Electronic Supplementary Information

Physical properties and nanostructuring of long-chained homobaric imidazolium ionic liquids

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Materials and methods

All chemicals were bought from VWR or Sigma Aldrich (unless stated otherwise) and were purified using standard purification techniques.[1] The solvents used for the syntheses were of 99 % purity and used without further purification. All the glassware were washed with absolute ethanol, followed by washes with decon-90 and de-ionised water.

Synthesis of alkylimidazoles

The procedure for the synthesis of *N*-alkylimidazoles was adapted from Lee *et. al*.[2] 1 equivalent of 1H-imidazole is mixed with 1.2 equivalents of NaOH in water (30% w/w) at room temperature. After 1H-imidazole is dissolved, 1 equivalent of alkyl bromide dissolved in tetrahydrofuran is added and the solution is brought to reflux. The progress of the reaction is monitored by ^{1}H NMR, until full conversion of 1H-imidazole is observed or until the reaction stops progressing. After completion of the reaction, tetrahydrofuran is removed *in vacuo* and the product is extracted with dichloromethane/water in order to remove the formed sodium bromide and unreacted 1H-imidazole. The dichloromethane is removed *in vacuo*, the product is stirred overnight over KOH pellets and then purified with vacuum distillation. The final *N*-alkylimidazole is received as a colourless viscous liquid.

1-isobutylimidazole [$C_{3,1}$im]. 1-bromo-2-methylpropane (50 mL, 459.8 mmol, 1.1 eq.) was added dropwise to a stirring solution of freshly distilled imidazole (28.4 g, 418 mmol, 1 eq.) in tetrahydrofuran (20 mL) and then aqueous NaOH (20 g, 501.6 mmol, 1.2 eq.) solution was added. The mixture was refluxed for 5 days, tetrahydrofuran was removed under reduced pressure and the residue was extracted with dichlorometane and water (3x25 mL each). The organic layer was dried over magnesium sulphate. Drying *in vacuo* resulted in a pale yellow solid. Recrystallising twice from toluene resulted in fine white powder (19.2 g, 246.6 mmol, 59% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.59 (s, 1H, imC(2)**H**), 7.12 (s, 1H, imC(4)**H**), 6.88 (s, 1H, imC(5)**H**), 3.75 (d, 2H, isobutyl-C(1)$\mathbf{H_2}$), 2.02-1.89 (m, 1H, isobutyl-C(2)**H**), 0.81 and 0.80 (singlets, 6H, isobutyl-C(3)$\mathbf{H_3}$ and C(3)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 137.64 (imC(2)), 128.24 (imC(4)), 119.63 (imC(5)), 53.23 (isobutyl-C(1)), 29.48 (isobutyl-C(2)), 19.52 (isobutyl-C(3,3)).

1-pentylimidazole [C_5im]. 1-bromopentane (30 mL, 234 mmol, 1.2 eq.) was added dropwise to a stirring solution of freshly distilled 1H-imidazole (13.3 g, 195 mmol, 1 eq.) in tetrahydrofuran (30 mL) and then aqueous NaOH (9.4 g, 234 mmol, 1.2 eq.) solution was added. The mixture was refluxed for 3 days, tetrahydrofuran was removed under reduced pressure and the residue was extracted with dichloromethane and water (3x25 mL each). The organic layer was dried over magnesium sulphate. Drying *in vacuo* resulted in an oily yellow liquid. Distilling under reduced pressure yielded a colourless
oily liquid (17.3 g, 125 mmol, 64% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 7.60 (s, 1H, imC(2)**H**), 7.15 (s, 1H, imC(4)**H**), 6.87 (s, 1H, imC(5)**H**), 3.93 (t, J = 7.1 Hz, 2H, pentyl-C(1)$\mathbf{H_2}$), 1.68 (p, J = 7.26 Hz, 2H, pentyl-C(2)$\mathbf{H_2}$), 1.21-1.11 (m, 2H, pentyl-C(4)$\mathbf{H_2}$), 0.84 (t, J = 7.24 Hz, 3H, pentyl-C(5)$\mathbf{H_3}$).

^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 137.19 (imC(2)), 128.31 (imC(4)), 119.20 (imC(5)), 45.88 (pentyl-C(1)), 30.28 (pentyl-C(2)), 28.12 (pentyl-C(3)), 21.61 (pentyl-C(4)), 13.85 (pentyl-C(5))
m/z (ES^+): 139.1 (100 %, M^+).

1-isopentylimidazole [$C_{4,1}$im]. 1-Bromo-3-methylbutane (30 mL, 234 mmol, 1.2 eq.) was added dropwise to a stirring solution of freshly distilled 1H-imidazole (13.3 g, 195 mmol, 1 eq.) in tetrahydrofuran (30 mL) and then aqueous NaOH (9.4 g, 234 mmol, 1.2 eq.) solution was added. The mixture was refluxed for 3 days, tetrahydrofuran was removed under reduced pressure and the residue was extracted with dichloromethane and water (3x25 mL each). The organic layer was dried over magnesium sulphate. Drying *in vacuo* resulted in an oily yellow liquid. Distilling under reduced pressure yielded a colourless oily liquid (16.4 g, 119 mmol, 61% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.62 (s, 1H, imC(2)**H**), 7.15 (t, J = 1.27 Hz, 1H, imC(4)**H**), 6.87 (t, J = 1.09 Hz, 1H, imC(5)**H**), 3.95 (t, J = 7.4 Hz, 2H, isopentyl-C(1)$\mathbf{H_2}$), 1.62-1.54 (m, 2H, isopentyl-C(2)$\mathbf{H_2}$), 1.44 (dh, J = 13.3, 6.6 Hz, 1H, isopentyl-C(3)**H**), 0.88 (d, 6H, isopentyl-C(4,4')$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 137.12 (imC(2)), 128.28 (imC(4)), 119.13 (imC(5)), 44.23 (isopentyl-C(1)), 39.48 (isopentyl-C(2)), 24.95 (isopentyl-C(3)), 22.11 (2C, isopentyl- C(4,4')).

1-cyclopentylimidazole [CycloC_5im]. Bromocyclopentane (30 mL, 279.8 mmol, 1.2 eq.) was added dropwise to a stirring solution of freshly distilled 1H-imidazole (15.8 g, 233 mmol, 1 eq.) in tetrahydrofuran (50 mL) and then aqueous NaOH (9.4 g, 234 mmol, 1.2 eq.) solution was added. The mixture was refluxed for 3 days, tetrahydrofuran was removed under reduced pressure and the residue was extracted with dichloromethane and water (3x25 mL each). The organic layer was dried over magnesium sulphate. Drying *in vacuo* resulted in an oily yellow liquid. Distilling under reduced pressure yielded a colourless oily liquid (17.7 g, 130 mmol, 56% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.67 (s, 1H, imC(2)**H**), 7.19 (s, 1H, imC(4)**H**), 6.88 (s, 1H, imC(5)**H**), 4.56-4.46 (m, 1H, cyclopentyl-C(1)**H**), 2.13-2.02 (m, 2H, cyclopentyl-C(2)$\mathbf{H_2}$), 1.80-1.556 (m, 6H, cyclopentyl-C(2-5)$\mathbf{H_2}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 136.11 (imC(2)), 128.43 (imC(4)), 117.71 (imC(5)), 57.42 (cyclopentyl-C(1)), 33.73 (2C, cyclopentyl-C(2,5)), 23.32 (2C, cyclopentyl-C(3,4)).
m/z (ES^+): 138.1 (100 %, M^+).

Synthesis of alkylimidazolium halides

The synthesis of the alkylimidazolium halides is described in detail in previous publications of our group.[3, 4]

The bromoalkanes were washed with concentrated sulphuric acid until the acid layer appeared colourless. Then they were washed with a saturated solution of sodium bicarbonate (until pH testing was slightly basic), followed by washes with de-ionised water. The organic phase was dried over anhydrous magnesium sulphate and distilled *in vacuo*.

1-alkylimidazoles were left overnight stirring over potassium hydroxide pellets and then distilled *in vacuo*.

1,2-Dimethylimidazole was recrystallized from toluene and then dried *in vacuo*.

