

Electronic Supplementary Information (ESI)

Fluorine-functionalized ionic liquids with high oxygen solubility

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General

1-(2-Chloroethyl)piperidine hydrochloride (98%), 1-(2-chloroethyl)pyrrolidine hydrochloride (98%), 2-chloro-N,N-diethylethylamine hydrochloride (99%), iodomethane (99%), 2,2,2-trifluoroethanol (99+%), 4,5,5,-octafluoro-1-pentanol (98%), hexafluorobutanoic acid (97+%) and heptadecafluorononanoic acid (97%) were obtained from Sigma-Aldrich (Diegem, Belgium). Lithium bis(trifluoromethylsulfonyl)imide (99%) was obtained from IoLiTec (Heilbronn, Germany). All chemicals were used as received without any further purification. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^1H , 75 MHz for ^{13}C). The ^{19}F spectra were recorded at a Bruker AMX 400 spectrometer (operating at 376 MHz for ^{19}F). The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ^1H and ^{13}C . All solutions were made in CDCl_3 or DMSO-d_6 . The spectra were analyzed with SpinWorks software. The Fourier Transform Infrared (FTIR) spectrum of the IL was recorded by a Bruker Vertex 70 spectrometer via the attenuated total reflectance (ATR) technique with a Bruker Platinum ATR accessory. The OPUS software package was used for analysis of the FTIR spectra. Thermogravimetric analysis (TGA) was performed using a TA instruments TGA Q500. CHN analysis (carbon, hydrogen, nitrogen) was performed on a CE Instruments EA-1110 element analyzer (Interscience, Louvain-la-Neuve, Belgium). It must be mentioned that it is very difficult to obtain reproducible CHN results for the highly fluorinated ionic liquids, even when a combustion catalyst was added to the compounds. Especially the value for hydrogen showed a lot of scattering between different measurements. For ionic liquids 3a, 3b and 4a no reproducible CHN results could be obtained. However, all other analytical evidence showed that these compounds were pure.

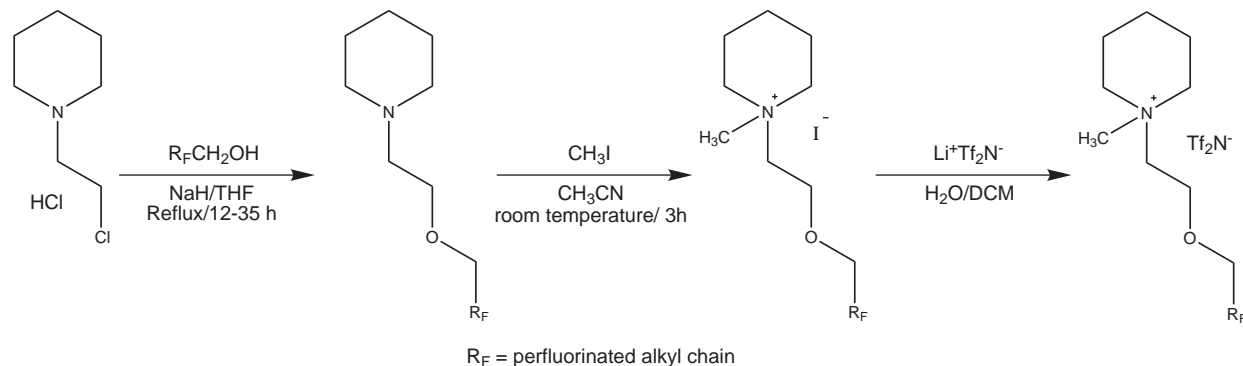


Figure S1: General reaction scheme for the synthesis of fluorinated cations. The synthesis illustrated for the example of the piperidine precursor.

