

Supporting Information

Synthesis and toxicity evaluation of hydrophobic Ionic Liquids for Volatile Organic Compounds biodegradation in a two-phase partitioning bioreactor.

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Procedures for IL synthesis

All chemical products were purchased from Sigma-Aldrich, Acros Organic and Alfa Aesar. Solvent or excess reagents were removed by evaporation under reduced pressure with a BUCHI rotavapor or a vacuum pump Edward RV5 (2-6.10⁻² mbar). Ultrasound bath was a Bransonic 1510 maintained at 25°C. ¹H NMR spectra were recorded on BRUKER AC 300 P (300 MHz) spectrometer, ¹³C NMR spectra on BRUKER AC 300 P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Data are given in the following order: δ value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons, coupling constants J is given in Hertz. Water contents were determined by titration with a Karl-Fischer 831 KF Coulometer and are given in ppm. Melting points were measured with a Leica VMHB System Kofler.

Synthesis of 3-Butyl-1-methylimidazolium chloride [Bmim][Cl]

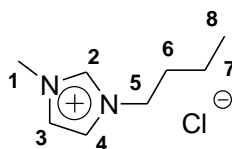


Figure 1 Chemical structure of [Bmim][Cl]

1-Methylimidazole purified by distillation under reduced pressure (0.63 mol, 1 eq) and 1-chlorobutane distilled under reduced pressure (0.94 mol, 1.5 eq) is heated at 90°C under argon atmosphere during 48 h. The excess of chlorobutane is removed under reduced pressure at 50°C during 16h and the product crystallizes to give a white solid (yield 99%). ¹H NMR δ

(acetone-d₆) : 0.98 (t, $J = 7.3$ Hz, 3H, H-8); 1.41 (tq, $J = 7.2, 7.4, 7.5$ Hz, 2H, H-7); 1.96 (tq, $J = 7.3, 7.5, 7.7$ Hz, 2H, H-6); 4.13 (s, 3H, H-1); 4.47 (t, $J = 7.2$ Hz, 2H, H-5); 7.84 (t, $J = 1.7$ Hz, 1H, H-4); 7.91 (t, $J = 1.7$ Hz, 1H, H-3); 10.85 (s, 1H, H-2). ¹³C NMR δ (acetone-d₆) : 13.74 (C-8); 19.96 (C-7); 32.88 (C-6); 36.37 (C-1); 49.79 (C-5); 123.00 (C-4); 124.30 (C-3); 139.32 (C-2).

Synthesis of 3-Butyl-1-methylimidazolium hexafluorophosphate [Bmim][PF₆]

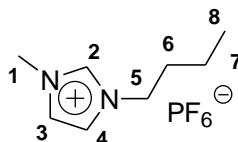


Figure 2 Chemical structure of [Bmim][PF₆]

3-butyl-1-methylimidazolium chloride (0.312 mol, 1 eq) is diluted in 50 mL of deionized water and potassium hexafluorophosphate (0.343 mol, 1.1 eq) in solution in 45 mL of deionized water is added and the mixture is agitated at room temperature during 24 h. The organic layer is washed three times with deionized water (70 mL). The residual water is removed under reduced pressure at 50°C for 12 h to give a viscous yellow liquid (yield 55%). ¹H NMR δ (acetone-d₆) : 0.98 (t, $J = 7.3$ Hz, 3H, H-8); 1.42 (tq, $J = 7.2, 7.4, 7.5$ Hz, 2H, H-7); 1.96 (tt, $J = 7.4, 7.5, 7.6$ Hz, 2H, H-6); 4.06 (s, 3H, H-1); 4.37 (t, $J = 7.3$ Hz, 2H, H-5); 7.69 (t, $J = 1.7$ Hz, 1H, H-4); 7.75 (t, $J = 1.7$ Hz, 1H, H-3); 8.94 (s, 1H, H-2). ¹⁹F NMR δ (acetone-d₆) : -73.57; -71.06. ³¹P NMR δ (acetone-d₆) : -144.31 (hept, $J = 707$ Hz). ¹³C NMR δ (acetone-d₆) : 13.66 (C-8); 19.91 (C-7); 32.62 (C-6); 36.49 (C-1); 50.16 (C-5); 123.28 (C-4); 124.63 (C-3); 137.26 (C-2). Water content: 7.03 ppm.

Synthesis of 3-Butyl-1-methylimidazolium bis(trifluoro-methylsulfonyl)imide [Bmim][NTf₂]

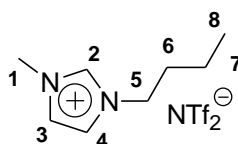


Figure 3 Chemical structure of [Bmim][NTf₂]

3-butyl-1-methylimidazolium chloride (0.312 mol, 1 eq) is diluted in 50 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (0.343 mol, 1.1 eq) in solution in 45 mL of deionized water is added slowly. The mixture is agitated at room temperature during 24 h. The organic layer is washed three times with deionized water (70 mL). The residual water is removed under reduced pressure at 50°C for 12h to give a low viscous yellow liquid (yield 91%). ¹H NMR δ (acetone-d₆) : 0.98 (t, $J = 7.3$ Hz, 3H, H-8); 1.42 (tq, $J = 7.2, 7.4, 7.5$ Hz, 2H, H-7); 1.96 (tt, $J = 7.4, 7.5, 7.5$ Hz, 2H, H-6); 4.09 (s, 3H, H-1); 4.39 (t, $J = 7.3$ Hz, 2H, H-5); 7.73 (t, $J = 1.8$ Hz, 1H, H-4); 7.79 (t, $J = 1.8$ Hz, 1H, H-3); 9.04 (s, 1H, H-2). ¹⁹F NMR δ (acetone-d₆) : -79.97. ¹³C NMR δ (acetone-d₆) : 13.57 (C-8); 19.90 (C-7); 32.66 (C-6); 36.56 (C-1); 50.22 (C-5); 120.91 (q, $^1J_{C-F} = 321$ Hz); 123.35 (C-4); 124.71 (C-3); 137.26 (C-2). Water content : 4.33 ppm.