[$C_{11}C_1$im]Br. 1-bromoundecane (16.5 mL, 79.6 mmol, 1.2 eq.) was added to a stirring solution of 1-methylimidazole (6.4 mL, 66.3 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield a white powder (15 g, 47.7 mmol, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.37 (s, 1H, imC(2)**H**), 7.50 (t, J = 1.77 Hz, 1H, imC(4)**H**), 7.35 (t, J = 1.77 Hz, 1H, imC(5)**H**), 4.29 (t, J = 7.52 Hz, 2H, undecyl C(1)$\mathbf{H_2}$), 4.11 (s, 3H, methyl C(1)$\mathbf{H_3}$), 1.89 (m, 2H, undecyl-C(2)$\mathbf{H_2}$), 1.35-1.17 (m, 16H, undecyl-C(3-10)$\mathbf{H_2}$), 0.84 (t, J = 13.66 Hz, 3H, undecyl-C(11)$\mathbf{H_3}$)
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 137.67 (imC(2)), 123.63 (imC(4)), 121.91 (imC(5)), 50.36 (methyl-C), 36.94 (undecyl-C(1)), 31.96, 30.39, 29.62, 29.58, 29.45, 29.37, 29.08, 26.36, 22.75 (9C, undecyl C(2-10)), 14.22 (undecyl-C(11)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[$C_{10}C_2$im]Br. 1-bromodecane (16.5 mL, 79.6 mmol, 1.2 eq.) was added to a stirring solution of 1-ethylimidazole (6.4 mL, 66.3 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield a viscous colourless liquid (15 g, 47.7 mmol, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.38 (s, 1H, imC(2)**H**), 7.62 (s, 1H, imC(4)**H**), 7.43 (s, 1H, imC(5)**H**), 4.39 (q, J = 7.6 Hz, 2H, ethyl-C(1)$\mathbf{H_2}$), 4.27 (t, J = 7.2 Hz, 2H, decyl-C(1)$\mathbf{H_2}$), 1.85 (m, 2H, decyl-C(2)$\mathbf{H_2}$), 1.54 (t, J = 7.6 Hz, 3H, ethyl-C(2)$\mathbf{H_3}$), 1.33-1.06 (m, 14H, decyl-C(3-9)H2), 0.79, (t, J = 6.4 Hz, 3H, decyl-C(10)H3).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 136.59 (imC(2)), 122.1 (imC(4)), 122.07 (imC(5)), 50.04 (ethyl-C(1)), 45.21 (decyl-C(1)), 31.78 (decyl-C(2)), 30.32 (decyl-C(3)), 29.4 (decyl-C(4)), 29.33 (decyl-C(5)), 29.19 (decyl-C(6)), 28.96 (decyl-C(7)), 26.22 (decyl-C(8)), 22.6 (decyl-C(9)), 15.71 (ethyl-C(2)), 14.07 (decyl-C(10)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[$C_{10}C_1C_1$im]Br. 1-bromodecane (20.8 mL, 99.8 mmol, 1.2 eq.) was added to a stirring solution of 1,2-dimethylimidazole (8 g, 83.2 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield a white solid (19 g, 59.9 mmol, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 7.75 (d, 1H, imC(4)**H**), 7.45 (d, 1H, imC(5)**H**), 4.17 (t, J = 7.2 Hz, 2H, decyl-C(1)$\mathbf{H_2}$), 4.01 (s, 3H, methyl-CH3), 2.80 (s, 3H, imC(2)-C$\mathbf{H_3}$), 1.79 (m, 2H, decyl-C(2)$\mathbf{H_2}$), 1.38-1.14 (m, 14H, decyl-C(3-9)H2), 0.85, (t, J = 7.0 Hz, 3H, decyl-C(10)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 143.84 (imC(2)), 126.59 (imC(4)), 119.57 (imC(5)), 49.61 (methyl-C(1)), 36.37 (decyl-C(1)), 31.91, 29.97, 29.53, 29.45, 29.31, 29.13, 26.48, 22.79 (decyl-C(2-9)), 14.19 (imC(2)-C), 11.18 (decyl-C(10)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[C_9C_3im]Br. 1-bromononane (17.8 mL, 93.2 mmol, 1.2 eq.) was added to a stirring solution of 1-propylimidazole (8.6 mL, 77.6 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield a viscous colourless liquid (17.7 g, 59 mmol, 76% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.31 (s, 1H, imC(2)**H**), 7.56 (t, J = 2 Hz, 1H, imC(4)**H**), 7.46 (t, J = 2 Hz, 1H, imC(5)**H**), 4.27 (t, J = 7.2 Hz, 4H, propyl-C(1)$\mathbf{H_2}$ & nonyl-C(1)$\mathbf{H_2}$), 1.98-1.75 (m, 4H, propyl-C(2)$\mathbf{H_2}$ & nonyl-C(2)$\mathbf{H_2}$), 1.34-1.05 (m, 12H, nonyl-C(3-8)$\mathbf{H_2}$), 0.9 (t, J = 7.2 Hz, 3H, propyl-C(3)$\mathbf{H_3}$), 0.77 (t, J = 6.8 Hz, 3H, nonyl-C(9)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, CDCl3) δH (ppm): 136.79 (imC(2)), 122.41 (imC(4)), 122.11 (imC(5)), 51.35 (propyl-C(1)), 50.01 (nonyl-C(1)), 31.68, 30.28, 29.24, 29.05, 28.91, 26.16, 23.66, 22.53 (8C, propyl-C(2) & nonyl-C(2-8)), 14.01 (propyl-C(3)), 10.65 (nonyl-C(9)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[$C_9C_{2,1}$im]Br. 1-bromononane (17.8 mL, 93.2 mmol, 1.2 eq.) was added to a stirring solution of 1-isopropylimidazole (8.6 mL, 77.6 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield a viscous colourless liquid (19.9 g, 62.8 mmol, 81% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.53 (s, 1H, imC(2)**H**), 7.56 (t, J = 1.86 Hz, 1H, imC(4)**H**), 7.43 (t, J = 1.83 Hz, 1H, imC(5)**H**), 4.87 (hept, J = 6.72 Hz, 1H, isopropyl-C(1)**H**), 4.32 (t, J = 7.4 Hz, 2H, nonyl-C(1)$\mathbf{H_2}$), 1.88 (m, 2H, nonyl-C(2)H2), 1.58 (d, 6H, isopropyl-C(2)$\mathbf{H_3}$ & C(2')$\mathbf{H_3}$) 1.36-1.13 (m, 12H, nonyl-C(3-8)$\mathbf{H_2}$), 0.81 (t, J = 7.0 Hz, 3H, nonyl-C(9)$\mathbf{H_3}$).
13C NMR (101 MHz, $CDCl_3$) δH (ppm): 136.18 (imC(2)), 122.09 (imC(4)), 120.56 (imC(5)), 53.32 (isopropyl-C(1)), 50.11 (nonyl-C(1)), 31.79, 30.39, 29.35, 29.17, 29.04, 26.31, 23.26, 22.64 (9C, isopropyl-C(2,2') & nonyl-C(2-8)), 14.11 (nonyl-C(9)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[C_8C_4im]Br. 1-bromooctane (20 mL, 115.8 mmol, 1.2 eq.) was added to a stirring solution of 1-butylimidazole (12.6 mL, 96.6 mmol, 1 eq.) in ethyl acetate (50 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield white crystals (m.p. 15 ^{o}C, 17.8 g, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 9.33 (s, 1H, imC(2)**H**), 7.84 (overlapping singlets, 2H, imC(4,5)**H**), 4.2-4.15 (overlapping triplets, 4H, butyl-C(1)$\mathbf{H_2}$ & octyl-C(1)$\mathbf{H_2}$), 1.82-1.74 (m, 4H, butyl-C(2)$\mathbf{H_2}$ & octyl-C(2)$\mathbf{H_2}$), 1.3-1.14 (m, 10H, butyl-C(3)$\mathbf{H_2}$ & octyl-C(3-7)$\mathbf{H_2}$), 0.89 (t, J = 7.6 Hz, 3H, butyl-C(4)$\mathbf{H_2}$), 0.84 (t, J = 6.8 Hz, 3H, octyl-C(8)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 135.98 (imC(2)), 122.46 (imC(4,5)), 48.81 (butyl-C(1)), 48.54 (octyl-C(1)), 31.29, 31.13, 29.27, 28.49, 28.28, 25.47, 22.06, 18.77 (8C, butyl-C(2,3) & octyl-C(2-7)), 13.95 (butyl-C(4)), 13.28 (octyl-C(8)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[$C_8C_{3,1}$im]Br. 1-bromooctane (20 mL, 115.8 mmol, 1.2 eq.) was added to a stirring solution of 1-isobutylimidazole (12.6 mL, 96.6 mmol, 1 eq.) in ethyl acetate (50 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line and left in the fridge for 48 h to yield white crystals (21.7 g, 68.6 mmol, 71% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.41 (s, 1H, imC(2)**H**), 7.52 (overlapping singlets, 2H, imC(4)**H** & imC(5)**H**), 4.30 (t, J = 7.38 Hz, 2H, octyl-C(1)**H_2**), 4.13 (d, 2H, isobutyl-C(1)**H_2**), 2.24-2.12 (m, 1H, isobutyl-C(2)**H**), 1.89-1.81 (m, 2H, octyl-C(2)**H_2**), 1.29-1.11 (m, 10H, octyl-C(3-7)**H_2**), 0.91 (d, 6H, isobutyl-C(3)**H_3** and C(3)**H_3**), 0.78(t, J = 7 Hz, 3H, octyl-C(8)**H_3**).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 137.15(imC(2)), 122.74 (imC(4)), 122.08 (imC(5)), 56.70 (isobutyl-C(1)), 50.02 (octyl-C(1)), 31.60, 30.33, 29.55, 28.99, 28.89, 26.16, 22.53 (7C, isobutyl-C(2) & octyl-C(2-7)), 19.44 (isobutyl-C(3,3)), 14.02 (octyl-C(8)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[C_7C_5im]Br. 1-bromoheptane (10 mL, 71.5 mmol, 1.2 eq.) was added to a stirring solution of 1-pentylimidazole (10 mL, 59.6 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a transparent liquid (15.3 g, 48.5 mmol, 73% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.44 (s, 1H, imC(2)**H**), 7.44 (s, 1H, imC(4)**H**), 7.42 (s, 1H, imC(5)**H**), 4.39-4.25 (overlapping triplets, 4H, pentyl-C(1)**H_2** & heptyl-C(1)**H_2**), 1.97-1.79 (m, 4H, pentyl-C(2)**H_2** & heptyl-C(2)**H_2**), 1.4-1.11 (m, 12H, pentyl-C(3,4)**H_2** & heptyl-C(3-6)**H_2**), 0.91-0.77 (overlapping triplets, 6H, pentyl-C(5)**H_3** & heptyl-C(7)**H_3**).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 137.17 (imC(2)), 122.1 (imC(4)), 122.05 (imC(5)), 50.22 (pentyl-C(1)), 50.19 (heptyl-C(1)), 31.59, 30.38, 30.06, 28.7, 28.33, 26.25, 22.56, 22.14 (8C, pentyl-C(2-4) & heptyl-C(2-6)), 14.09 (pentyl-C(5)), 13.91 (heptyl-C(7)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[$C_7C_4C_1$im]Br. 1-bromoheptane (10 mL, 71.5 mmol, 1.2 eq.) was added to a stirring solution of 1-butyl-2-methylimidazole (8.2 g, 59.6 mmol, 1 eq.) in ethyl acetate (30 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a transparent liquid (14.6 g, 45.9 mmol, 77% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.71 (s, 2H, imC(4)**H** & imC(5)**H**), 4.13-4.07 (overlapping triplets, 4H, butyl-C(1)**H_2** & heptyl-C(1)**H_2**), 2.62 (s, 3H, im(C2')-C**H_3**), 1.76-1.64 (m, 4H, butyl-C(2)H2 & heptyl-C(2)H2), 1.33-1.17 (m, 10H, butyl-C(3)H2 & heptyl-C(3-6)**H_2**), 0.94-0.82 (overlapping triplets, 6H, butyl-C(4)**H_3** & heptyl-C(7)**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 143.64 (imC(2)), 121.28 (2C, imC(4) & imC(5)), 47.49, 47.28 (2C, butyl-C(1) & heptyl-C(1)), 31.08, 29.05, 28.13, 25.56, 21.97, 18.93, 13.93, 13.43, 9.18 (10C, butyl-C(2-4) & heptyl-C(2-7) & imC(2)-C').
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[$C_7C_{4,1}$im]Br. 1-bromoheptane (10 mL, 71.5 mmol, 1.2 eq.) was added to a stirring solution of 1- isopentylimidazole (8.2 g, 59.6 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a transparent liquid (13.8 g, 43.5 mmol, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.46 (s, 1H, imC(2)**H**), 7.5-7.47 (overlapping triplets, 2H, imC(4)**H** & imC(5)**H**), 4.36-4.27 (overlapping triplets, 4H, isopentyl-C(1)$\mathbf{H_2}$ & heptyl-C(1)$\mathbf{H_2}$), 1.92-1.73 (m, 4H, isopentyl-C(2)$\mathbf{H_2}$ & heptyl-C(2)$\mathbf{H_2}$), 1.59 (dh, J = 13.4, 6.7 Hz, 1H, isopentyl-C(3)**H**), 1.33-1.13 (m, 8H, heptyl-C(3-6)$\mathbf{H_2}$), 0.92 (d, 6H, isopentyl-C(4,4')$\mathbf{H_3}$), 0.8 (t, J = 6.8 Hz, 3H, heptyl-C(7)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 137.03 (imC(2)), 128.19 (imC(4)), 119.15 (imC(5)), 50.08, 48.49 (isopentyl-C(1) & heptyl-C(1))), 38.93, 31.52, 30.36, 28.64, 26.18, 25.56, 22.48 (7C, isopentyl-C(2,3) & heptyl-C(2-6)), 22.28 (2C, isopentyl-C(4,4')), 14.02 (heptyl-C(7)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[C_7CycloC_5im]Br. 1-bromoheptane (10 mL, 71.5 mmol, 1.2 eq.) was added to a stirring solution of 1-cyclopentylimidazole (8.1 g, 59.6 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a transparent liquid (12.9 g, 41.1 mmol, 69% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 9.43 (s, 1H, imC(2)**H**), 7.91 (t, J = 1.83, 1H, imC(4)**H**), 7.87 (t, J = 1.80 Hz, 1H, imC(5)**H**), 4.77 (p, J = 7 Hz, 1H, cyclopentyl-C(1)**H**), 4.16 (t, J = 7.32 Hz, 2H, heptyl-C(1)$\mathbf{H_2}$), 2.24-2.13 (m, 2H, heptyl-C(2)$\mathbf{H_2}$), 1.92-1.59 (m, 8H, cyclopentyl-C(2-5)$\mathbf{H_2}$), 1.33-1.55 (m, 8H, heptyl-C(3-6)$\mathbf{H_2}$), 0.84 (t, J = 6.8 Hz, 3H, heptyl- C(7)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.18 (imC(2)), 122.58 (imC(4)), 121.30 (imC(5)), 60.55, 48.81 (2C, cyclopentyl-C(1) & heptyl-C(1)), 32.54, 31.00, 29.30, 27.99, 25.46, 23.06, 21.95 (9C, cyclopentyl-C(2-5) & heptyl-C(2-6)), 13.89 (heptyl-C(7)).
m/z (ES^+): 235.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

