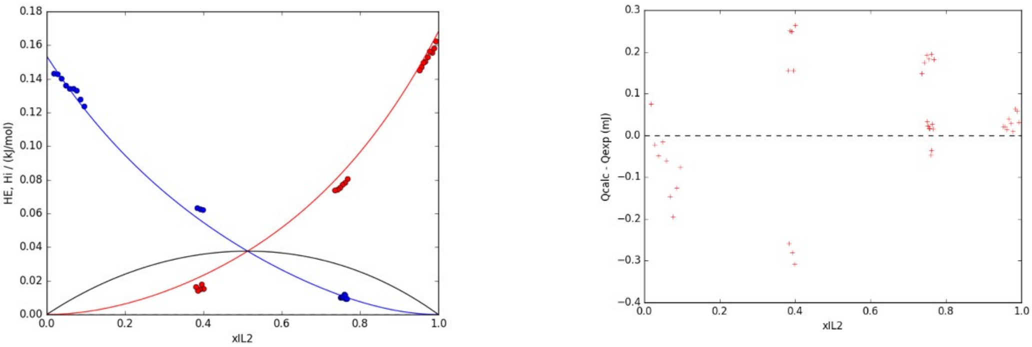
n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mail	Q / mJ
1.10792E-04	1.75575E-03	1.38438E-02	0.00000E+00	18.01
1.24636E-04	1.75575E-03	1.38438E-02	0.00000E+00	17.83
1.38480E-04	1.75575E-03	1.38438E-02	0.00000E+00	17.33
9.21164E-04	1.04553E-03	0.00000E+00	2.00732E-02	5.977
9.21164E-04	1.06560E-03	0.00000E+00	2.00732E-02	5.853
9.21164E-04	1.08568E-03	0.00000E+00	2.00732E-02	5.462
9.21164E-04	1.10586E-03	1.93896E-02	0.00000E+00	12.76
9.40554E-04	1.10586E-03	1.93896E-02	0.00000E+00	12.53
9.59943E-04	1.10586E-03	1.93896E-02	0.00000E+00	12.43
9.79333E-04	1.10586E-03	1.93896E-02	0.00000E+00	12.33
9.98722E-04	1.10586E-03	1.93896E-02	0.00000E+00	12.17

$[(C_7O_3)imC_1imC_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$

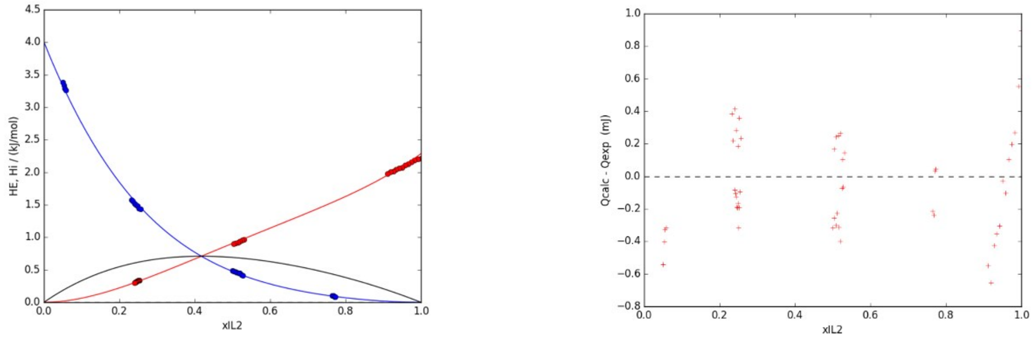
n_{1c} / mol	n_{2c} / mol	n_{1d} mmol	n_{2d} mail	Q / mJ
4.43000E-05	1.81000E-03	7.39000E-03	7.38000E-03	9.050
5.17000E-05	1.82000E-03	7.39000E-03	7.38000E-03	8.800
5.91000E-05	1.82000E-03	7.39000E-03	7.38000E-03	8.530
1.29000E-03	1.76000E-05	0.00000E+00	1.76000E-02	107.0
1.29000E-03	3.52000E-05	0.00000E+00	1.76000E-02	102.0
1.29000E-03	5.28000E-05	0.00000E+00	1.76000E-02	96.90
1.29000E-03	7.03000E-05	0.00000E+00	1.76000E-02	96.00
1.29000E-03	8.79000E-05	0.00000E+00	1.76000E-02	89.90
1.29000E-03	1.06000E-04	0.00000E+00	1.76000E-02	84.80
1.29000E-03	1.23000E-04	0.00000E+00	1.76000E-02	82.40
7.39000E-04	8.26000E-04	0.00000E+00	1.76000E-02	17.20
7.39000E-04	8.44000E-04	0.00000E+00	1.76000E-02	16.90
7.39000E-04	8.62000E-04	0.00000E+00	1.76000E-02	16.60

Figure S7
Partial molar enthalpies, HEi, of the components of the mixtures [and enthalpies of mixing, ΔmixH, of each system. Lines are the Redlich-Kister fitting curves with the parameters reported in Table S4 and ■, ● are experimental data. In the graphs of the right hand side are plotted the differences between the experimental heat effects, Qexp, and the ones calculated, Qcalc, with the fitting parameters collected in Table S4.