Synthesis and characterization

For the synthesis of the fluorinated cations a general synthetic procedure was followed: (1) synthesis of the fluorinated amino ether, (2) synthesis of the iodide salt and (3) preparation of the final Tf_2N^- product by a metathesis reaction with $\text{Li}^+\text{Tf}_2\text{N}^-$. The first step, the synthesis of the fluorinated amino ether was based on a modification of a procedure described by Kim *et al.*¹ Instead of 1.25 equivalents of NaH, we found that 1.5 to 1.8 equivalents gave higher yields. The workup was done by column chromatography with $\text{Et}_2\text{O}:\text{MeOH}$ (95:5) as the eluent; the fluorinated amino ether eluted in the last fraction. For the second step, the formation of the iodide salt, the fluorinated ether was dissolved in acetonitrile and cooled down in an icebath. Iodomethane (1 eq.) was added to the solution in small portions. After addition, the reaction mixture was stirred for 3 hours or until the amine has reacted completely, as monitored via TLC analysis. After reaction, the solvent was evaporated to give the pure iodide ionic liquid. The third and final step was the transformation of the iodide ionic liquid into the bis(trifluoromethylsulfonyl)imide ionic liquid. Therefore the iodide salt was dissolved in 30 mL of water and mixed with a water solution of lithium bis(trifluoromethylsulfonyl)imide (1.5 eq.) causing an immediate formation of an ionic liquid phase on the bottom of the flask. After stirring for 30 minutes, dichloromethane was added. The organic phase was separated and washed with 50 mL of distilled water. After the AgNO_3 test on the washing water gave

a negative result for iodide ions, the solvent was evaporated to yield a pure ionic liquid. The detailed synthesis and characterization of precursor molecules and ionic liquids is described below.

Precursor molecules

Precursors for IL 1a

***N*-((trifluoroethoxy)ethyl)piperidine** Sodium hydride (3.33 g, 139.0 mmol) in dry tetrahydrofuran (60 mL) was cooled down to 0 °C. 2,2,2-Trifluoroethanol (7.93 mL, 108.6 mmol) was added dropwise and the mixture was stirred at room temperature for 1 hour. Subsequently, 1-(2-chloroethyl)piperidine hydrochloride (20.0 g, 108.6 mmol) was added and the mixture was stirred for an additional 1 hour at room temperature. Afterwards, the mixture was stirred at 78 °C for 11 hours and at 65 °C for 23 hours. After this time, water was added to the mixture and the product was extracted with dichloromethane and a redish oil was obtain. Dissolution of the oil in dichloromethane and filtration yielded the unreacted piperidine substrate that was filtered off and an oil that was purified on silica gel. Two subsequent column chromatography purifications were applied. First one in pure dichloromethane and thereafter one in 20% heptane/ethyl acetate to yield a slightly yellow oil. Some of the product was lost on solvent evaporation, a mass of 4.05 g and yield 12% was obtained. The synthesis of this compound was based on the procedure from the paper of Kim *et al.*¹ ¹H NMR (300 MHz, CDCl₃): δ = 3.86 (q, 2H), 3.74 (q, 2H), 2.58 (t, 2H), 2.43 (t, 4H), 1.58 (m, 4H), 1.44 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 119.9 (q), 70.5 (s), 68.5 (q), 58.4 (s), 54.9 (s), 25.9 (s), 24.2 (s) ppm.

***N*-((Trifluoroethoxy)ethyl)-*N*-methylpiperidinium iodide** *N*-((trifluoroethoxy)ethyl)-piperidine (4.47 g, 22.7 mmol) was dissolved in 150 mL of acetonitrile and cooled down in an ice bath. Iodomethane (1.41 mL, 22.7 mmol) was added in small portions to the solution. After addition the reaction mixture was stirred for 3 hours or until *N*-((trifluoroethoxy)ethyl)piperidine reacted completely, as monitored via thin-layer chromatography. ¹H NMR

(300 MHz, CDCl₃): δ = 4.13 (m, 2H), 4.06 (q, 2H, J = 8.9 Hz), 3.64 (t, 2H, J = 4.0 Hz), 3.41 (m, 4H), 3.12 (s, 3H), 1.89 (t, 4H, J = 5.2 Hz), 1.65 (m, 2H) ppm.