Synthesis of 1-Butyl-3-methylimidazolium nonafluorobutylsulfonate [Bmim][NfO]

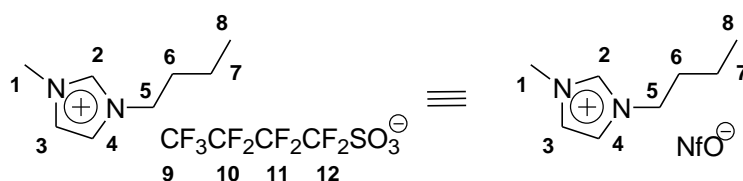


Figure 4 Chemical structure of [Bmim][NfO]

3-butyl-1-methylimidazolium chloride (91.48 mmol, 1 eq) is diluted in 100 mL of deionized water and potassium nonafluorobutane sulfonate (91.48 mmol, 1 eq) is added slowly at 0°C. The mixture is agitated at room temperature during 45 h. Dichloromethane (80mL) is added and the organic layer is washed with deionized water (3 x 15mL). The residual water is removed under reduced pressure at 60°C for 7 h to give a high viscous yellow liquid (yield 94%). Mp = 20°C. ^1H NMR δ (acetone- d_6): 0.95 (t, J = 7.4 Hz, 3H, H-8); 1.39 (tq, J = 7.2, 7.5, 7.7 Hz, 2H, H-7); 1.93 (tt, J = 7.4, 7.6, 7.6 Hz, 2H, H-6); 4.06 (s, 3H, H-1); 4.37 (t, J = 7.3 Hz, 2H, H-5); 7.73 (t, J = 1.7 Hz, 1H, H-4); 7.80 (t, J = 1.7 Hz, 1H, H-3); 9.11 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6): -126.65; -122.09; -115.53; -81.85. ^{13}C NMR δ (acetone- d_6): 13.60 (C-8); 19.93 (C-7); 32.75 (C-6); 36.56 (C-1); 50.14 (C-5); 109.98 (ttq, J = 3.0, 34.0, 269.4 Hz, CF_2); 111.87 (ttt, J = 3.8, 34.0, 265.6 Hz, CF_2); 115.01 (tt, J = 33.2, 289.8 Hz, CF_2); 118.54 (tq, J = 34.0, 287.5 Hz, CF_3); 123.38 (C-4); 124.73 (C-3); 137.69 (C-2). Water content: 6.4 ppm.

Synthesis of 3-Isopentyl-1-methylimidazolium bromide [iPtMim][Br]

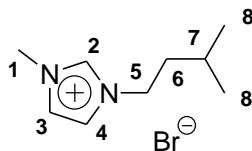


Figure 5 Chemical structure of [iPtMim][Br]

1-Methylimidazole purified by distillation under reduced pressure (109.61 mmol, 1 eq) is cooled at 0°C and 1-bromo-3-methylbutane distilled under reduced pressure (120.57 mmol, 1.1 eq) is added slowly. The mixture is heated at 110°C under argon atmosphere during 23h. The excess of 1-bromo-3-methylbutane is removed under reduced pressure at 60°C during 6 h to give a yellow viscous oil (yield 99%). ^1H NMR δ (acetone- d_6): 0.99-1.01 (2s, 2x3H, H-8); 1.67 (hept, J = 6.6 Hz, 1H, H-7); 1.90 (dt, J = 6.9, 7.4 Hz, 2H, H-6); 4.15 (s, 3H, H-1); 4.53 (dd, J = 7.6, 7.6 Hz, 2H, H-5); 7.96 (t, J = 1.7 Hz, 1H, H-4); 8.07 (t, J = 1.8 Hz, 1H, H-3); 10.38 (s, 1H, H-2). ^{13}C NMR δ (acetone- d_6): 22.59 (C-8); 26.07 (C-7); 36.58 (C-1); 39.62 (C-6); 48.56 (C-5); 123.22 (C-4); 124.47 (C-3); 138.47 (C-2).

Synthesis of 3-Isopentyl-1-methylimidazolium hexafluorophosphate [iPtMim][PF₆]

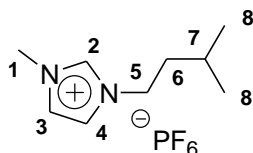


Figure 6 Chemical structure of [iPtmmim][PF₆]

3-isopentyl-1-methylimidazolium bromide (109.07 mmol, 1 eq) is diluted in 39 mL of deionized water and potassium hexafluorophosphate (119.97 mmol, 1.1 eq) is added slowly at 0°C. The mixture is agitated at room temperature during 44 h. Dichloromethane (190mL) is added and after decantation and separation, the organic layer is washed with deionized water (3 x 60 mL). The residual water is removed under reduced pressure at 60°C for 7 h to give a pale yellow oil (yield 95%). ¹H NMR δ (acetone-d₆) : 0.99-1.01 (2s, 2x3H, H-8); 1.69 (hept, *J* = 6.7 Hz, 1H, H-7); 1.89 (m, 2H, H-6); 4.08 (s, 3H, H-1); 4.41 (m 2H, H-5); 7.72 (t, *J* = 1.8 Hz, 1H, H-4); 7.79 (t, *J* = 1.8 Hz, 1H, H-3); 9.00 (s, 1H, H-2). ¹⁹F NMR δ (acetone-d₆) : -73.64; -71.13. ³¹P NMR δ (acetone-d₆) : -144.30 (hept, *J* = 707 Hz). ¹³C NMR δ (acetone-d₆) : 22.37 (C-8); 26.06 (C-7); 36.58 (C-1); 39.44 (C-6); 48.88 (C-5); 123.36 (C-4); 124.76 (C-3); 137.36 (C-2). Water content : 7.9 ppm.