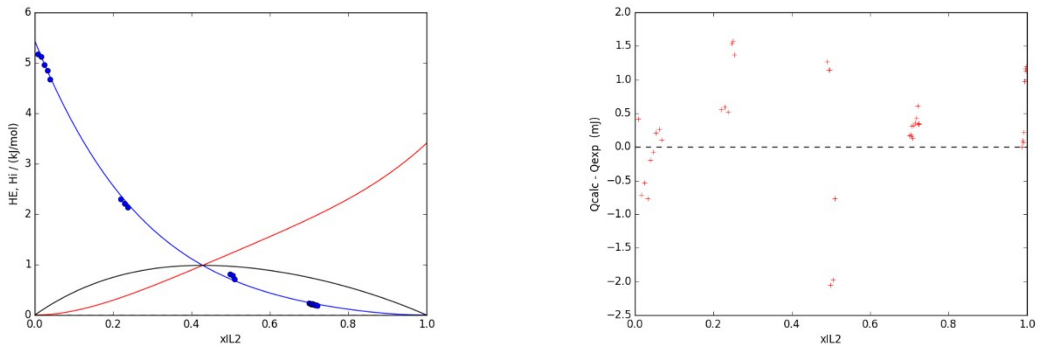
$[(C_3O)C_1im]_{(1-x)}[C_2C_1im]_x[NTf_2]$; IL2 = $[C_2C_1im][NTf_2]$



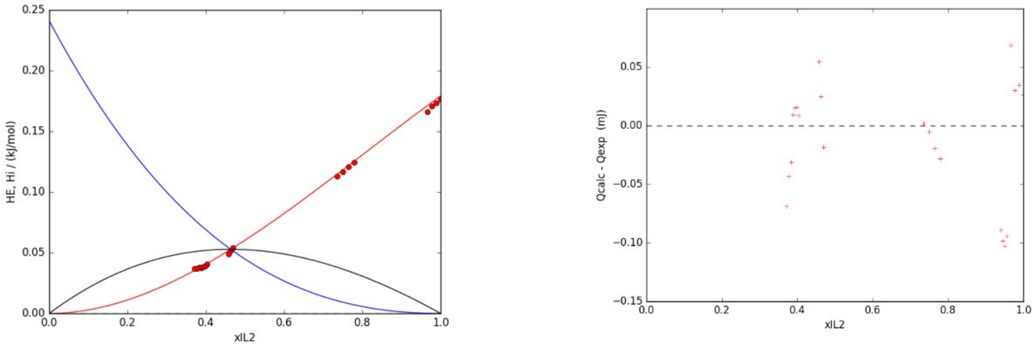
$[(C_3O)C_1im]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$; IL2 = $[C_{10}C_1im][NTf_2]$



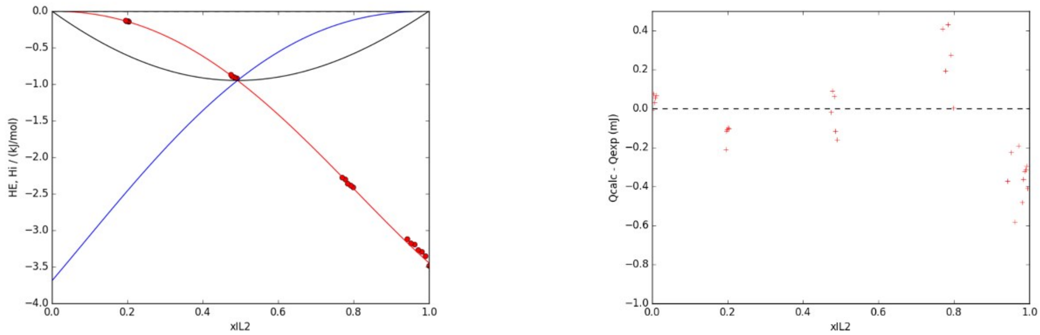
$[(C_3Oim)_2C_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[C_{10}C_1im][NTf_2]$