[C_6C_6im]Br. 1-bromohexane (10 mL, 71.5 mmol, 1.2 eq.) was added to a stirring solution of 1-hexylimidazole (10 mL, 59.6 mmol, 1 eq.) in ethyl acetate (20 mL) according to the general procedure. The salt was dried overnight on the Schlenk Line to yield a transparent liquid (15.3 g, 48.5 mmol, 73% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δH (ppm): 10.52 (s, 1H, imC(2)**H**), 7.39 (d, J = 1.6 Hz, 2H, imC(4,5)**H**), 4.34 (t, J = 7.6 Hz, 4H, hexyl-C(1)$\mathbf{H_2}$), 1.91 (q, 4H, hexyl-C(2)$\mathbf{H_2}$), 1.3 (m, 12H, hexyl-C(3-5)$\mathbf{H_2}$), 0.85 (t, J = 6.8 Hz, 6H, hexyl-C(6)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, $CDCl_3$) δH (ppm): 137.39 (imC(2)), 121.99 (imC(4,5)), 50.30 (hexyl-C(1)), 31.17 (hexyl-C(2)), 32.05 (hexyl-C(3)), 25.98 (hexyl-C(4)), 22.47 (hexyl-C(5)), 14.01 (hexyl-(C(6)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 80.9 (100 %, M^-).

Synthesis of dialkylimidazolium bis(trifluoromethylsulfonyl)imides ([NTf_2])
1 equivalent of dialkylimidazolium halide is dissolved in dichloromethane and to that an aqueous solution of 1.2 equivalents of Li[NTf_2] is added. The reaction mixture is left in vigorous stirring at room temperature overnight. Then the aqueous layer is removed with a canula and the dichloromethane layer is washed with water until the silver nitrate halide test of the water phase is negative. The dichloromethane is then

dried over magnesium sulfate and dried *in vacuo*. The final ionic liquid is received as a colourless viscous liquid.