Synthesis of 3-Butenyl-1-methylimidazolium bromide [Butenylmim][Br]

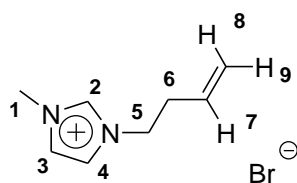


Figure 7 Chemical structure of [Butenylmim][Br]

1-bromobutene purified by distillation (32.5 mmol, 1,1 eq) is added at 0°C slowly on 1-methylimidazole previously distilled under reduced pressure (29.6 mmol, 1 eq). The mixture is agitated under argon atmosphere at room temperature for 48 h and at 40°C for 24 h. After removing the excess of 1-bromobutene under vacuum, the product is obtained as a viscous pale yellow liquid (yield 85%). ¹H NMR δ (acetone-d₆) : 2.76 (dtt, *J* = 1.3, 6.9, 6.9 Hz, 2H, H-6); 4.15 (s, 3H, H-1); 4.58 (t, *J* = 6.9 Hz, 2H, H-5); 4.90 (ddt, *J* = 1.0, 1.8, 10.2 Hz, 1H, H-9); 5.01 (ddt, *J* = 1.5, 1.8, 17.1 Hz, 1H, H-8); 5.92 (ddt, *J* = 6.9, 10.2, 17.1 Hz, 1H, H-7); 7.93 (t, *J* = 1.7 Hz, 1H, H-4); 8.06 (t, *J* = 1.7 Hz, 1H, H-3); 10.33 (s, 1H, H-2). ¹³C NMR δ (acetone-d₆) : 34.20 (C-6); 35.82 (C-1); 48.31 (C-5); 117.92 (C-8); 122.58 (C-4); 123.46 (C-3); 133.73 (C-7); 137.50 (C-2).

Synthesis of 3-Butenyl-1-methylimidazolium hexafluorophosphate [Butenylmim][PF₆]

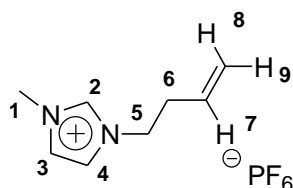


Figure 8 Chemical structure of [Butenylmim][PF₆]

3-butenyl-1-methylimidazolium bromide (25 mmol, 1 eq) is diluted in 10 mL of deionized water and potassium hexafluorophosphate (27.6 mmol, 1.1 eq) in solution in 6 mL of deionized water is added and the mixture is agitated at room temperature during 48 h. The organic layer is washed three times with deionized water (2 mL). The residual water is removed under reduced pressure at 40°C for 11 h to give a viscous yellow liquid (yield 87%). ^1H NMR δ (acetone- d_6) : 2.73 (pseudo quadruplet, $J = 6.9$ Hz, 2H, H-6); 4.09 (s, 3H, H-1); 4.49 (t, $J = 6.9$ Hz, 2H, H-5); 5.11 (m, 2H, H-8); 5.86 (ddt, $J = 6.9, 10.3, 17.2$ Hz, 2H, H-7); 7.74 (s, 1H, H-4); 7.80 (s, 1H, H-3); 9.05 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6) : -73.70; -71.19. ^{31}P NMR δ (acetone- d_6) : 144.30 (hept, $J = 707$ Hz). ^{13}C NMR δ (acetone- d_6) : 34.75 (C-6); 36.48 (C-1); 49.61 (C-5); 119.36 (C-8); 123.24 (C-4); 124.26 (C-3); 134.05 (C-7); 137.17 (C-2). Water content : 16.5 ppm.

Synthesis of 3-Butenyl-1-methylimidazolium bis(trifluoromethylsulfonyl)imide [Butenylmim][NTf₂]

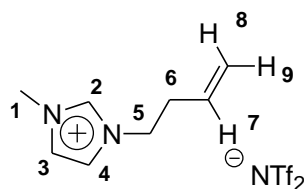


Figure 9 Chemical structure of [Butenylmim][NTf₂]

3-butenyl-1-methylimidazolium bromide (42.31 g, 194.88 mmol, 1 eq) is diluted in 76 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (61.54 g, 214.37 mmol, 1.1 eq) is added and the mixture is agitated at room temperature during 78h. Dichloromethane (30 mL) is added and the organic layer is washed three times with deionized water (35 mL). The solvent is removed under reduced pressure and the product is dried under vacuum at 60°C for 24h to give a viscous pale yellow liquid (yield 99%). ^1H NMR δ (acetone- d_6) : 2.73 (q, $J = 6.9$ Hz, 2H, H-6); 4.05 (s, 3H, H-1); 4.45 (t, $J = 6.9$ Hz, 2H, H-5); 5.13 (m, 2H, H-8,9); 5.86 (m, 1H, H-7); 7.68 (s, 1H, H-4); 7.74 (s, 1H, H-3); 8.97 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6) : -79.91. ^{13}C NMR δ (acetone- d_6) : 34.88 (C-6); 36.60 (C-1); 49.70 (C-5); 119.23 (C-8); 120.90 (q, $J = 321$ Hz, CF₃); 123.43 (C-4); 124.67 (C-3); 133.94 (C-7); 137.25 (C-2). Water content : 38.2 ppm.

Synthesis of 3-Butenyl-1-methylimidazolium nonafluorobutylsulfonate [Butenylmim][NfO]

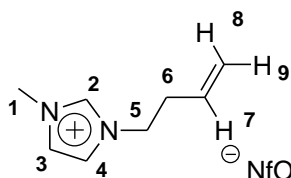


Figure 10 Chemical structure of [Butenylmim][NfO]

3-butenyl-1-methylimidazolium bromide (42.18g, 194.28 mmol, 1 eq) is diluted in 76 mL of deionized water and potassium nonafluorobutylsulfonyl (72.28g, 213.71 mmol, 1.1 eq) is added and the mixture is agitated at room temperature during 48 h. The organic layer is

washed three times with deionized water (50 mL). The residual water is removed under reduced pressure at 40°C for 30 h to give a viscous pale liquid (yield 80%). ^1H NMR δ (acetone- d_6) : 2.71 (tq, $J = 1.3, 6.9$ Hz, 2H, H-6); 4.05 (s, 3H, H-1); 4.45 (t, $J = 6.9$ Hz, 2H, H-5); 5.10 (m, 2H, H-8); 5.86 (ddt, $J = 6.9, 10.3, 17.2$ Hz, 2H, H-7); 7.72 (s, 1H, H-4); 7.79 (s, 1H, H-3); 9.11 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6) : -126.62; -122.06; -115.54; -81.84. ^{13}C NMR δ (acetone- d_6) : 34.95 (C-6); 36.53 (C-1); 49.55 (C-5); 118.95 (C-8); 123.47 (C-4); 124.63 (C-3); 134.22 (C-7); 137.72 (C-2). Water content : 13.7 ppm.