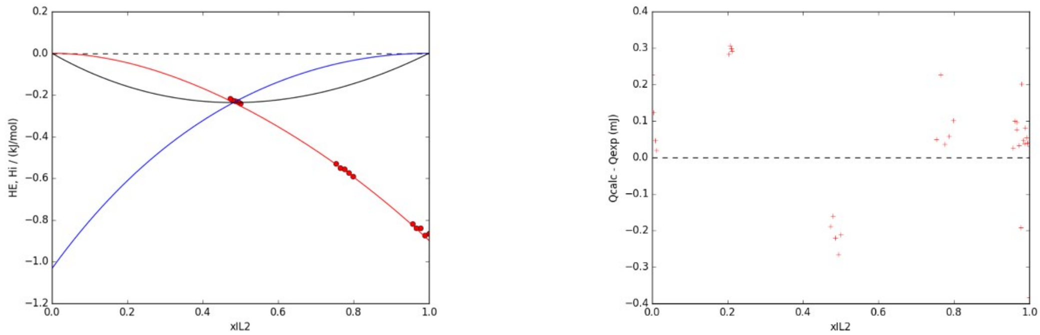
$[(C_3Oim)_2C_1]_{(1-x)}[(C_3O)C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[(C_3Oim)_2C_1][NTf_2]$



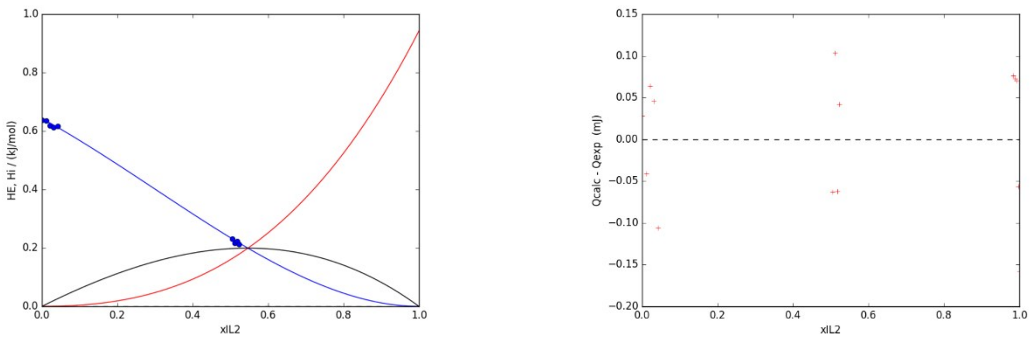
$[(C_3Oim)_2C_1]_{(1-x)}[(C_7O_3)C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[(C_3Oim)_2C_1][NTf_2]$



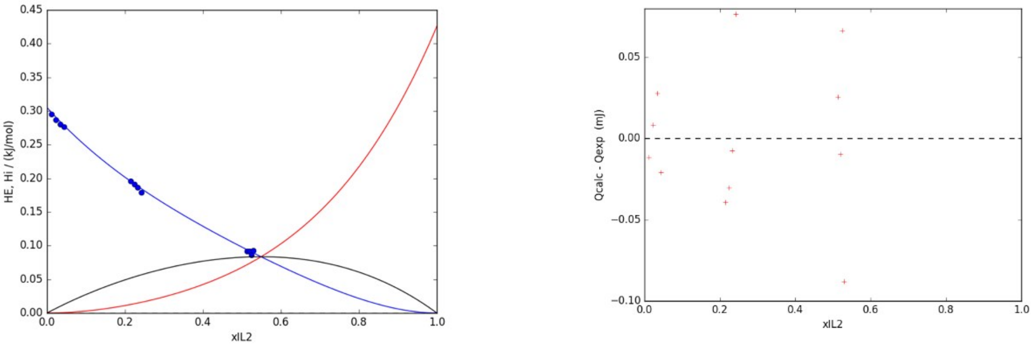
$[(C_3Oim)_2C_1]_{(1-x)}[(C_5O_2)C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[(C_3Oim)_2C_1][NTf_2]$