[$C_{11}C_1$im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.4 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_{11}C_1$im][Br] (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (3 g, 5.6 mmol, 89% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.6 (s, 1H, imC(2)**H**), 7.35 (t, J = 1.79 Hz, 1H, imC(4)**H**)), 7.32 (t, J = 1.83 Hz, 1H, imC(5)**H**), 4.17 (t, J = 7.47 Hz, 2H, undecyl-C(1)$\mathbf{H_2}$), 3.96 (s, 3H, methyl-C(1)$\mathbf{H_3}$), 1.87 (m, 2H, undecyl-C(2)$\mathbf{H_2}$), 1.40-1.20 (m, 16H, undecyl-C(3-10)$\mathbf{H_2}$), 0.89 (t, J = 6.80 Hz, 3H, undecyl-C(11)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 136.10 (imC(2)), 123.86 (imC(4)), 122.86 (imC(5)), 119.9 (q, J_{CF} = 321.19 Hz, 2C, NTf_2), 50.32 (methyl-C), 36.41 (undecyl-C(1)), 31.98, 30.18, 29.62, 29.55, 29.38, 28.96, 26.21 (9C, undecyl-C(2-10)), 14.19 (undecyl-C(11)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[$C_{10}C_2$im][NTf_2]. Lithiums bis(trifluoromethylsulfonyl)imide (2.1 g, 7.2 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_{10}C_2$im][Br] (2 g, 6 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.5 g, 5 mmol, 79% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 8.75 (s, 1H, imC(2)**H**), 7.38 (t, J = 1.8 Hz, 1H, imC(4)**H**), 7.32 (t. J = 1.8 Hz, 1H, imC(5)**H**), 4.24 (q, J = 7.6 Hz, 2H, ethyl-C(1)$\mathbf{H_2}$), 4.15 (t, J = 7.6 Hz, 2H, decyl-C(1)$\mathbf{H_2}$), 1.84 (m, 2H, decyl-C(2)H2), 1.53 (t, J = 7.6 Hz, 3H, ethyl-C(2)$\mathbf{H_3}$), 1.38-1.14 (m, 14H, decyl-C(3-9)$\mathbf{H_2}$), 0.85, (t, J = 6.8 Hz, 3H, decyl-C(10)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.08 (imC(2)), 122.50 (imC(4)), 122.23(imC(5)), 119.93(q, J_{CF} = 322 Hz, 2C, NTf_2), 50.30 (ethyl-C(1)), 45.37 (decyl-C(1)), 31.91, 30.18, 29.48, 29.36, 29.29, 28.93, 26.20, 22.72, (8C, decyl-C(2-9)), 15.26 (ethyl-C(2)), 14.14 (decyl-C(10)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[$C_{10}C_1C_1$im][NTf_2]. Lithiums bis(trifluoromethylsulfonyl)imide (2.1 g, 7.2 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_{10}C_1C_1$im][Br] (2 g, 6 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.5 g, 4.9 mmol, 82% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.18 (d, 1H, imC(4)**H**), 7.15 (d, 1H, imC(5)**H**), 4.00 (t, J = 7.2 Hz, 2H, decyl-C(1)$\mathbf{H_2}$), 3.76 (s, 3H, methyl-C$\mathbf{H_3}$), 2.56 (s, 3H, imC(2)-C$\mathbf{H_3}$), 1.75 (m, 2H, decyl-C(2)$\mathbf{H_2}$), 1.37-1.16 (m, 14H, decyl-C(3-9)H2), 0.85, (t, J = 7.0 Hz, 3H, decyl-C(10)$\mathbf{H_3}$).

^{13}C NMR (101 MHz, DMSO d6) δH (ppm): 142.89 (imC(2)), 122.59 (imC(4)), 120.84(im C(5)), 119.85(q, J_{CF} = 321.65 Hz, 2C, NTf_2), 48.88 (methyl-C(1)), 35.30 (decyl-C(1)), 31.88, 29.60, 29.48, 29.36, 29.27, 28.99, 26.31, 22.70, (8C, decyl-C(2-9)), 14.13 (imC(2)-C), 9.54 (decyl-C(10)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[C_9C_3im][NTf_2]. Lithiums bis(trifluoromethylsulfonyl)imide (2.2 g, 7.2 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_9C_3im]Br (2 g, 6 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.8 g, 5 mmol, 84% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 8.77 (s, 1H, imC(2)**H**), 7.36 (t, J = 2 Hz, 1H, imC(4)**H**), 7.34 (t, J = 1.6 Hz, 1H, imC(5)**H**), 4.24-4.08 (overlapping triplets, 4H, propyl-C(1)$\mathbf{H_2}$ & nonyl-C(1)$\mathbf{H_2}$), 1.99-1.77 (m, 4H, propyl-C(2)$\mathbf{H_2}$ & nonyl-C(2)$\mathbf{H_2}$), 1.40-1.14 (m, 12H, nonyl-C(3-8)$\mathbf{H_2}$), 0.94 (t, J = 7.2 Hz, 3H, propyl-C(3)$\mathbf{H_3}$), 0.85 (t, J = 6.8 Hz, 3H, nonyl-C(9)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.43 (imC(2)), 122.57 (imC(4)), 122.49 (imC(5)), 119.93 (q, J_{CF} = 322 Hz, 2C, NTf_2), 51.64 (propyl-C(1)), 50.28 (nonyl-C(1)), 31.83, 30.21, 29.31, 29.16, 28.92, 26.15, 23.58, 22.68 (8C, propyl-C(2) & nonyl-C(2-8)), 14.12 (propyl-C(3)), 10.46 (nonyl-C(9)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[$C_9C_{2,1}$im][NTf_2]. Lithiums bis(trifluoromethylsulfonyl)imide (2.2 g, 7.2 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_9C_{2,1}$im]Br (2 g, 6 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.9 g, 5 mmol, 92% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 9.23 (s, 1H, imC(2)**H**), 7.89 (t, J = 1.83 Hz, 1H, imC(4)**H**), 7.80 (t, J = 1.83 Hz, 1H, imC(5)**H**), 4.62 (hept, J = 6.66 Hz, 1H, isopropyl-C(1)**H**), 4.13 (t, 2H, nonyl-C(1)$\mathbf{H_2}$), 1.86-1.74 (m, 2H, nonyl-C(2)$\mathbf{H_2}$), 1.48 (d, 2H, isopropyl-C(2)$\mathbf{H_3}$ & C(2')$\mathbf{H_3}$), 1.35-1.17 (m, 12H, nonyl-C(3-8)$\mathbf{H_2}$), 0.85 (t, J = 7.0 Hz, 3H, nonyl-C(9)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 134.69 (imC(2)), 122.50 (imC(4)), 120.59 (imC(5)), 119.49 (q, J_{CF} = 322.1 Hz, 2C, NTf_2), 52.23 (isopropyl-C(1)), 48.91 (nonyl-C(1)), 31.21, 29.26, 28.72, 28.55, 28.31, 25.51, 22.24, 22.06 (9C, isopropyl-C(2,2') & nonyl-C(2-8)), 13.85 (nonyl-C(9)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[C_8C_4im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_8C_4im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the

ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.5 g, 5 mmol, 80% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 8.76 (s, 1H, imC(2)**H**), 7.35 (t, J = 2 Hz, 1H, imC(4)**H**), 7.34 (t, J = 1.6 Hz, 1H, imC(5)**H**), 4.2-4.1 (overlapping triplets, 4H, butyl-C(1)$\mathbf{H_2}$ & octyl-C(1)$\mathbf{H_2}$), 1.93-1.73 (m, 4H, butyl-C(2)$\mathbf{H_2}$ & octyl-C(2)$\mathbf{H_2}$), 1.43-1.15 (m, 12H, butyl-C(3)$\mathbf{H_2}$ & octyl-C(3-7)$\mathbf{H_2}$), 0.94 (t, J = 7.6 Hz, 3H, butyl-C(4)$\mathbf{H_3}$), 0.85 (t, J = 6.8 Hz, 3H, octyl-C(8)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.39 (imC(2)), 122.57 (imC(4)), 122.49 (imC(5)), 119.94 (q, J_{CF} = 322 Hz, 2C, NTf_2), 50.27 (butyl-C(1)), 50.00 (octyl-C(1)), 32.09, 31.68, 30.20, 29.01, 28.86, 26.14, 22.62, 19.40 (8C, butyl-C(2,3) & octyl-C(2-7)), 14.07 (butyl-C(4)), 13.28 (octyl-C(8)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[$C_8C_{3,1}$im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [C8C3,1im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (3 g, 5.8 mmol, 93% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 8.77 (s, 1H, imC(2)**H**), 7.35 (t, J = 1.83 Hz, 1H, imC(4)**H**), 7.33 (t, J = 1.83 Hz, 1H, imC(5)**H**), 4.17 (t, J = 7.43 Hz, 2H, octyl-C(1)$\mathbf{H_2}$), 3.99 (d, 2H, isobutyl-C(1)$\mathbf{H_2}$), 2.17-2.06 (m, 1H, isobutyl-C(2)**H**), 1.87-1.79 (m, 2H, octyl-C(2)$\mathbf{H_2}$), 1.32-1.17 (m, 10H, octyl-C(3-7)$\mathbf{H_2}$), 0.93 (d, 6H, isobutyl-C(3)$\mathbf{H_3}$ & C(3)$\mathbf{H_3}$), 0.85 (t, J = 7 Hz, 3H, octyl-C(8)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.69 (imC(2)), 122.97 (imC(4)), 122.46 (imC(5)), 119.94 (q, J_{CF} = 321.6 Hz, 2C, NTf_2), 57.03 (isobutyl-C(1)), 50.29 (octyl-C(1)), 31.68, 30.22, 29.53, 29.02, 28.86, 26.11, 22.62 (7C, isobutyl-C(2) & octyl-C(2-7)), 19.23 (isobutyl-C(3,3)), 14.08 (octyl-C(8)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[C_5C_5im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_7C_5im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.9 g, 5.6 mmol, 89% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 8.76 (s, 1H, imC(2)**H**), 7.35 (m, 2H, imC(4)**H** & imC(5)**H**), 4.18-4.13 (overlapping triplets, 4H, pentyl-C(1)$\mathbf{H_2}$ & heptyl-C(1)$\mathbf{H_2}$), 1.88-1.80 (m, 4H, pentyl-C(2)$\mathbf{H_2}$ & heptyl-C(2)$\mathbf{H_2}$), 1.39-1.18 (m, 12H, pentyl-C(3,4)$\mathbf{H_2}$ & heptyl-C(3-6)$\mathbf{H_2}$), 0.90-0.81 (overlapping triplets, 6H, pentyl-C(5)$\mathbf{H_3}$ & heptyl-C(7)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.36 (imC(2)), 122.53 (imC(4)), 122.50 (imC(5)), 119.91 (q, J_{CF} = 321.24 Hz, 2C, NTf_2), 50.24 (pentyl-C(1) & heptyl-C(1)), 31.51, 30.19, 29.88, 28.56, 28.17, 26.08, 22.50, 22.00 (8C, pentyl-C(2-4) & heptyl-C(2-6)), 14.01 (pentyl-C(5)), 13.74 (heptyl-C(7)).