Precursors for IL 1b

***N*-((2,2,3,3,4,4,5,5,-octafluoropentoxy)ethyl)piperidine** Sodium hydride (4.0 g of 60% suspension, 100 mmol) in dry tetrahydrofuran (60 mL) was cooled down to 0 °C. 2,2,3,3,4,4,5,5,-Octafluoro-1-pentanol (7.73 mL, 55.5 mmol) was added dropwise and the mixture was stirred at room temperature for 1 hour. Subsequently, *N*-(2-chloroethyl)piperidine hydrochloride (10.23 g, 55.5 mmol) was added and the mixture was stirred for one additional hour at room temperature. Afterwards, the mixture was refluxed at 78 °C for 3 hours and at 65 °C overnight. After this time, water was added to the mixture and the product was extracted with diethyl ether. The residue was chromatographed on silica gel in diethyl ether. A second column chromatography step was needed to purify the product. ¹H NMR (300 MHz, CDCl₃): δ = 6.08 (tt, 1H, J_1 = 51.8 Hz, J_2 = 5.3 Hz), 4.24 (t, 2H, J = 13.9 Hz), 4.15 (t, 2H, J = 5.8 Hz), 4.12 (t, 2H, J = 5.8 Hz), 3.92 (m, 4H), 3.84 (m, 4H), 2.33 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 115.5 (m), 109.3 (m), 107.6, 105.9, 70.8 (s), 67.7 (t), 58.3 (s), 54.9 (s), 25.9 (s), 24.2 (s) ppm.

***N*-((2,2,3,3,4,4,5,5,-octafluoropentoxy)ethyl)-*N*-methylpiperidinium iodide** *N*-((2,2,3,3,4,4,5,5,-octafluoropentoxy)ethyl)piperidine (6.20 g, 18.0 mmol) was dissolved in 100 mL of acetonitrile and cooled down in an ice bath. Iodomethane (1.12 mL, 18.0 mmol) was added in small portions. After addition the reaction mixture was stirred for 3 hours. Subsequently the solvent was evaporated to give a yellow solid in a quantitative yield. ¹H NMR (300 MHz, methanol-*d*₄): δ = 6.59 (tt, 1H, J_1 = 51.2 Hz, J_2 = 5.7 Hz), 4.20 (t, 2H, J = 13.6 Hz), 4.14 (br t, 2H), 3.73 (t, 2H, J = 4.50 Hz), 3.48 (m, 4H), 3.18 (s, 3H), 1.95 (m, 4H), 1.73 (m, 2H) ppm.

Precursors for IL 2a

***N*-((Trifluoroethoxy)ethyl)pyrrolidine** Sodium hydride, 60% suspension in mineral oil (4.34 g, 106 mmol) in dry tetrahydrofuran (60 mL) was cooled down to 0 °C. 2,2,2-Trifluoroethanol (4.30 mL, 59 mmol) was added dropwise and the mixture was stirred at room temperature for 1 hour. Subsequently, 1-(2-chloroethyl)pyrrolidine hydrochloride (10.0 g, 59 mmol) was added and the mixture was stirred for one additional hour at room temperature. Afterwards, the mixture was stirred at 70 °C for 18 hours. After this time, water was added to the mixture and the product was extracted with diethyl ether. After evaporation of the solvents, the crude product was re-dissolved in diethyl ether and purified by chromatography on a silica gel column resulting in a yellow oil with a mass of 2.59 g and a yield of 22%. ¹H NMR (300 MHz, CDCl₃): δ = 3.86 (q, 2H, J = 8.7 Hz), 3.76 (t, 2H, J = 5.8 Hz), 2.57 (t, 2H, J = 5.8 Hz), 2.57 (m, 4H), 1.79 (m, 4H) ppm.