Synthesis of 3-(1-methoxyethyl)-1-methylimidazolium bromide [MeOEmim][Br]

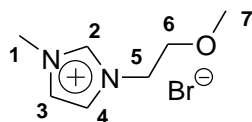


Figure 11 Chemical structure of [MeOEmim][Br]

1-Methylimidazole purified by distillation under reduced pressure (50.73 mmol, 1 eq) and 2-bromoethyl methyl ether distilled under reduced pressure (60.88 mmol, 1.2 eq) is heated at 40°C under argon atmosphere during 48 h. The excess of 2-bromoethyl methyl ether is removed under reduced pressure at 40°C during 10h and the product crystallizes to give a beige solid (yield 96%). ^1H NMR δ (acetone- d_6) : 3.39 (s, 3H, H-7); 3.87 (dt, $J = 5.0$ Hz, 2H, H-5); 4.16 (s, 3H, H-1); 4.69 (dt, $J = 5.0$ Hz, 2H, H-6); 7.90 (t, $J = 1.7$ Hz, 1H, H-4); 7.98 (t, $J = 1.7$ Hz, 1H, H-3); 10.14 (s, 1H, H-2). ^{13}C NMR δ (acetone- d_6) : 36.60 (C-1); 50.03 (C-5); 58.86 (C-7); 71.00 (C-6); 123.77 (C-4); 124.19 (C-3); 138.59 (C-2).

Synthesis of 3-(1-methoxyethyl)-1-methylimidazolium bis(trifluoro-methylsulfonyl)imide [MeOEmim][NTf₂]

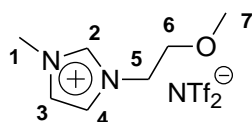


Figure 12 Chemical structure of [MeOEmim][NTf₂]

3-(1-methoxyethyl)-1-methylimidazolium bromide (48.89 mmol, 1 eq) is diluted in 15 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (49.89 mmol, 1.1 eq) in solution in 5 mL of deionized water is added slowly. The mixture is agitated at room temperature during 18h. The organic layer is washed with deionized water (3 mL). The residual water is removed under reduced pressure at 50°C for 6 h to give a low viscous brown liquid (yield 89%). ^1H NMR δ (acetone- d_6) : 3.38 (s, 3H, H-7); 3.84 (dd, $J = 4.8, 4.9$ Hz, 2H, H-5); 4.10 (s, H, H-1); 4.55 (dd, $J = 4.8, 4.9$ Hz, 2H, H-6); 7.71 (t, $J = 1.8$ Hz, 1H, H-4); 7.75 (t, $J = 1.8$ Hz, 1H, H-3); 9.01 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6) : -79.96. ^{13}C NMR δ (acetone- d_6) : 36.65 (C-1); 50.42 (C-5); 58.84 (C-7); 70.73 (C-6); 120.96 (q, $^1J_{\text{C-F}} = 321$ Hz); 123.92 (C-4); 124.48 (C-3); 137.75 (C-2). Water content : 5.6 ppm.

Synthesis of 3-(1-methoxyethyl)-1-methylimidazolium nonafluorobutylsulfonate [MeOEmim][NfO]

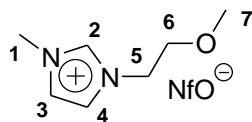


Figure 13 Chemical structure of [MeOEmim][NfO]

3-(1-methoxyethyl)-1-methylimidazolium bromide (179.91 mmol, 1 eq) is diluted in 200 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (197.9 mmol, 1.1 eq) is added slowly. The mixture is agitated at room temperature during 28 h. Dichloromethane is added (180 mL) and after decantation, the organic layer is washed three times with deionized water (50 mL). The residual water is removed under reduced pressure at 50°C for 24 h to give a viscous brown liquid (yield 64%). ¹H NMR δ (acetone-d₆) : 3.37 (s, 3H, H-7); 3.83 (dd, *J* = 4.8, 4.9 Hz, 2H, H-5); 4.08 (s, H, H-1); 4.54 (dd, *J* = 4.8, 4.9 Hz, 2H, H-6); 7.74 (t, *J* = 1.8 Hz, 1H, H-4); 7.77 (t, *J* = 1.8 Hz, 1H, H-3); 9.08 (s, 1H, H-2). ¹⁹F NMR δ (acetone-d₆) : -126.62, 122.07, 115.56, 81.55. ¹³C NMR δ (acetone-d₆) : 36.57 (C-1); 50.26 (C-5); 58.79 (C-7); 70.81 (C-6); 111.91-120.49 (CF₃CF₂CF₂CF₂); 123.88 (C-4); 124.46 (C-3); 138.03 (C-2). Water content : 11.6 ppm.

Synthesis of 3-(1-ethoxyethyl)-1-methylimidazolium chloride [EtOEmim][Cl]

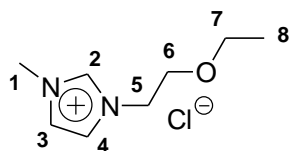


Figure 14 Chemical structure of [EtOEmim][Cl]

1-Methylimidazole purified by distillation under reduced pressure (165.62 mmol, 1 eq) and 2-chloroethyl ethyl ether distilled under reduced pressure (190.46 mmol, 1.15 eq) is heated at 90°C under argon atmosphere during 48 h. The excess of 2-chloroethyl ethyl ether is removed under reduced pressure at 60°C during 16 h and the product is obtained as an orange gel (yield 98%). ¹H NMR δ (acetone-d₆) : 1.16 (t, *J* = 7.0 Hz, 3H, H-8); 3.57 (q, *J* = 7.0 Hz, 2H, H-7); 3.90 (dt, *J* = 5.0 Hz, 2H, H-5); 4.14 (s, 3H, H-1); 4.68 (dt, *J* = 5.0 Hz, 2H, H-6); 7.89 (t, *J* = 1.7 Hz, 1H, H-4); 7.96 (t, *J* = 1.7 Hz, 1H, H-3); 10.72 (s, 1H, H-2). ¹³C NMR δ (acetone-d₆) : 15.35 (C-8); 36.39 (C-1); 50.07 (C-5); 58.86 (C-7); 71.00 (C-6); 123.74 (C-4); 123.99 (C-3); 139.49 (C-2).

