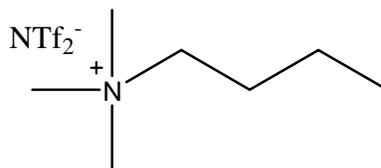


Supporting information

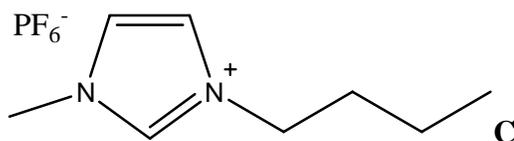
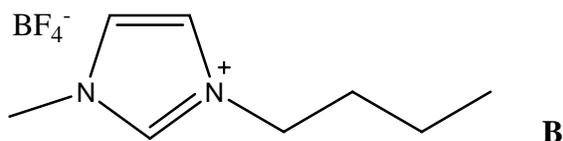
Synthesis

N-trimethyl-*N*-butylammonium bis(trifluoromethylsulfonyl)imide [tmba][NTf₂] (**A**)

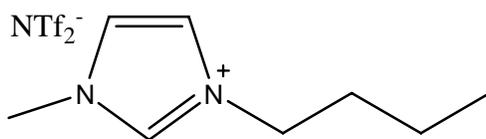


In a sealed flask, to one equivalent of chlorobutane was added 2 equivalents of trimethylamine (45wt% aqueous solution) and the minimum volume of acetonitrile in order to obtain a monophasic reaction medium. The flask was heated up to 70°C for one night. After elimination of volatiles and solvents under vacuum, the residue was washed with diethyl ether and recrystallised from acetone leading to a white solid. It was dissolved in the minimum of distilled water and 1.1 equivalents of lithium bis(trifluoromethylsulfonyl)imide as well. The two water solutions were mixed. After 2 hours of stirring at room temperature, the [tmba][NTf₂] was extracted with methylene chloride and this last solution dried with Na₂SO₄. Solvent was removed by vacuum distillation giving a water like free flowing liquid which was dried under high vacuum at 60°C for 3 hours. *Yield*: 85%. ¹H NMR (300 MHz, Acetone-d₆) δ: 0.95 (t, 3H); 1.40-1.59 (m, 2H); 1.88-2.11 (m, 2H); 3.42 (s, 9H); 3.60-3.75 (m, 2H). ¹³C RMN (75 MHz, Acetone-d₆) δ: 14.1; 20.6; 25.8; 53.9 (t, J_{C-N}= 4.1 Hz); 67.7; 121.8 (q, J_{CF}=321.0 Hz). ¹⁹F RMN (376 MHz, Acetone-d₆): δ -80.3. HRMS(FAB) for (2C⁺, NTf₂⁻)⁺: Calculated 512.2051, Found 512.2069

1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] (**B**) and *1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆]* (**C**) are commercially available from Merck KGaA and were used without further purification. The other ionic liquids were synthesized according to protocols developed in the laboratory.

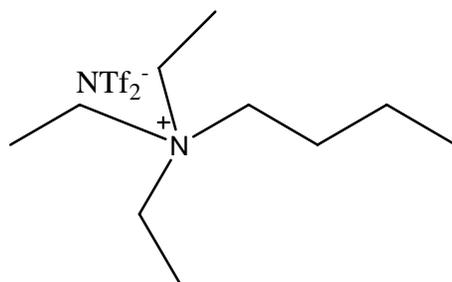


1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**D**)



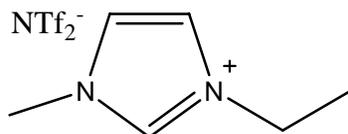
0.1 mole (8.21g) of freshly distilled 1-methylimidazole was mixed, under argon with 1 equivalent (9.26g) of 1-chlorobutane in a sealed flask which was then heated up to reflux temperature for 3 days. After cooling, the product was washed 3 times with 20 ml of hot ethyl acetate. The salt was purified by recrystallisation in a 1/1 mixture of acetonitrile/ethyl acetate to give 14.1g of product of a white powder. 0.05 mole of this product (8.725g) was dissolved in 75 ml water. 0.055 mole (15.77 g) of powdered lithium bis(trifluoromethylsulfonyl)imide was added to the mixture. The ionic liquid **D** immediately separated from the aqueous phase. After decantation and washing with distilled water, **D** (20.5g) was dried under vacuum for several hours at 60°C. Yield: 98%. ¹H NMR (300 MHz, Acetone d₆), δ: 0.96 (t, 3H, J= 7.3Hz); 1.30 (m, 2H); 1.95 (m, 2H), 4.02 (s, 3H); 4.32 (t, J = 7.3 Hz, 2 H); 7.70 (m, 2 H); 8.94 (s, 1H); ¹³C NMR (50.32 MHz, Acetone d₆), δ: 13.6 ; 19.9 ; 32.7 ; 36.6, 50.3 ; 119.7 (q, J_{C-F} = 321.2 Hz) ; 123.4 ; 124.8 ; 137.3. HRMS(FAB) for (2C⁺, NTf₂⁻)⁺: Calculated 558.1643, Found 558.1640