***N*-((Trifluoroethoxy)ethyl)-*N*-methyl pyrrolidinium iodide** *N*-((Trifluoroethoxy)ethyl)pyrrolidine (5.18 g, 26.2 mmol) was dissolved in acetonitrile and cooled to 0 °C in an ice bath. Iodomethane (1.63 mL, 26.2 mmol) was added in small portions. The resulting solution was stirred at room temperature for 3 hours. Evaporation of the solvent yielded a dark orange solid with a mass of 7.74 g and a yield of 87%. ¹H NMR (300 MHz, D₂O): δ = 4.11 (broad t, 2H), 4.04 (q, 2H, J = 8.9 Hz), 3.64 (t, 2H, J = 4.5 Hz), 3.56 (m, 4H), 3.08 (s, 3H), 2.20 (m, 4H) ppm.

Precursors for IL 2b

***N*-((2,2,3,3,4,4,5,5,-octafluoropentoxy)ethyl)pyrrolidine** Sodium hydride (2.20 g, 91.9 mmol) in dry tetrahydrofuran (60 mL) was cooled down to 0 °C. 2,2,3,3,4,4,5,5-Octafluoro-1-pentanol (10.23 mL, 73.52 mmol) was added dropwise and the mixture was stirred at room temperature for 1 hour. Subsequently *N*-(2-chloroethyl)pyrrolidine hydrochloride (12.50 g, 73.52 mmol) was added and the mixture was stirred for an additional hour at room temperature. Next the mixture was refluxed at 70 °C for 2 hours and at 65 °C for 22 hours. After this

time, water was added to the mixture and the product was extracted with dichloromethane. The dichloromethane phase was dried with MgSO_4 . The residue was purified by chromatography on a silica gel column in ethyl acetate. Further purification was done using a second column chromatography step using 7:3 heptane:ethyl acetate as eluent. This resulted in a yellow oil with a mass of 5.24 g and a yield of 21%. The synthesis of this compound was based on the procedure from the paper of Kim *et al.*¹ ^1H NMR (300 MHz, CDCl_3): $\delta = 6.12$ (tt, 1H), 3.98 (t, 2H), 3.74 (t, 2H), 2.71 (t, 2H), 2.55 (m, 4H), 1.78 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 118.1$ (m), 115.3 (m), 113.0 (m), 110.9 (m), 110.2 (m), 107.7 (m), 105.2 (m), 72.2 (s), 67.7 (t), 55.3 (s), 54.6 (s), 23.5 (s) ppm.

***N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-*N*-methylpyrrolidinium iodide** *N*-((2,2,3,3,4,4,5,5,-octafluoropentoxy)ethyl)pyrrolidine (4.10 g, 12.4 mmol) was dissolved in 150 mL of acetonitrile and cooled down in an ice bath. Iodomethane (0.98 mL, 12.4 mmol) was added in small portions to the solution. After addition, the reaction mixture was stirred for 3 hours or until *N*-((2,2,3,3,4,4,5,5,-octafluoropentoxy)ethyl)pyrrolidine reacted completely, as monitored via thin-layer chromatography. After evaporation of the solvent, the pure iodide ionic liquid was obtained with a mass of 5.60 g and a yield of 96%. ^1H NMR (300 MHz, CDCl_3): $\delta = 6.07$ (tt, 1H), 4.23 (t, 2H), 4.13 (m, 4H), 3.88 (m, 4H), 3.35 (s, 3H), 2.32 (m, 4H) ppm.