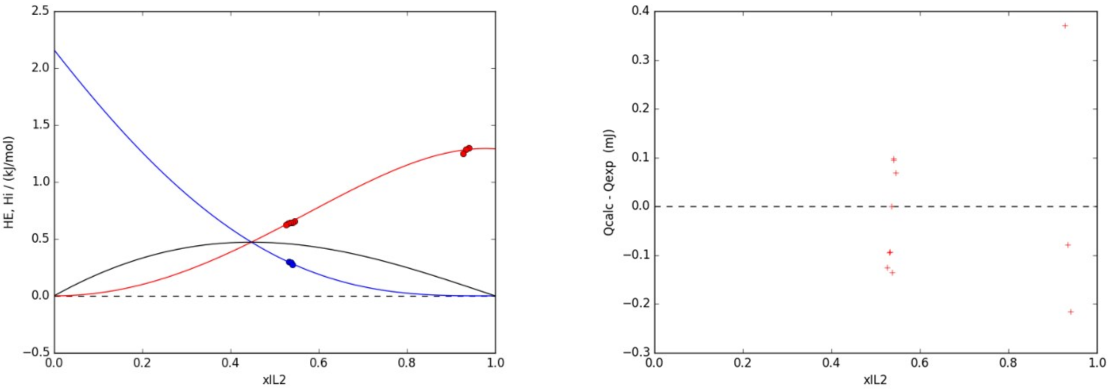
$[C_{10}imC_1imC_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[C_{10}C_1im]$ $[NTf_2]$



$[C_{10}C_1C_1biim]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$; IL2 = $[C_{10}C_1im]$ $[NTf_2]$



$[(C_7O_3)C_1im]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[C_{10}C_1im]$ $[NTf_2]$



$[(C_7O_3)imC_1imC_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$; IL2 = $[C_{10}C_1im]$ $[NTf_2]$

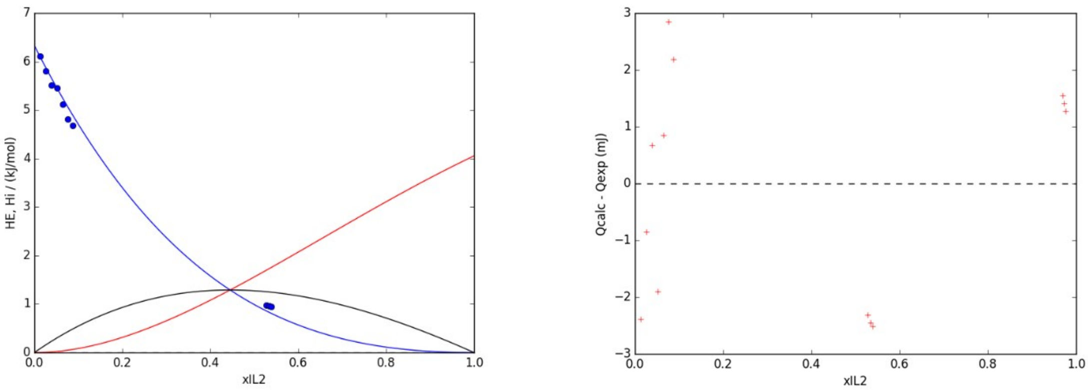


Table S13
Parameters obtained for the fitting of the partial IL excess enthalpies with the Redlich-Kister equation corresponding to the systems studied in this work.

System	a_0	a_1	a_2
$[(C_3O)C_1im]_{(1-x)}[C_2C_1im]_x[NTf_2]$	+ 0.14996	- 0.00646	+ 0.00900
$[(C_3O)C_1im]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$	+ 2.76041	+ 0.85944	+ 0.38433
$[(C_3Oim)_2C_1]_{(1-x)}[C_{10}C_1im]_x [NTf_2]_{(2-x)}$	+ 3.86665	+ 1.01538	+ 0.55669
$[(C_3Oim)_2C_1]_{(1-x)}[(C_3O)C_1im]_x[NTf_2]_{(2-x)}$	+ 0.21027	+ 0.03092	- 0.00014
$[(C_3Oim)_2C_1]_{(1-x)}[(C_7O_3)C_1im]_x[NTf_2]_{(2-x)}$	- 3.78385	- 0.18174	+ 0.13038
$[(C_3Oim)_2C_1]_{(1-x)}[(C_5O_2)C_1im]_x[NTf_2]_{(2-x)}$	- 0.94444	- 0.06775	- 0.02090
$[C_{10}imC_1imC_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$	+ 0.78975	- 0.14987	+ 0.00305
$[C_{10}C_1C_1biim]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$	+ 0.33121	- 0.06027	+ 0.03413
$[(C_7O_3)C_1im]_{(1-x)}[C_{10}C_1im]_x[NTf_2]$	+ 1.86422	+ 0.43468	- 0.13858
$[(C_7O_3)imC_1imC_1]_{(1-x)}[C_{10}C_1im]_x[NTf_2]_{(2-x)}$	+ 5.09528	+ 1.13648	+ 0.09566

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