m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[$C_7C_4C_1$im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_7C_4C_1$im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.8 g, 5.5 mmol, 88% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 7.68 (s, 2H, imC(4)**H** & imC(5)**H**), 4.12-4.06 (overlapping triplets, 4H, butyl-C(1)$\mathbf{H_2}$ & heptyl-C(1)$\mathbf{H_2}$), 2.61 (s, 3H, im(C2')-C$\mathbf{H_3}$), 1.76-1.64 (m, 4H, butyl-C(2)$\mathbf{H_2}$ & heptyl-C(2)$\mathbf{H_2}$), 1.33-1.2 (m, 10H, butyl-C(3)$\mathbf{H_2}$ & heptyl-C(3-6)$\mathbf{H_2}$), 0.93-0.82 (overlapping triplets, 6H, butyl-C(4)$\mathbf{H_3}$ & heptyl-C(7)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 143.62 (imC(2)), 121.25 (2C, imC(4) & imC(5)), 121.09 (q, J_{CF} = 321.24 Hz, 2C, NTf_2), 47.50, 47.29 (2C, butyl-C(1) & heptyl-C(1)), 31.08, 29.04, 28.13, 25.56, 21.97, 18.93, 13.88, 13.36, 9.09 (10C, butyl-C(2-4) & heptyl-C(2-7) & imC(2)-C').
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[$C_7C_{4,1}$im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [$C_7C_{4,1}$im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.7 g, 5.3 mmol, 84% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 9.21 (s, 1H, imC(2)**H**), 7.81-7.77 (overlapping triplets, 2H, imC(4)**H** & imC(5)**H**), 4.20-4.12 (overlapping triplets, 4H, isopentyl-C(1)$\mathbf{H_2}$ & heptyl-C(1)$\mathbf{H_2}$), 1.84-1.65 (m, 4H, isopentyl-C(2)$\mathbf{H_2}$ & heptyl-C(2)$\mathbf{H_2}$), 1.49 (dh, J = 13.3, 6.7 Hz, 1H, isopentyl-C(3)**H**), 1.33-1.15 (m, 8H, heptyl-C(3-6)$\mathbf{H_2}$), 0.91 (d, 6H, isopentyl-C(4,4')**H3**), 0.85 (t, J = 6.8 Hz, 3H, heptyl-C(7)$\mathbf{H_3}$).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.92 (imC(2)), 122.45 (2C, imC(4) & imC(5)), 119.49 (q, J_{CF} = 321.65 Hz, 2C, NTf_2), 48.88, 47.29 (isopentyl-C(1) & heptyl-C(1))), 38.02, 31.02, 29.25, 27.97, 25.42, 24.82, 22.48, 21.95 (9C, isopentyl-C(2,3) & heptyl-C(2-6) & isopentyl-C(4,4')), 13.85 (heptyl-C(7)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[C_7CycloC_5im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_7CycloC_5im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After the purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.92 g, 5.67 mmol, 90% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 9.23 (s, 1H, imC(2)**H**), 7.85 (t, J = 1.84, 1H, imC(4)**H**), 7.81 (t, J = 1.82 Hz, 1H, imC(5)**H**), 4.73 (p, J = 7 Hz, 1H, cyclopentyl-C(1)**H**), 4.13 (t, J = 7.31 Hz, 2H, heptyl-C(1)$\mathbf{H_2}$), 2.25-2.13 (m, 2H, heptyl-C(2)$\mathbf{H_2}$), 1.91-1.61 (m,

8H, cyclopentyl-C(2-5)**H_2**), 1.33-1.18 (m, 8H, heptyl-C(3-6)**H_2**), 0.86 (t, J = 6.8 Hz, 3H, heptyl-C(7)**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.12 (imC(2)), 122.60 (imC(4)), 121.29 (imC(5)), 121.09 (q, J_{CF} = 322 Hz, 2C, NTf_2), 60.61, 48.91 (2C, cyclopentyl-C(1) & heptyl-C(1)), 32.53, 31.01, 29.28, 28.00, 25.49, 23.07, 21.97 (9C, cyclopentyl-C(2-5) & heptyl-C(2-6)), 13.88 (heptyl-C(7)).
m/z (ES^+): 235.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

[C_6C_6im][NTf_2]. Lithium bis(trifluoromethylsulfonyl)imide (2.2 g, 7.6 mmol, 1.1 eq.) was slowly added to a stirring solution of [C_6C_6im]Br (2 g, 6.3 mmol, 1 eq.) in dichloromethane according to the general procedure. After purification steps, the ionic liquid was dried overnight on the Schlenk Line to yield a viscous colourless liquid (2.6 g, 5.1 mmol, 81% yield).
^{1}H NMR (400 MHz, DMSO-d_6) δH (ppm): 8.83 (s, 1H, imC(2)**H**), 7.32 (d, J = 1.6 Hz, 2H, im C(4,5)**H**), 4.18 (t, J = 7.6 Hz, 4H, hexyl-C(1)**H_2**), 1.94-1.67 (m, 4H, hexyl-C(2)**H_2**), 1.31 (s, 12H, hexyl-C(3-5)**H_2**), 0.87, (t, J = 6.8 Hz, 6H, hexyl-C(6)**H_3**).
^{13}C NMR (101 MHz, DMSO-d_6) δH (ppm): 135.7 (imC(2)), 122.38 (imC(4,5)), 119.97 (q, J_{CF} = 322 Hz, 2C, NTf_2), 50.36 (hexyl-C(1)), 31.06 (hexyl-C(2)), 30.20 (hexyl-C(3)), 25.84 (hexyl-C(4)), 22.42 (hexyl-C(5)), 13.92 (hexyl-C(6)).
m/z (ES^+): 237.2 (100 %, M^+).
m/z (ES^-): 279.8 (100 %, M^-).