N-triethyl-N-butylammonium bis(trifluoromethylsulfonyl)imide (**E**)



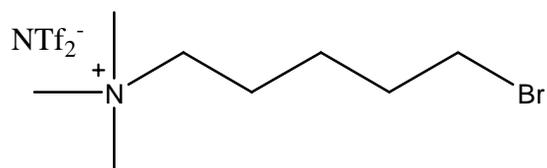
The same protocol as for [tmba][NTf₂] **A** was applied except that trimethylamine was replaced by triethylamine. Yield: 83% ; ¹H NMR (300MHz, acetone d₆), δ : 1.02 (t, J=7.3Hz, 3H) ; 1.40-1.50 (m, 11H) ; 1.70-1.90 (m, 2H) ; 3.30-3.60 (m, 8H) ; ¹³C NMR: (50MHz, acetone d₆), δ : 6.48 ; 12.59 ; 19.05 ; 22.97 ; 52.43 ; 56.40 ; 119.77 (q, J_{CF}=320.0Hz). HRMS(FAB) for (2C⁺, NTf₂⁻)⁺ Calculated 596.2985, Found 596.2975

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**F**)



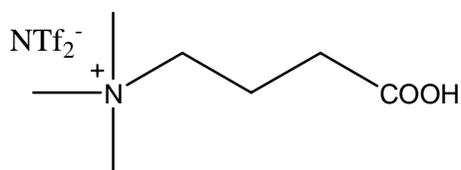
The same protocol as for **D** was used except that 1-chlorobutane was replaced by 1-chloroethane. ¹H NMR (300MHz, acetone-d₆) δ : 9.10 (s, 1H), 7.78 (t, 1H, J = 2.2 Hz), 7.71 (t, 1H, J = 2.2 Hz), 4.39 (q, 2H, J = 9.3 Hz), 4.05 (s, 3H), 1.56 (t, 3H, J = 9.0 Hz). ¹³C NMR: (50MHz, acetone d₆), δ : 136.52, 124.22, 122.52, 120.62(q, J_{c-F} = 319.9 Hz), 45.22, 36.06, 14.99. ¹⁹F-NMR (Acetone-d₆, δ(ppm) relative to CFCl₃): -79.80. HRMS(FAB) for C₁₄H₂₂N₅S₂O₄F₆ [2C⁺, NTf₂⁻]⁺ Calcd: 502,1017, Found: 502, 1013.

N-bromopentyl-N-trimethyl bis(trifluoromethylsulfonyl)imide (**G**)

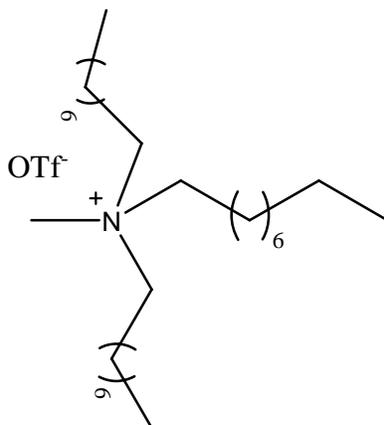


0.6 mol (41 ml) of 45% aqueous solution of trimethylamine was introduced in a flask and heated at 40°C. The vapours of trimethylamine were dried by flowing through a glass tube filled up with KOH pellets and transferred to a flask containing 0.2 mol of dibromopentane in 100 ml of anhydrous THF under stirring. After reaction, the solid was filtered and washed with ether. The white solid was drying under vacuum. Anion metathesis was achieved with the same protocol as **D**. Yield: 84%; ¹H NMR (300MHz, acetone d₆) δ: 1.40-1.70 (m, 2H); 1.90-2.20 (m, 4H); 3.35 (s, 9H); 3.50-3.70 (m, 4H); ¹³C NMR (50MHz, acetone d₆) δ: 23.13; 25.86; 33.24; 34.58; 54.06 (t, J_{C-N}= 4.0Hz); 67.65; 121.37 (q, J_{CF}= 320.9Hz). HRMS(FAB) for [2C⁺, NTf₂⁻]⁺: Calcd: 696.0575, Found: 696.0588