Synthesis of 3-(1-ethoxyethyl)-1-methylimidazolium bis(trifluoro-methylsulfonyl)imide [EtOEmim][NTf₂]

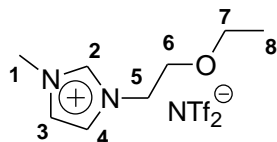


Figure 15 Chemical structure of [EtOEmim][NTf₂]

3-(1-ethoxyethyl)-1-methylimidazolium chloride (161.5 mmol, 1 eq) is diluted in 70 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (177.65 mmol, 1.1 eq) is added

slowly at 0°C. The mixture is agitated at room temperature during 72 h. Dichloromethane is added (25 mL) and the organic layer is washed three times with deionized water (25 mL). The residual water is removed under reduced pressure at 60°C for 10 h to give a low viscous yellow liquid (yield 95%). ¹H NMR δ (acetone-d6) : 1.17 (t, *J* = 7.0 Hz, 3H, H-8); 3.56 (q, *J* = 7.0 Hz, 2H, H-7); 3.88 (dd, *J* = 5.0 Hz, 2H, H-5); 4.10 (s, H, H-1); 4.55 (dd, *J* = 5.0 Hz, 2H, H-6); 7.71 (m, 1H, H-4); 7.76 (m, 1H, H-3); 9.01 (s, 1H, H-2). ¹⁹F NMR δ (acetone-d6) : -79.87. ¹³C NMR δ (acetone-d6) : 15.22 (C-8); 36.65 (C-1); 50.65 (C-5); 66.97 (C-6); 68.72 (C-7); 120.98 (q, ¹*J*_{C-F} = 321 Hz); 123.98 (C-4); 124.47 (C-3); 137.72 (C-2). Water content : 4.6 ppm.

Synthesis of 3-(1-methoxyethoxyethyl)-1-methylimidazolium bromide [MeOC₂OC₂mim][Br]

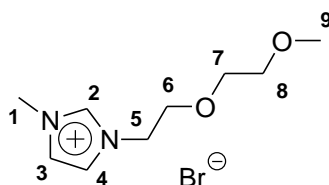


Figure 16 Chemical structure of [MeOC₂OC₂mim][Br]

1-methoxyethoxyethyl bromide purified by distillation under reduced pressure (25.75 mmol, 1,4 eq) is added at 0°C slowly on 1-methylimidazole previously distilled under reduced pressure (18.40 mmol, 1 eq). The mixture is agitated under argon atmosphere at room temperature for 48 h and at 40°C for 24 h. After removing the excess of 1-methoxyethoxyethyl bromide under vacuum, the product is diluted in water (25 mL) and washed three times with diethylether (12 mL). The water is removed under vacuum to give the desired product as a brown oil (yield 85%). ¹H NMR δ (acetone-d6) : 3.32 (s, 3H, H-9); 3.53 (ddd, *J* = 4.4, 4.9, 6.3 Hz, 2H, H-7/8); 3.70 (ddd, *J* = 4.4, 4.9, 6.3 Hz, 2H, H-7/8); 3.97 (t, *J* = 4.9 Hz, 2H, H-6); 4.15 (s, 3H, H-1); 4.67 (t, *J* = 4.9 Hz, 2H, H-5); 7.87 (t, *J* = 1.6 Hz, 1H, H-4); 7.96 (t, *J* = 1.6 Hz, 1H, H-3); 10.04 (s, 1H, H-2). ¹³C NMR δ (acetone-d6) : 35.75 (C-1); 49.19 (C-5); 57.93 (C-9); 68.69-69.87-71.53 (C-6-7-8); 122.91 (C-4); 123.24 (C-3); 137.75 (C-2).

Synthesis of 3-(1-methoxyethoxyethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide [MeOC₂OC₂mim][NTf₂]

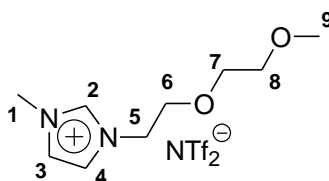


Figure 17 Chemical structure of [MeOC₂OC₂mim][NTf₂]

3-(1-methoxyethoxyethyl)-1-methylimidazolium bromide (78.86 mmol, 1 eq) is diluted in 40 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (86.74 mmol, 1.1 eq) is added slowly. The mixture is agitated at room temperature during 4 days. Dichloromethane (40 mL) is added and the organic layer is washed 3 times with deionized water (30 mL). The

crude is diluted in 50 mL of acetonitrile. The mixture is filtered on 3 cm of alumina and 0.5 cm of activated charcoal and rinsed with 150 mL of acetonitrile. After removing the solvent under reduced pressure, the residual water is removed under vacuum at 50°C during 5 h to give a low viscous brown liquid (yield 89%). ^1H NMR δ (acetone- d_6) : 3.30 (s, 3H, H-9); 3.50 (ddd, $J = 4.4, 4.9, 6.3$ Hz, 2H, H-7/8); 3.65 (ddd, $J = 4.4, 4.9, 6.3$ Hz, 2H, H-7/8); 3.92 (t, $J = 4.9$ Hz, 2H, H-6); 4.06 (s, 3H, H-1); 4.53 (t, $J = 4.9$ Hz, 2H, H-5); 7.70 (t, $J = 1.6$ Hz, 1H, H-4); 7.76 (t, $J = 1.6$ Hz, 1H, H-3); 9.01 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6) : -79.89. ^{13}C NMR δ (acetone- d_6) : 35.43 (C-1); 49.10 (C-5); 57.56 (C-9); 68.03-69.57-71.10 (C-6-7-8); 119.69 (CF_3 , $J = 321$ Hz); 122.73 (C-4); 123.21 (C-3); 136.56 (C-2). Water content : 9.13 ppm.