TGA Analysis

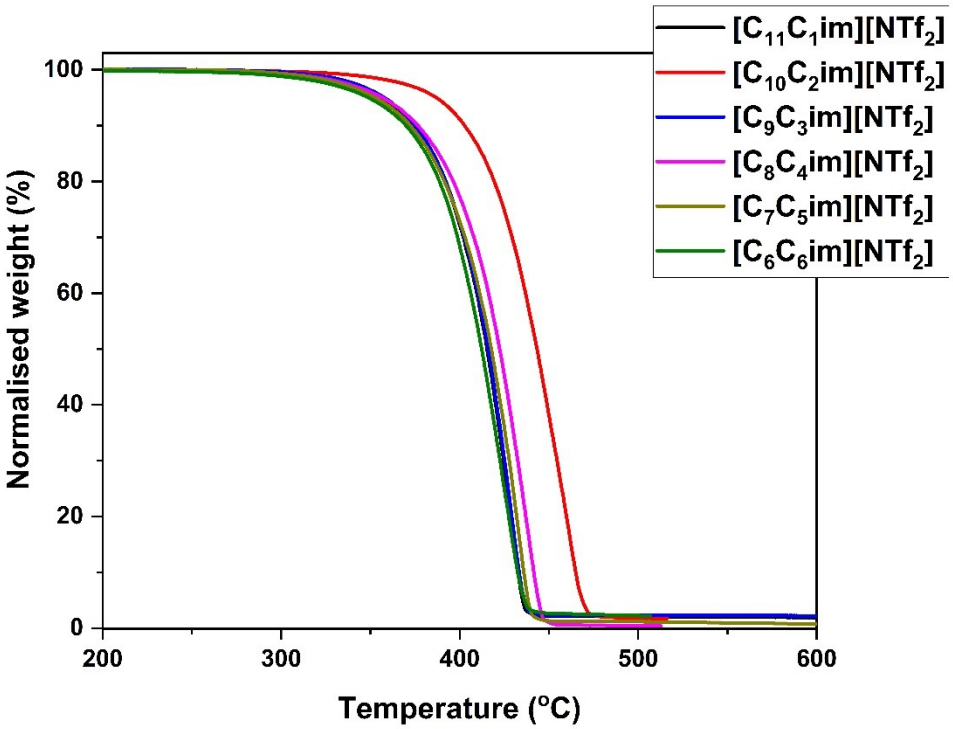

Figure S1. Thermogram of the linear-chained ionic liquids.

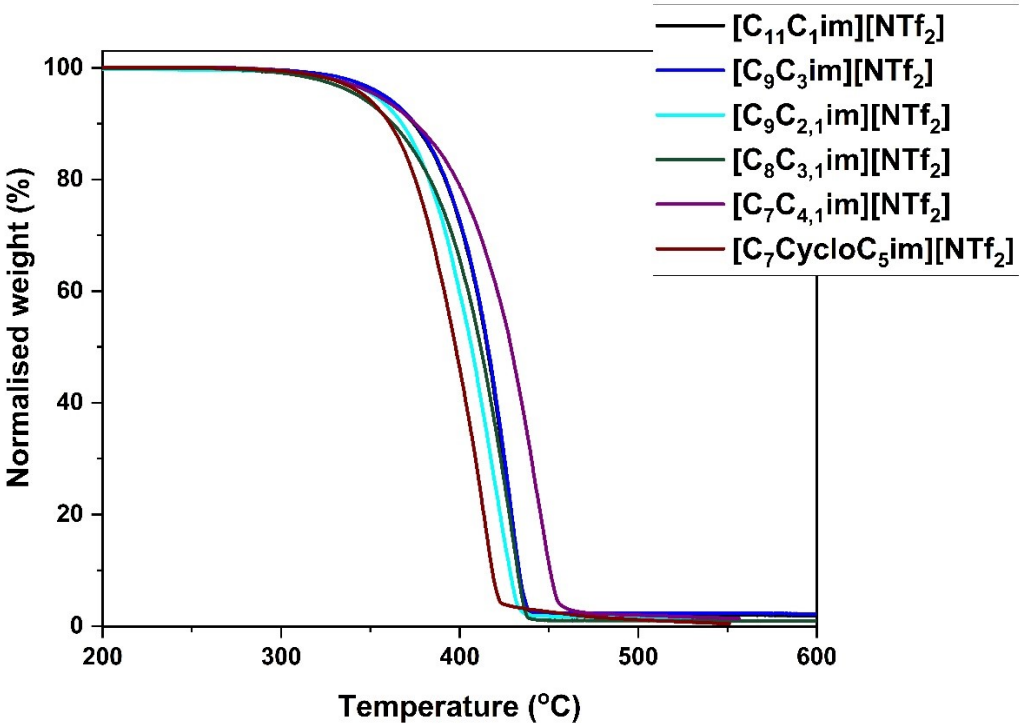

Figure S2. Thermogram of the branched-chained ionic liquids.

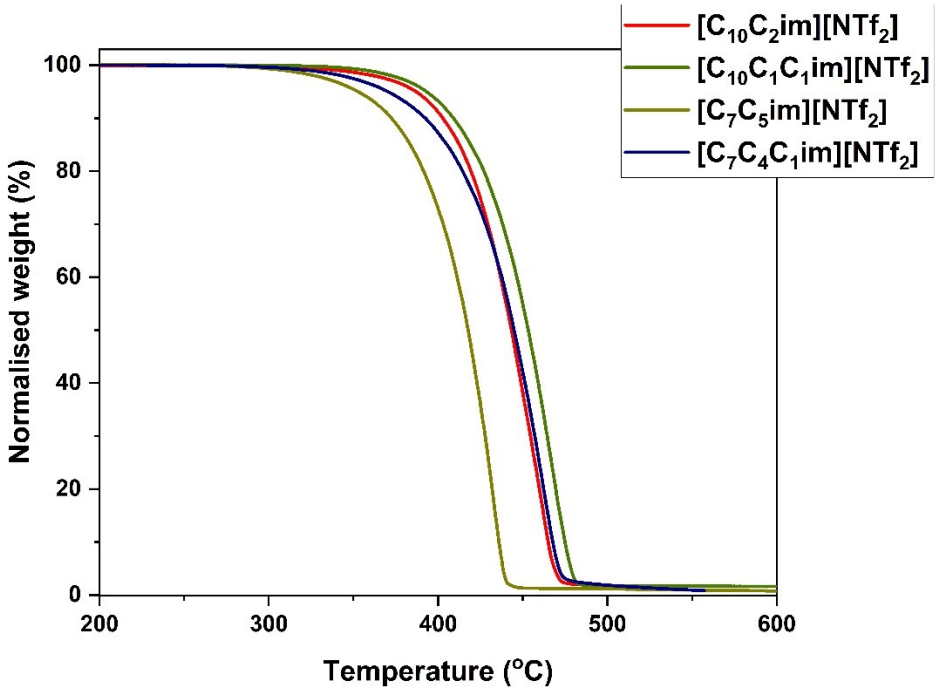

Figure S3. Thermogram of the C^2-methylated ionic liquids compared to their non-methylated analogues.

Density measurements

All studied densities showed linear dependency to temperature increase. Therefore, a straight line was fitted to the experimental data according to Equation (S1).

$$\rho = a + bT \tag{S1}$$

Where ρ is mass density in g mL^{-1}, α and b are the linear fit parameters in g mL^{-1} and g mL^{-1} K^{-1} and T temperature in K accordingly. T is sample temperature in K. Tables S1 and S2 show the experimental data and fitting parameters for the studied ILs.
The relative deviations of the density, δ, were calculated using Equation S2:

$$\delta = \frac{100(Y_{exp} - Y_{Cal})}{Y_{cal}} \tag{S2}$$

Where Y denotes ρ, Y_{exp} is the experimental values, Y_{cal} is the calculated values obtained by the linear fitting of densities against temperature.
Absolute average deviation (AAD%) between the measured and fitted data are calculated using Equation S3.

$$AAD = \frac{100}{N}\sum_{i=1}^{N}\left(\frac{\left|\rho_{exp_i} - \rho_{cal_i}\right|}{\rho_{exp_i}}\right) \tag{S3}$$

Table S1. Experimental densities of the studied ionic liquids in the temperature range of 293 – 373 K. The deviations indicated are relative to the fitting polynomials with coefficients listed in Table S2.