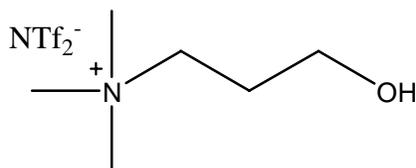
3-carboxy-propyl-N-trimethylammonium bis(trifluoromethylsulfonyl)imide (H)



A aqueous solution of 0.2 mol of trimethylamine (30 ml at 6.65M) and 0.1 mol of 1-bromobutyrate (14.3ml) was refluxed for 24hours. The solvent was eliminated under vacuum and a white solid was obtained after washing with ether (3 times). The solid was dissolved in 15 ml of bromhydric acid solution (6N) and was refluxed for 12hours. The solvent was eliminated under vacuum and a white solid was obtained after washing with ether (3 times) and drying under vacuum. To a solution of this salt (17.7 mmol) in water (10ml) was added 19.5 mmol of LiNTf₂ solubilized in water (10ml). After 2 hours of reaction at room temperature, the two phases were separated. The ionic liquid phase was extracted with methylene chloride. After elimination of solvents under vacuum, the product **H** was dried under vacuum. Yield: 88%; NMR ¹H (200MHz, Acetone d₆) δ: 2.15-2.30 (m, 2H); 2.5 (t, J= 6.7Hz, 2H); 3.40 (s, 9H); 3.55-3.70 (m, 2H); NMR ¹³C (50MHz, Acetone d₆) δ: 19.52; 23.73; 54.09 (t, J_{C-N}= 4.0Hz); 67.02 (t, J_{C-N}= 3.0Hz); 118.4(q C-F, J = 324,0 Hz); 172.89. HRMS(FAB) for (2C⁺, NTf₂⁻)⁺ Calculated 572.1530, Found 572.1534

N-methyl-*N*- trioctylammonium trifluoromethanesulfonate (**I**)

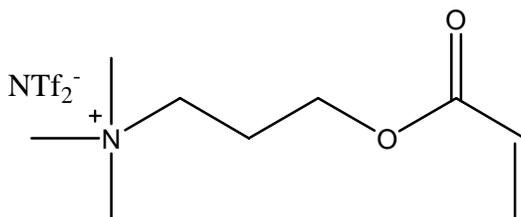
A solution of Aliquat 336 (Sigma Aldrich, 10mmol) in H₂O (50mL) and a solution of Ba(TfO)₂ (12mmol) in H₂O (50mL) were mixed with stirring at RT. After 2 h, CH₂Cl₂ (100mL) were added and the aqueous solution was washed with CH₂Cl₂ (2 x 30mL). The organic layers were combined and evaporated. The liquid salt was dried for 4h at 100°C at a pressure of 0.05mmHg to afford [Oct₃NMe][TfO] (92%) as a pale yellow liquid. ¹H NMR (300MHz acetone-*d*₆): 0.88(t, 9H, J = 6.7Hz), 1.25-1.55(m, 36H), 1.89(m, 6H), 3.25 (s, 3H), 3.44-3.55(m, 6H). ¹³C (Acetone-*d*₆): 14.08, 22.32, 22.89, 26.50, 32.06, 32.18, 54.18, 61.71, 121.46, (q, J = 319.5Hz), 122.48. ¹⁹F (Acetone-*d*₆): -79.37. HRMS(FAB) for [2C⁺, TfO⁻]: Calculated 922.7484, Found 922.7469.

(3-hydroxy-propyl)-trimethylammonium bis(trifluoromethylsulfonyl)imide (**J**)

The same protocol used for [tmba][NTf₂] was applied except that chlorobutane was replaced by 1-chloropropan-3-ol. Clear oil. Yield: 90%. ¹H NMR (200 MHz, Acetone-*d*₆) δ: 3.35 (s, 9H); 4.14-4.40 (m, 2H); 4.05-4.63(m, 2H). ¹³C RMN (50MHz, Acetone *d*₆): 29.14 ; 54.27 (t ; J_{C-N}=4.1Hz) ; 60.05 ;