Synthesis of 3-(1-butyronitrile)-1-methylimidazolium bromide [CNC₃mim][Br]

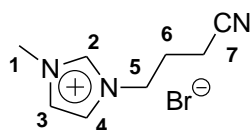


Figure 18 Chemical structure of [CNC₃mim][Br]

1-Methylimidazole purified by distillation under reduced pressure (128 mmol, 1 eq) and 4-bromopropionitrile distilled under reduced pressure (141 mmol, 1.1 eq) are heated at 85°C under argon atmosphere during 2.5 h. The excess of 4-bromopropionitrile is removed under reduced pressure at 50°C during 1 h. Acetonitrile (10 mL) is added and after 2.5 h in an ultrasound bath at 25°C, the crystallized product is collected by filtration under argon. This operation is repeated once and the product is obtained after drying under reduced pressure for 5 h as a beige solid (yield 95%). ^1H NMR δ (acetone- d_6) : 2.40 (pseudoquintuplet, $J = 7.0$ Hz, 2H, H-6); 2.78 (t, $J = 7.3$ Hz, 2H, H-5); 4.11 (s, 3H, H-1); 4.68 (t, $J = 7.0$ Hz, 2H, H-7); 7.80 (t, $J = 1.8$ Hz, 1H, H-4); 8.00 (t, $J = 1.8$ Hz, 1H, H-3); 10.14 (s, 1H, H-2). ^{13}C NMR δ (D_2O) : 13.65 (C-7); 25.00 (C-6); 35.70 (C-1); 47.97 (C-5); 119.94 (CN); 122.19 (C-4); 123.90 (C-3); 136.24 (C-2).

3-(4-butyronitrile)-1-methylimidazolium bis(trifluoromethylsulfonyl)-imide [CNC₃mim][NTf₂]

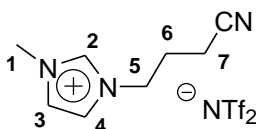


Figure 19 Chemical structure of [CNC₃mim][NTf₂]

3-(4-Butyronitrile)-1-methylimidazolium bromide (185.39 mmol, 1 eq) is diluted in 94 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (203.93 mmol, 1.1 eq) is added slowly. The mixture is agitated at room temperature during 48 h. Dichloromethane (25 mL) is added and after decantation, the organic layer is washed three times with 20 mL of deionized water. The residual water is removed under reduced pressure at 50°C for 28 h to give a white powder (yield 88%). ^1H NMR δ (acetone- d_6) : 2.36 (pseudoquintuplet, 2H, H-6); 2.66 (pseudotriplet, 2H, H-5); 4.06 (s, 3H, H-1); 4.51 (t, $J = 7.1$ Hz, 2H, H-7); 7.71 (t, $J = 1.8$ Hz,

1H, H-4); 7.78 (t, $J = 1.8$ Hz, 1H, H-3); 9.02 (s, 1H, H-2). ^{19}F NMR δ (acetone- d_6) : -79.88. ^{13}C NMR δ (acetone- d_6) : 14.43 (C-7); 26.75 (C-6); 36.73 (C-1); 49.16 (C-5); 114.53 (CN); 120.91 ($J = 321$ Hz, CF_3); 123.44 (C-4); 125.06 (C-3); 137.69 (C-2). Water content : 8.0 ppm.

Synthesis of 1-octylisoquinolinium bromide [OctIq][Br]

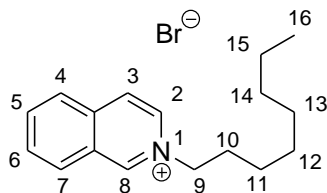


Figure 20 Chemical structure of [OctIq][Br]

1-Octyl bromide purified by distillation under reduced pressure (115.78 mmol, 1.2 eq) is added at 0°C slowly on 1-methylimidazole previously distilled under reduced pressure (96.49 mmol, 1 eq). The mixture is agitated under argon atmosphere at 90°C for 19 h. Acetone (5-10 mL) is added and the excess of 1-octyl bromide is removed under vacuum. An orange gel is obtained (yield 99%). ^1H NMR δ (acetone- d_6) : 0.87 (m, 3H, H-16); 1.25-1.58 (m, 10H, H-11-15); 2.25 (m, 2H, H-10); 5.15 (t, $J = 7.5$ Hz, 2H, H-9); 8.11-9.17, 11.26 (m, 7H, H-2-8). ^{13}C NMR δ (acetone- d_6) : 14.47 (C-16); 23.27 (C-15); 26.88 (C-14); 29.89 (C-12-13); 32.47 (C-10-11); 61.72 (C-9); 127.00-151.20 (C-2-8).

Synthesis of 1-octylisoquinolinium bis(trifluoromethyl-sulfonyl)imide [OctIq][NTf₂]

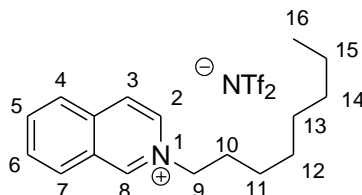


Figure 21 Chemical structure of [OctIq][NTf₂]

1-octylisoquinolinium bromide (96.16 mmol, 1 eq) is diluted in 250 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (105.78 mmol, 1.1 eq) is added slowly at 0°C . The mixture is agitated at room temperature during 72 h. Dichloromethane (100 mL) is added and after decantation, the organic layer is washed with deionized water (3 x 50 mL). The residual water is removed under reduced pressure at 60°C for 10 h to give an orange liquid (yield 95%). ^1H NMR δ (acetone- d_6) : 0.90 (t, $J = 6.9$ Hz, 3H, H-16); 1.30-1.53 (m, 10H, H-11-15); 2.24 (m, 2H, H-10); 4.99 (t, $J = 7.5$ Hz, 2H, H-9); 8.13-8.90, 10.09 (m, 7H, H-2-8). RMN ^{19}F δ (acetone- d_6) : -79.90. ^{13}C NMR δ (acetone- d_6) : 14.33 (C-16); 23.24-32.41 (C-10-15); 62.80 (C-9); 121.02 (CF_3 , $J = 321$ Hz); 128.36-150.63 (C-2-8). Water content : 5.6 ppm.