Precursors for IL 3a

***N,N*-diethyl-*N*-((trifluoroethoxy)ethyl)amine** Sodium hydride, 60% suspension in mineral oil (3.22 g, 80.5 mmol) in dry tetrahydrofuran (25 mL) was cooled down to 0 °C. 2,2,2-trifluoroethanol (4.70 mL, 64.4 mmol) was added dropwise and the mixture was stirred at room temperature for 1 hour. Subsequently, (2-chloroethyl)-*N,N*-diethylammonium hydrochloride (11.08 g, 64.4 mmol) was added and the mixture was stirred for one additional hour at room temperature. Afterwards, the mixture was stirred at 78 °C for 3 hours and at 70 °C for 17 hours. After this time, water was added to the mixture and the product was

extracted with diethyl ether, to give a light yellow oil. A column chromatography step (100% diethyl ether) gave an impure product as the last fraction. A second column chromatography step (2% ethanol/dichloromethane) was applied to yield the product as a transparent oil. Some product was lost on solvent evaporation and a total mass of 4.05 g and a yield of 12% was obtained. ^1H NMR (300 MHz, CDCl_3): $\delta = 3.86$ (q, 2H, $J = 8.6$ Hz), 3.70 (t, 2H, $J = 5.5$ Hz), 2.69 (t, 2H, $J = 5.8$ Hz), 2.59 (q, 4H, $J = 6.7$ Hz), 1.04 (t, 6H, $J = 6.7$ Hz) ppm.

***N,N*-diethyl-*N*-methyl-*N*-((trifluoroethoxy)ethyl)ammonium iodide** A solution of *N,N*-diethyl-*N*-((trifluoroethoxy)ethyl)amine (0.63 g, 3.16 mmol) in ethanol, remaining from the column chromatography, and acetonitrile was cooled down in an ice bath. Then iodomethane (0.12 mL, 3.16 mmol) was added dropwise. After the addition, the ice bath was removed and the solution was stirred at room temperature for 3 hours. Evaporation of the solvent gave a yellow oil in a quantitative yield. ^1H NMR (300 MHz, CDCl_3): $\delta = 4.27$ (t, 2H, $J = 4.4$ Hz), 4.05 (q, 2H, $J = 8.5$ Hz), 3.97 (t, 2H, $J = 4.4$ Hz), 3.67 (q, 4H, $J = 7.2$ Hz), 3.34 (s, 21H), 1.43 (t, 6H, $J = 7.2$ Hz) ppm.

Precursors for IL 3b

***N,N*-diethyl-*N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)amine** Sodium hydride, 60% suspension in mineral oil (2.20 g, 55.0 mmol) in dry tetrahydrofuran (60 mL) was cooled down to 0 °C. 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (5.67 mL, 40.8 mmol) was added dropwise and the mixture was stirred at room temperature for 1 hour. Subsequently, (2-chloroethyl)-*N,N*-diethylammonium hydrochloride (8.12 g, 40.8 mmol) was added and the mixture was stirred for one additional hour at room temperature and for 16 hours at 73 °C. After this time, water was added to the mixture and the product was extracted with diethyl ether. After evaporation of the solvent, the crude product was re-dissolved in diethyl ether and purified by chromatography on two subsequent columns in diethyl ether. A yellow oil was obtained with a mass of 2.70 g and a yield of 20%. ^1H NMR (300 MHz, CDCl_3): $\delta = 6.11$ (tt, 1H, $J_1 = 51.7$ Hz, $J_2 = 5.6$ Hz), 3.97 (t, 2H, $J = 13.9$ Hz), 3.68 (t, 2H, $J = 5.8$ Hz),

2.67 (t, 2H, $J = 5.9$ Hz), 2.56 (q, 2H, $J = 6.9$ Hz), 1.02 (t, 6H, $J = 6.9$ Hz) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 115.5$ (m), 111.0 (m), 107.7 (t), 105.2 (t), 71.7 (s), 67.8 (t), 52.3 (s), 47.6 (s), 11.7 (s) ppm.