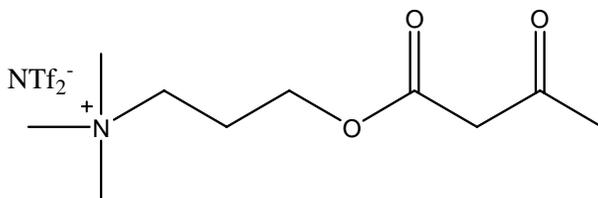
66.09 ; 121.05 (q, $J_{CF}=321.2\text{Hz}$). HRMS(FAB) for $(2\text{C}^+, \text{NTf}_2^-)^+$ *Calculated 516.1631, Found 516.1623*

(3-acryloyloxy-propyl)-trimethylammonium bis(trifluoromethylsulfonyl)imide (K)



To 1 equivalent of (**J**) dissolved in acetonitrile were added 2 equivalents of acryloyl chloride and 5 equivalents of potassium carbonate. After 3 hours at 80°C, solvent and excess of acryloyl chloride were removed in vacuo. The residue was then washed with diethyl ether, in order to eliminate traces of acryloyl chloride. The residue was triturated with methylene chloride and the potassium carbonate was filtrated. Methylene chloride was removed under vacuum yielding a clear oil. *Yield: 90%. ¹H NMR (200 MHz, Acetone-*d*₆) δ: 2.22- 2.25 (m, 2H) ; 3.25 (s , 9H) ; 3.60-3.75 (m, 2H) ; 4.15 (t, 2H, J= 6,0Hz) ; 5.80(dd, 1H, J₁=1.9 Hz, J₂=10.7 Hz) ; 6.05 (dd, 1H, J₁=17.2 Hz, J₂=10.7 Hz) ; 6.15 (dd, 1H, J₁=1.9 Hz, J₂=17.2 Hz).* HRMS(FAB) for C⁺ *Calculated 172.1338, Found 172.1346*

(3-acetoacetoxy-propyl)-trimethylammonium bis(trifluoromethylsulfonyl)imide (L)



To one equivalent of (**J**) dissolved in acetonitrile were added 1,1 equivalent of diketene. Then, the solution was heated up to 100°C for 3 hours. Afterwards, solvent was eliminated under vacuum and excess of diketene was eliminated by washing with ether. *¹H NMR (200 MHz, Acetone-*d*₆) δ: 2.01-2.19*

(m, 2H), 2.35(s, 3H), 3.02(s, 9H), 3.19-3.27(m, 2H), 3.44(s, 2H), 4.02 (t, 2H). ¹³C NMR (50MHz, Acetone-d₆) δ: 24.02, 28.84, 50.32, 54.21, 60.12, 64.52, 166.98, 200.27

Characterisation of RTIL

All ionic liquids used in this paper were saturated in water. We decided to work with saturated ionic liquids to be sure that the water content is equivalent in macro or micro scale. Otherwise, as we worked with tiny droplets, we assumed that the high ratio surface/volume could lead to a very quick absorption of water.

For the RTIL and TSIL used in Figure 2 (electrowetting curves), we measured the water content by Karl Fisher. The RTIL were dissolved in methanol, with a known water content. One mL of this solution was injected in a Coulometric Karl Fisher Titrator (GRScientific). All measurements were repeated at least 5 times.

[tmba][NTf ₂]	[bmim][BF ₄]	[bmim][PF ₆]	[bmim][NTf ₂]	[C ₁₀ H ₂₀ NO ₃][NTf ₂]	[C ₉ H ₁₇ NO ₂][NTf ₂]
2952 ppm	13250 ppm	3329 ppm	1528 ppm	16943 ppm	12349 ppm

Comparison of the obtained molecular ions in macro and micro scale by ESI/MS

	Compound	Theoretical m/z (amu)	Found m/z (amu)	MS2 ^(b)	MS3
Macro scale	4a	486.24	486.55	427.36	369.18
Micro scale			486.55	428.27	370.18
Macro scale	4b	519.16	519.08-521.04 ^(a)	461.18	403.09
Micro scale			519.06-521.04 ^(a)	462.00	-
Macro scale	4c	441.25	441.18	382.27	324.18
Micro scale			441.18	382.18	324.27
Macro scale	7a	486.24	486.12	427.27	369.18
Micro scale			486.12	427.27	369.18
Macro scale	7b	519.16	519.06-521.02 ^(a)	461.18	403.09
Micro scale			519.06-521.02 ^(a)	461.18	403.09

(a) For those compounds, two isotopes were obtained due to the Br atom

(b) This ion corresponds to the departure of the N(Me)₃ fragment