Synthesis of 1-methoxyethylisoquinolinium bromide [MeOEIq][Br]

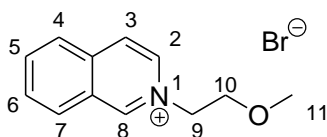


Figure 22 Chemical structure of [MeOEIq][Br]

2-Bromoethyl ethyl ether purified by distillation under reduced pressure (159 mmol, 1.18 eq) is added at 0°C slowly on 1-methylimidazole previously distilled under reduced pressure (135 mmol, 1 eq). The mixture is agitated under argon atmosphere at 40°C for 94 h. The excess of 2-bromoethyl ethyl ether is removed under vacuum at 40°C for 5 h. Acetonitrile (10 mL) is added and after 3.5 h in an ultrasound bath at 25°C, the solvent and volatile impurities are removed under reduced pressure at RT. A beige solid is obtained (yield 97%). ¹H NMR δ (acetone-d₆): 3.39 (s, 3H, H-11); 4.12 (pseudotriplet, *J* = 4.9 Hz, 2H, H-9); 5.32 (pseudotriplet, *J* = 5.0 Hz, 2H, H-10); 8.12-9.09, 10.93 (m, 7H, H-2-8). ¹³C NMR δ (acetone-d₆): 59.06 (C-11); 61.51 (C-9); 71.50 (C-10); 126.50-137.90 (C-2-8).

Synthesis of 1-(1-methoxyethyl)-isoquinolinium bis(trifluoromethyl-sulfonyl)imide [MeOEIq][NTf₂]

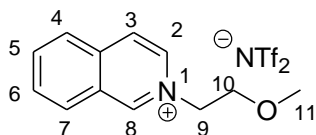


Figure 23 Chemical structure of [MeOEIq][NTf₂]

1-(1-methoxyethyl)-isoquinolinium bromide (130.3 mmol, 1 eq) is diluted in 270 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (145.47 mmol, 1.1 eq) is added slowly. The mixture is agitated at room temperature during 48 h. Dichloromethane (135 mL) is added and after decantation, the organic layer is washed with deionized water (3 x 70 mL). The residual water is removed under reduced pressure at 50°C for 28 h to give a light brown oil (yield 95%). ¹H NMR δ (acetone-d₆): 3.36 (s, 3H, H-11); 4.09 (pseudotriplet, 2H, H-9); 5.14 (pseudotriplet, 2H, H-10); 8.13-8.85, 10.02 (H-2-8). RMN ¹⁹F δ (acetone-d₆): -79.79. ¹³C NMR δ (acetone-d₆): 58.18 (C-11); 61.43 (C-9); 70.20 (C-10); 120.11 (CF₃, *J* = 321 Hz); 126.16-137.79, 150.28 (C-2-8). Water content: 8.53 ppm.

Synthesis of 1-butyl-1H-[1,2,4]triazole

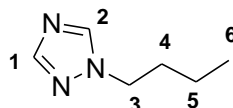


Figure 24 Chemical structure of 1-butyl-1H-[1,2,4]triazole

1,2,4-Triazole (25 g, 361.95 mmol, 1 eq) is diluted at -40°C in a solution of MeONa/MeOH 25% wt. (82.76 mL, 361.95 mmol, 1 eq) and 1-butylbromide (38.87 mL, 361.95 mmol, 1 eq) is added dropwise. The mixture is allowed to come back at RT and agitation is purchased 2h. Then the mixture is agitated at 60°C for 24h. After filtration, the solvent is removed under reduced pressure. The crude is diluted in dichloromethane (120 mL) and washed five times

with deionized water (60 mL). The organic layer is dried with MgSO_4 and the solvent is removed under vacuum. The product is isolated by distillation under vacuum as a colorless liquid (yield 98%). ^1H NMR δ (acetone- d_6) : 0.96 (t, $J = 7.3$ Hz, 3H, H-6); 1.34 (m, 2H, H-5); 1.88 (m, 2H, H-4); 4.26 (t, $J = 7.0$ Hz, 2H, H-3); 7.89 (s, 1H, H-2); 8.36 (s, 1H, H-1). ^{13}C NMR δ (acetone- d_6) : 13.74 (C-6); 20.24 (C-5); 32.59 (C-4); 49.54 (C-3); 144.29 (C-1); 152.27 (C-2).

Synthesis of 1-butyl-3-methyl-1H-[1,2,4]triazolium iodide [BMTriaz][I]

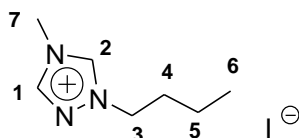


Figure 25 Chemical structure of [BMTriaz][I]

Butyltriazolium (20 g, 159.77 mmol, 1 eq) is diluted in acetonitrile (200 mL) and methyl iodide (18.9 mL, 303.57 mmol, 1.9 eq) is added dropwise. The mixture is agitated at 60°C for 18h. The solvent is removed under reduced pressure and the product is dried under vacuum to give a yellow powder (yield 98%). ^1H NMR δ (acetone- d_6) : 0.98 (t, $J = 7.3$ Hz, 3H, H-6); 1.44 (m, 2H, H-5); 2.07 (m, 2H, H-4); 4.23 (s, 3H, H-7); 4.61 (t, $J = 7.0$ Hz, 2H, H-3); 9.21 (s, 1H, H-2); 10.68 (s, 1H, H-1). ^{13}C NMR δ (acetone- d_6) : 12.54 (C-6); 18.67 (C-5); 29.98 (C-4); 33.93 (C-7); 52.16 (C-3); 145.30 (C-1).