***N,N*-diethyl-*N*-methyl-*N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)ammonium iodide** *N,N*-diethyl-*N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)amine (2.70 g, 8.15 mmol) was dissolved in acetonitrile and cooled down in an ice bath. Iodomethane (0.51 mL, 8.15 mmol) was added in small portions to the solution. After addition the reaction mixture was stirred for 3 hours or until the substrates have reacted completely, as monitored via thin-layer chromatography. Subsequently, the solvent was evaporated to obtain the pure iodide ionic liquid with a mass of 3.85 g and a yield of 99%. ^1H NMR (300 MHz, D_2O): $\delta = 6.43$ (tt, 1H, $J_1 = 51$ Hz, $J_2 = 5.8$ Hz), 4.13 (t, 2H, $J = 14.3$ Hz), 4.02 (br, 2H), 3.50 (t, 2H, $J = 3.8$ Hz), 3.35 (q, 4H, $J = 7.1$ Hz), 2.95 (s, 3H), 1.25 (t, 6H, $J = 7.1$ Hz) ppm.

Precursors for IL 4b

Potassium heptadecafluorononanoate Heptadecafluorononanoic acid (13.94 g, 30.0 mmol) was dissolved in ethanol (50 mL) and KOH (1.68 g, 30.0 mmol) dissolved in a minimal amount of water was added. After 1 hour of stirring or when the pH of the solution reached approx. 7.5 (as tested with a pH indicator strip), the solvents were carefully evaporated (foaming occurred upon evaporation). The solid product was dried overnight in a vacuum oven at 50°C and a white solid was obtained in a quantitative yield.

Fluorinated ionic liquids

1a: *N*-((trifluoroethoxy)ethyl)-*N*-methylpiperidinium bis(trifluoromethylsulfonyl)imide

N-((trifluoroethoxy)ethyl)-*N*-methylpiperidinium iodide (7.66 g, 21.7 mmol) was dissolved in 30 mL of water and mixed with a water solution of lithium bis(trifluoromethylsulfonyl)imide (6.85 g, 23.8 mmol) causing an immediate occurrence of an ionic liquid phase on the

bottom of the flask. After stirring for 30 minutes, dichloromethane was added, the organic phase was separated and washed with 50 mL of distilled water. The AgNO_3 test performed on the last water portion from the washing gave a negative result for iodide ions. The solvent was evaporated to yield an orange-brown liquid ($m = 10.0$ g, yield: 91%). ^1H NMR (300 MHz, CDCl_3 , Figure S13a): $\delta = 4.12$ (t, 2H, $J = 4.4$ Hz), 3.93 (q, 2H, $J = 8.4$ Hz), 3.70 (t, 2H, $J = 4.4$ Hz), 3.45 (m, 4H), 3.16 (s, 3H), 1.95 (m, 4H), 1.75 (m, 2H) ppm. ^{13}C NMR (75 MHz, acetone- d_6 , Figure S13b): $\delta = 123.5$ (q), 119.7 (q), 68.4 (q), 65.5 (s), 63.1 (t), 62.8 (s), 50.0 (s), 20.6 (s), 20.0 (s) ppm. ^{19}F NMR (565 MHz, acetone- d_6 , Figure S13c): $\delta = -73.6$ (t), -78.6 (s) ppm. IR (ATR, cm^{-1}): 2955, 1348 (S=O), 1279, 1177 (S=O), 1133, 1053, 514 (C-F). CHN, with catalyst,% (calculated): C: 28.51 (28.46), H: 5.07 (3.78), N: 5.42 (5.53). MS-ESI (positive mode), found: $m/z = 226.2$ (M_{cation}) and $m/z = 731.9$ ($2M_{\text{cation}} + M_{\text{anion}}$).

1b: *N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-*N*-methylpiperidinium bis(trifluoromethylsulfonyl)imide