T / K	ρ / g mL^{-1}	δ / %	T / K	ρ / g mL^{-1}	δ / %
	[C_6C_6im][NTf_2]			[C_9C_3im][NTf_2]	
293.152	1.260479	0.02	293.133	1.261407	-0.01
298.154	1.256178	0.008	298.153	1.257586	0.02
303.146	1.251897	-0.0004	303.154	1.253362	0.01
313.154	1.243420	-0.008	313.154	1.244789	-0.002
232.154	1.234990	-0.01	232.154	1.236340	-0.009
333.154	1.226634	-0.01	333.154	1.227983	-0.008
343.155	1.218284	-0.01	343.155	1.219597	-0.01
353.154	1.209989	-0.004	353.154	1.211283	-0.005
363.154	1.201719	0.005	363.154	1.203011	0.002
373.154	1.193492	0.02	373.155	1.194770	0.01
	[C_7C_5im][NTf_2]			[$C_{10}C_2$im][NTf_2]	
293.154	1.263651	0.02	293.148	1.262695	0.02
298.154	1.259332	0.007	298.154	1.258374	0.008
303.154	1.255506	0.001	303.154	1.254101	0.002
313.154	1.246545	-O.008	313.154	1.245522	-0.01
232.154	1.238082	-0.01	232.154	1.237131	-0.01
333.154	1.229696	-0.01	333.154	1.228742	-0.01
343.155	1.221310	-0.01	343.154	1.220375	-0.01
353.154	1.212973	-0.004	353.154	1.212049	-0.004
363.154	1.204680	0.005	363.154	1.203769	0.006
373.154	1.196418	0.02	373.155	1.195519	0.02
	[C_8C_4im][NTf_2]			[$C_{11}C_1$im][NTf_2]	
293.153	1.260370	0.01	293.150	1.257213	0.02
298.154	1.256083	0.007	298.154	1.252918	0.008
303.154	1.251820	0.0008	303.154	1.248638	0.0008
313.154	1.243346	-0.008	313,154	1.240144	-0.008
232.154	1.234918	-0.01	323,154	1.231699	-0.01
333.154	1.226564	-0.01	333,154	1.223328	-0.01
343.155	1.218222	-0.009	343,154	1.214970	-0.01
353.154	1.209916	-0.004	353,154	1.206653	-0.004
363.154	1.201661	0.005	363.154	1.198384	0.005
373.154	1.193418	0.02	373.155	1.190152	0.02
	[$C_9C_{2,1}$im][NTf_2]			[$C_7C_4C_1$im][NTf_2]	
293.150	1.263239	0.02	293.150	1.274651	0.01
298.154	1.258901	0.008	298.151	1.270366	0.007
303.154	1.254590	0.001	303.152	1.266107	0.0008
313.154	1.246023	-0.009	313.152	1.257633	-0.008
323.154	1.237510	-0.01	323.152	1.249226	-0.01
333.154	1.229086	-0.01	333.152	1.240882	-0.01
343.155	1.220662	-0.01	343.152	1.232559	-0.008
353.154	1.212294	-0.004	353.152	1.224265	-0.003
363.154	1.203966	0.005	363.152	1.216006	0.005
373.154	1.195684	0.02	373.152	1.207781	0.02

$[C_7C_{4,1}im][NTf_2]$			$[C_7CycloC_5im][NTf_2]$		
293.149	1.260520	0.02	293.148	1.311707	0.02
298.152	1.256236	0.008	298.152	1.307320	0.008
303.152	1.251958	0.0002	303.152	1.302979	0.001
313.152	1.243483	-0.009	313.152	1.294289	-0.009
323.152	1.235072	-0.01	323.152	1.285693	-0.01
333.152	1.226743	-0.01	333.151	1.277130	-0.01
343.152	1.218394	-0.01	343.152	1.268656	-0.01
353.152	1.210106	-0.01	353.152	1.260192	-0.004
363.152	1.201849	-0.004	363.152	1.251777	0.005
373.152	1.193634	0.02	373.152	1.243411	0.02
$[C_{10}C_1C_1im][NTf_2]$			$[C_8C_{3,1}im][NTf_2]$		
293.149	1.275398	0.02	293.153	1.25836	0.02
298.154	1.271142	0.009	298.154	1.253997	0.008
303.154	1.266908	0.002	303.154	1.249716	-0.0002
313.154	1.258472	-0.01	313.154	1.241216	-0.01
323.154	1.250125	-0.01	323.154	1.232797	-0.01
333.155	1.241849	-0.01	333.155	1.224470	-0.01
343.154	1.233594	-0.01	343.154	1.216129	-0.01
353.154	1.225385	-0.003	353.154	1.207853	-0.005
363.154	1.217206	0.006	363.154	1.19963	0.007
373.154	1.209058	0.02	373.154	1.191436	0.02

Table S2. Parameters A_0 and A_1 from linear functions used to fit the experimental densities, $\rho = \alpha + bT$, as a function of temperature from 293 – 373 K and absolute average deviation (AAD).

Sample	α / g mL^{-1}	b / g mL^{-1} K^{-1}	AAD%
$[C_6C_6im][NTf_2]$	1.5057	$-8.3730x10^{-4}$	0.009
$[C_7C_5im][NTf_2]$	1.5098	$-8.4046x10^{-4}$	0.009
$[C_8C_4im][NTf_2]$	1.5055	$-8.3691x10^{-4}$	0.009
$[C_9C_3im][NTf_2]$	1.5068	$-8.3673x10^{-4}$	0.009
$[C_{10}C_2im][NTf_2]$	1.5086	$-8.3956x10^{-4}$	0.01
$[C_{11}C_1im][NTf_2]$	1.5028	$-8.3841x10^{-4}$	0.009
$[C_9C_{2,1}im][NTf_2]$	1.5106	$-8.4457x10^{-4}$	0.01
$[C_7C_4C_1im][NTf_2]$	1.5195	$-8.3582x10^{-4}$	0.009
$[C_7C_{4,1}im][NTf_2]$	1.5054	$-8.3608x10^{-4}$	0.009
$[C_7CycloC_5im][NTf_2]$	1.5618	$-8.5388x10^{-4}$	0.01
$[C_{10}C_1C_1im][NTf_2]$	1.5183	$-8.2922x10^{-4}$	0.01
$[C_8C_{3,1}im][NTf_2]$	1.5032	$-8.3615x10^{-4}$	0.01

Viscosity measurements

The experimental viscosity data were fitted to Vogel – Fulcher – Tammann (VFT) equation shown below (Equation S4).

$$\eta = A_\eta exp\left(\frac{B_\eta}{T - T_{0\eta}}\right) \quad \text{(S4)}$$

Where A_η, B_η and $T_{0\eta}$ are the adjustable parameters determined by the regression of the set of the experimental data.

Table S3. Experimental viscosities of studied ionic liquids in the temperature range of 293 – 363 K. The deviations indicated are relative to the fitting polynomials with coefficients listed in Table S4.

T / K	η / mPa s	δ / %	T / K	η / mPa s	δ / %
	$[C_6C_6im][NTf_2]$			$[C_9C_3im][NTf_2]$	
293.152	139.3	-0.1	293.133	133.5	-0.1
298.154	106.4	-0.06	298.153	102.7	0.02
303.146	83.20	0.4	303.154	80.97	0.8
313.154	52.79	0.3	313.154	51.43	-0.08
232.154	34.58	-2.1	232.154	33.93	-2.3
333.154	24.62	-0.7	333.154	24.22	-1.1
343.155	18.17	0.4	343.155	18.03	0.7
353.154	13.94	2.1	353.154	13.87	2.7
363.154	10.82	2.3	363.154	10.80	3.3
	$[C_7C_5im][NTf_2]$			$[C_{10}C_2im][NTf_2]$	
293.152	144.2	0.006	293.148	124.0	0.04
298.154	110.2	-0.005	298.154	95.83	-0.09
303.146	86.00	-0.3	303.154	75.38	-0.07
313.154	54.91	0.5	313.154	48.91	0.5
232.154	35.77	-1.5	232.154	32.55	-1.1
333.154	25.38	0.8	333.154	23.46	1.1
343.154	18.70	3.4	343.154	17.55	3.7
353.154	14.07	5.1	353.154	11.20	-11.9
363.154	10.68	4.9	363.154	10.61	8.3
	$[C_8C_4im][NTf_2]$			$[C_{11}C_1im][NTf_2]$	
293.153	138.2	-0.06	293.150	142.3	-0.1
298.154	105.9	0.09	298.154	108.4	-0.05
303.154	82.69	0.3	303.154	84.35	0.2
313.154	52.79	0.5	313,154	53.39	0.3
232.154	34.56	-2.0	323,154	34.86	-2.0
333.154	24.57	-0.9	333,154	24.66	-1.0
343.155	18.22	0.6	343,154	18.19	0.3
353.154	13.96	2.3	353,154	13.93	2.1
363.154	10.81	2.3	363.154	10.81	2.4
	$[C_9C_{2,1}im][NTf_2]$			$[C_7C_4C_1im][NTf_2]$	
293.153	153.0	0.1	293.150	215.9	-0.1