Synthesis of 1-butyl-3-methyl-1H-[1,2,4]triazolium bis(trifluoromethylsulfonyl)imide [BMTriaz][NTf₂]

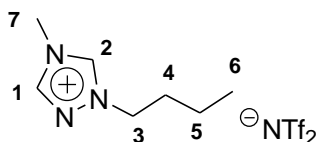


Figure 26 Chemical structure of [BMTriaz][NTf₂]

Butyl-methyl-triazolium iodide (42.68 g, 159.78 mmol, 1 eq) is diluted in deionized water (85 mL) and bis(trifluoromethylsulfonyl)imide (50.46 g, 175.76 mmol, 1.1 eq) is added slowly. The mixture is agitated at room temperature for 48h. Dichloromethane is added (30 mL) and the organic layer is washed with water (3 x 25 mL). The product is dried under vacuum at 40°C for 30h to give a yellow liquid (yield 96%). ^1H NMR δ (acetone- d_6) : 0.96 (t, $J = 7.3$ Hz, 3H, H-6); 1.41 (m, 2H, H-5); 2.02 (t, $J = 7.0$ Hz, 2H, H-4); 4.17 (s, 3H, H-7); 4.56 (t, $J = 7.2$ Hz, H-3); 9.05 (s, 1H, H-2); 9.96 (s, 1H, H-1). RMN ^{19}F δ (acetone- d_6) : -79.95. ^{13}C NMR δ (acetone- d_6) : 13.57 (C-6); 19.84 (C-5); 31.35 (C-4); 34.90 (C-7); 53.01 (C-3); 120.89 (q, $J = 321$ Hz, CF_3) ; 143.66 (C-1); 146.34 (C-2). Water content: 12.6 ppm.

Synthesis of 1-butyl-3-(1,1,2-trifluoro-1-butenyl)-1H-[1,2,4]triazolium bromide

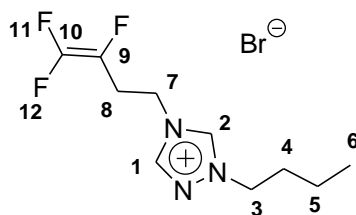


Figure 27 Chemical structure of $[\text{CF}_2\text{CFEBTriaz}][\text{Br}]$

Butyltriazolium (14.29 g, 114.16 mmol, 1 eq) and 4-bromo-1,1,2-trifluoro-1-butene (22.65 g, 119.87 mmol, 1.05 eq) is added dropwise at 0°C . The mixture is agitated at 85°C for 24h. The conversion rate stagnates after 24h so the excess of reagents is removed under reduced pressure at 60°C for 16h. Acetonitrile (10 mL) is added and the flask is placed in an ultrasound bath for 1h. The product is dried under vacuum with vigorous stirring for 2h to give a white powder (yield 93%). ^1H NMR δ (acetone- d_6): 1.00 (t, $J = 7.3$ Hz, 3H, H-6); 1.45 (m, 2H, H-5); 2.05 (m, 2H, H-4); 3.35 (m, 2H, H-8); 4.64 (t, $J = 7.1$ Hz, 2H, H-3); 4.87 (t, $J = 6.9$ Hz, 2H, H-7); 9.59 (s, 1H, H-2); 11.76 (s, 1H, H-1). RMN ^{19}F δ (acetone- d_6): -175.76 (dd, $J = 32.8, 114.0$ Hz, F-9); -122.95 (dd, $J = 83.3, 114.0$ Hz, F-12); -104.02 (dd, $J = 32.8, 83.3$ Hz, F-11). ^{13}C NMR δ (acetone- d_6): 13.67 (C-6); 19.98 (C-5); 27.75 (dd, $J = 2.4, 21.0$ Hz, C-8); 30.62 (C-4); 45.18 (C-7); 52.94 (C-3); 144.42 (C-1); 145.60 (C-2).

Synthesis of 1-butyl-3-(1,1,2-trifluoro-1-butenyl)-1H-[1,2,4]triazolium bis(trifluoromethylsulfonyl)imide $[\text{CF}_2\text{CFEBTriaz}][\text{NTf}_2]$

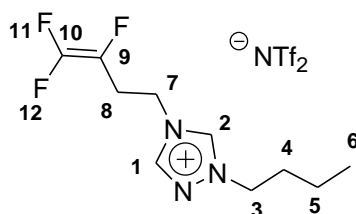


Figure 28 Chemical structure of $[\text{CF}_2\text{CFEBTriaz}][\text{NTf}_2]$

1-Butyl-3-(1,1,2-trifluoro-1-butenyl)-1H-[1,2,4]triazolium bromide (33.52 g, 106.70 mmol, 1 eq) is diluted in 57 mL of deionized water and lithium bis(trifluoromethylsulfonyl)imide (33.69 g, 117.37 mmol, 1.1 eq) is added and the mixture is agitated at room temperature during 72h. Dichloromethane (30 mL) is added and the organic layer is washed three times with deionized water (25 mL). The solvent is removed under reduced pressure and the product is dried under vacuum at 60°C for 24h to give a viscous pale yellow liquid (yield 95%). ^1H NMR δ (acetone- d_6): 1.05 (t, $J = 7.3$ Hz, 3H, H-6); 1.49 (m, 2H, H-5); 2.11 (m, 2H, H-4); 3.30 (m, 2H, H-8); 4.66 (t, $J = 7.1$ Hz, 2H, H-3); 4.90 (t, $J = 6.9$ Hz, 2H, H-7); 9.31 (s, 1H, H-2); 10.21 (s, 1H, H-1). RMN ^{19}F δ (acetone- d_6): -176.36 (dd, $J = 32.8, 114.0$ Hz, F-9); -122.96 (dd, $J = 83.3, 114.0$ Hz, F-12); -103.62 (dd, $J = 32.8, 83.3$ Hz, F-11); -79.95 (CF_3). ^{13}C NMR δ (acetone- d_6): 13.47 (C-6); 19.80 (C-5); 27.75 (dd, $J = 2.4, 21.6$ Hz, C-8); 31.22 (C-4); 45.27 (C-7); 53.31 (C-3); 120.83 (q, $J = 321$ Hz, CF_3); 143.23 (C-1); 145.53 (C-2); 124.48-128.53, 150.69-158.74 (C-9,10). Water content: 26.9 ppm.