N-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-*N*-methylpiperidinium iodide (8.78 g, 18.1 mmol) was dissolved in 50 mL of ethanol and mixed with an ethanol solution of lithium bis(trifluoromethylsulfonyl)imide (5.73 g, 19.9 mmol). After stirring for 15 minutes, the solvent was evaporated, the residue dissolved in dichloromethane and washed in 3 portions with 80 mL of distilled water. The AgNO_3 test performed on the last water portion from washing gave negative result for iodide ions. The solvent was evaporated to yield a yellow liquid ($m = 9.94$ g, yield: 86%). ^1H NMR (300 MHz, methanol- d_4 , Figure S14a): $\delta = 6.57$ (tt, 1H, $J_1 = 51$ Hz, $J_2 = 5.4$ Hz), 4.18 (t, 2H, $J = 14.4$ Hz), 4.23 (br t, 2H), 3.70 (t, 2H, $J = 4.3$ Hz), 3.49 (m, 4H), 3.18 (s, 3H), 1.95 (m, 4H), 1.73 (m, 2H) ppm. ^{19}F NMR (565 MHz, methanol- d_4 , Figure S14c): $\delta = -79.4$ (s, 6F), -119.9 (m, 2F), -125.1 (m, 2F), -130.3 (m, 2F), -138.5 (d, 2F) ppm. IR (ATR, cm^{-1}): 2980, 1349 (S=O), 1280, 1175 (S=O), 1131, 1052, 511 (C-F). CHN, with catalyst,% (calculated): C: 26.93 (28.49), H: 4.05 (3.16), N: 4.35 (4.39). MS-ESI (positive mode), found: $m/z = 358.5$ (M_{cation}) and $m/z = 996.0$ ($2M_{\text{cation}} + M_{\text{anion}}$).

2a: *N*-((trifluoroethoxy)ethyl)-*N*-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide

N-((trifluoroethoxy)ethyl)-*N*-methyl pyrrolidinium iodide (7.74 g, 22.8 mmol) was dissolved in water and mixed with a water solution of lithium bis(trifluoromethylsulfonyl)imide (7.21 g, 25.1 mmol). After stirring for 15 minutes, dichloromethane was added to the solution, the organic phase separated and washed with water until the AgNO₃ test gave a negative result (m = 10.89 g, yield: 97%). ¹H NMR (300 MHz, acetone-*d*₆, Figure S15a): δ = 4.32 (m, 2H), 4.20 (q, 2H, *J* = 8.9 Hz), 3.94 (t, 2H, *J* = 4.6 Hz), 3.84 (m, 4H), 3.37 (s, 3H), 2.36 (m, 4H) ppm. ¹³C NMR (75 MHz, acetone-*d*₆, Figure S15b): δ = 125.0 (q), 121.0 (q), 68.5 (q), 67.1 (s), 66.3 (t), 64.1 (t), 49.5 (t), 22.2 (s) ppm. ¹⁹F NMR (565 MHz, acetone-*d*₆, Figure S15c): δ = -73.6 (t), -78.6 (s) ppm. IR (ATR, cm⁻¹): 2981, 1348 (S=O), 1280, 1175 (S=O), 1131, 1052, 512 (C-F). CHN, with catalyst, % (calculated): C: 26.81 (26.83), H: 4.71 (3.48), N: 4.56 (5.69). MS-ESI (positive mode), found: m/z = 212.2 (M_{cation}) and m/z = 704.0 (2M_{cation} + M_{anion}).

2b: *N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

N-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-*N*-methylpyrrolidinium iodide (5.60 g, 11.9 mmol) was dissolved in 30 mL of ethanol and mixed with an ethanol solution lithium bis(trifluoromethylsulfonyl)imide (3.75 g, 13.1 mmol). After stirring for 15 minutes, the solvent was evaporated, the residue dissolved in dichloromethane and washed in 3 portions with 80 mL of distilled water. The AgNO₃ test performed on the last water portion from washing gave negative result for iodide ions. The solvent was evaporated to yield a brown liquid which was dried in vacuum at 70 °C overnight (m = 6.98 g, yield: 94%). ¹H NMR (300 MHz, acetone-*d*₆, Figure S16a): δ = 6.73 (tt, 1H, *J*₁ = 510 Hz, *J*₂ = 5.3 Hz), 4.32 (br t, 2H), 4.30 (t, 2H, *J* = 14.5 Hz), 3.93 (t, 2H, *J* = 4.6 Hz), 3.83 (m, 4H), 3.36 (s, 3H), 2.35 (m, 4H), ppm. ¹³C NMR (75 MHz, acetone-*d*₆, Figure S16b): δ = 121.1 (q), 116.6 (t), 111.9 (m),