298.154	116.0	-0.2	298.151	160.1	0.1
303.154	89.90	-0.1	303.152	121.1	0.1
313.154	56.87	0.7	313.152	73.51	0.6
323.154	36.78	-1.4	323.152	45.96	-2.3
333.124	25.93	0.7	333.152	31.48	-1.3
343.154	19.05	3.3	343.152	22.61	0.1
353.154	14.35	5.1	353.152	16.90	2.0
363.154	1.84	4.5	363.152	12.96	3.3
			373.152	10.10	3.5
	$[C_7C_{4,1}im][NTf_2]$			$[C_7CycloC_5im][NTf_2]$	
293.149	165.2	-0.1	293.148	148.9	-0.7
298.152	124.7	0.06	298.152	113.2	0.6
303.152	96.06	0.2	303.152	87.97	1.5
313.152	60.08	0.6	313.152	55.92	2.0
323.152	38.56	-2.3	323.152	36.49	-1.8
333.152	27.03	-1.2	333.151	25.92	-2.5
343.152	19.78	0.07	343.152	19.19	-3.5
353.152	15.04	1.8	353.152	14.76	-4.3
363.152	11.68	2.8	363.152	11.61	-5.7
373.152	9.205	2.7	373.152	9.247	-8.3
	$[C_{10}C_1C_1im][NTf_2]$			$[C_8C_{3,1}im][NTf_2]$	
293.149	292.2	-0.02	293.153	211.4	-0.2
298.154	212.4	-0.07	298.154	156.6	0.3
303.154	158.6	0.2	303.154	118.0	0.3
313.154	94.15	0.9	313.154	70.97	0.3
323.154	57.61	-2.2	323.154	44.21	2.6
333.155	38.8	-1.2	333.155	30.27	1.3
343.154	27.37	-0.3	343.154	21.73	0.3
353.154	20.18	1.2	353.154	16.23	2.2
363.154	15.44	3.2	363.154	12.52	4.3
373.154	12.12	5.0	373.154	9.782	5.0

Table S4. Parameters A_η, B_η and $T_{0\eta}$ from Vogel-Tammann-Fulcher (VTF) functions used to fit the experimental viscosities, $\eta = A_\eta EXP(B_\eta/(T-T_{0\eta}))$, as a function of temperature from 293 – 363 K and absolute average deviation (AAD%).

Sample	A_η / mPa s	B_η / K	$T_{0\eta}$ / K	AAD%
$[C_6C_6im][NTf_2]$	0.0728	1021.04	158.05	0.9
$[C_7C_5im][NTf_2]$	0.0261	1357.68	135.60	1.8
$[C_8C_4im][NTf_2]$	0.0689	1042.06	156.12	1.0
$[C_9C_3im][NTf_2]$	0.0610	1087.38	151.78	1.2
$[C_{10}C_2im][NTf_2]$	0.0390	1229.75	140.66	3.0
$[C_{11}C_1im][NTf_2]$	0.0723	1016.58	159.15	1.0
$[C_9C_{2,1}im][NTf_2]$	0.0338	1254.12	144.12	1.0
$[C_7C_4C_1im][NTf_2]$	0.0635	1057.42	163.13	1.0
$[C_7C_{4,1}im][NTf_2]$	0.0764	1004.32	162.38	1.0
$[C_7CycloC_5im][NTf_2]$	0.3210	627.890	191.00	2.5
$[C_{10}C_1C_1im][NTf_2]$	0.0734	1038.13	167.91	1.0
$[C_8C_{3,1}im][NTf_2]$	0.0608	1051.02	164.28	1.3

Table S5. Water content of the studied ionic liquids after the viscosity and density measuremets.

Sample	Water content (ppm)	Water content (% w/w)
$[C_6C_6im][NTf_2]$	86	< 0.0086
$[C_7C_5im][NTf_2]$	153	< 0.015
$[C_8C_4im][NTf_2]$	83	< 0.0083
$[C_9C_3im][NTf_2]$	290	< 0.029
$[C_{10}C_2im][NTf_2]$	200	< 0.020
$[C_{11}C_1im][NTf_2]$	238	< 0.024
$[C_9C_{2,1}im][NTf_2]$	32	0.0032
$[C_7C_4C_1im][NTf_2]$	51	< 0.0051
$[C_7C_{4,1}im][NTf_2]$	105	< 0.015
$[C_7CycloC_5im][NTf_2]$	65	0.0065
$[C_{10}C_1C_1im][NTf_2]$	50	< 0.005
$[C_8C_{3,1}im][NTf_2]$	13	= 0.0013

SAXS patterns

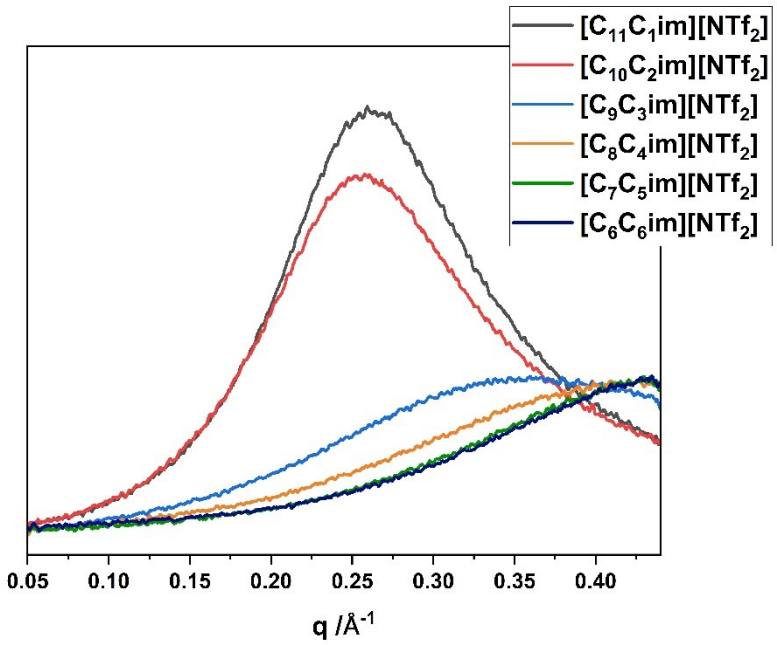

Figure S4. SAXS patterns of the linear-chained ionic liquids.

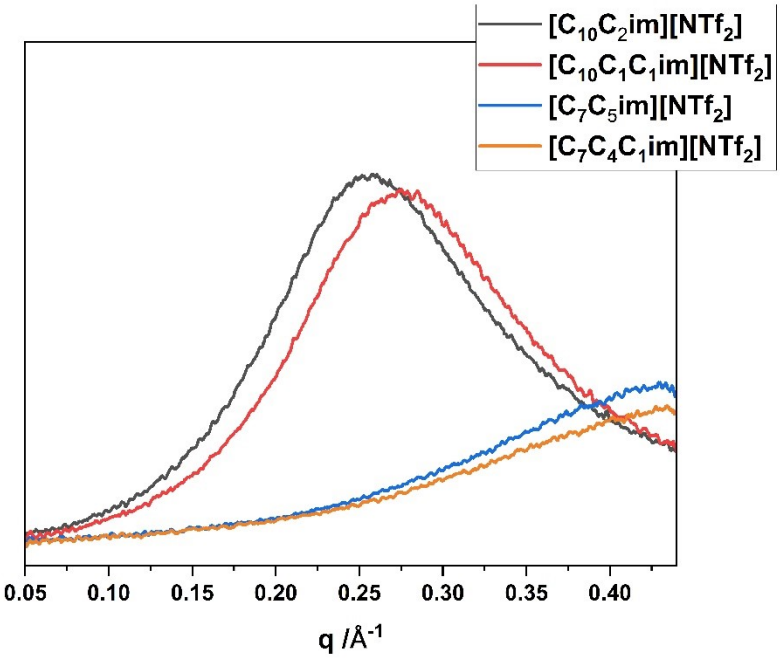

Figure S5. SAXS patterns of the C^2-methylated ionic liquids compared with their non-methylated analogues.

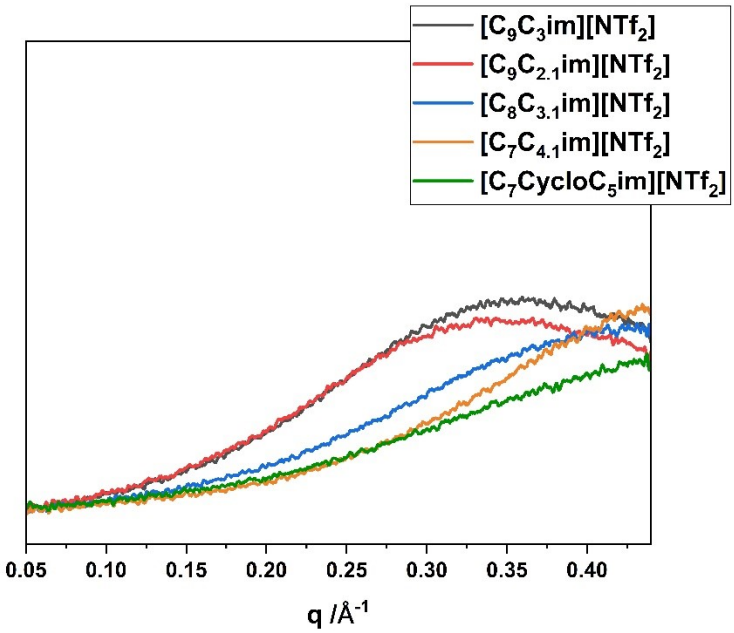

Figure S6. SAXS patterns of the branched-chained ionic liquids compared with their linear-chained analogues.

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