109.2 (t), 106.6 (t), 68.2 (t), 67.5 (br), 66.3 (s), 64.2 (br), 49.6 (br), 22.2 (s) ppm. ^{19}F NMR (565 MHz, acetone- d_6 , Figure S16c): $\delta = -78.7$ (s), -119.4 (m), -124.5 (m), -129.6 (m), -137.8 (d) ppm. IR (ATR, cm^{-1}): 2970, 1349 (S=O), 1279, 1170 (S=O), 1132, 1054, 514 (C-F). CHN, with catalyst, % (calculated): C: 26.93 (26.93), H: 4.20 (2.91), N: 4.35 (4.49). MS-ESI (positive mode), found: $m/z = 344.3$ (M_{cation}) and $m/z = 967.9$ ($2M_{\text{cation}} + M_{\text{anion}}$).

3a: *N,N*-diethyl-*N*-methyl-*N*-((trifluoroethoxy)ethyl)ammonium bis(trifluoromethylsulfonyl)imide

N,N-diethyl-*N*-methyl-*N*-((trifluoroethoxy)ethyl)ammonium iodide (1.08 g, 3.17 mmol) and lithium bis(trifluoromethylsulfonyl)imide were dissolved together in water and stirred for 10 minutes at ambient temperature. After this time, dichloromethane (50 mL) was added and the resulting two-phase mixture was stirred vigorously for 10 minutes. After this time, the mixture was taken up in a separation funnel, the dichloromethane phase was separated and the water phase was washed once with dichloromethane. The combined dichloromethane phases were then washed with water until the AgNO_3 test gave a negative result for iodides. Evaporation of the mixture yielded the pure product, a yellow liquid ($m = 1.32$ g, yield: 83%). ^1H NMR (300 MHz, acetone- d_6 , Figure S17a): $\delta = 4.29$ (m, 2H), 4.18 (q, 2H, $J = 8.9$ Hz), 3.84 (t, 2H, $J = 4.7$ Hz), 3.68 (q, 4H, $J = 7.3$ Hz), 3.29 (s, 3H), 1.43 (t, 6H, $J = 7.3$ Hz) ppm. ^{13}C NMR (75 MHz, acetone- d_6 , Figure S17b): $\delta = 123.9$ (q), 120.2 (q), 67.7 (q), 65.4 (s), 59.9 (t), 57.5 (s), 47.7 (t), 7.27 (s) ppm. ^{19}F NMR (565 MHz, acetone- d_6 , Figure S17c): $\delta = -75.0$ (t), -80.0 (s) ppm. IR (ATR, cm^{-1}): 2958, 1348 (S=O), 1280, 1176 (S=O), 1132, 1052, 512 (C-F). No reproducible CHN analysis results could be obtained for this compound.

3b: *N,N*-diethyl-*N*-methyl-*N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)ammonium bis(trifluoromethylsulfonyl)imide

N,N-diethyl-*N*-methyl-*N*-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)ammonium iodide (3.85 g, 8.14 mmol) was dissolved in 30 mL of ethanol and mixed with an ethanol solution of lithium bis(trifluoromethylsulfonyl)imide (2.56 g, 8.95 mmol). After stirring for 15 minutes, the solvent was evaporated, the residue dissolved in dichloromethane and washed in 3 portions with 80 mL of distilled water. The AgNO₃ test performed on the last water portion from washing gave a negative result for iodide ions. The solvent was evaporated to yield a yellow liquid (m = 4.45 g, yield: 87%). ¹H NMR (300 MHz, acetone-*d*₆, Figure S18a): δ = 6.74 (tt, 1H, *J*₁ = 51 Hz, *J*₂ = 5.5 Hz), 4.31 (t, 2H, br), 4.29 (t, 2H, *J* = 14.4 Hz), 3.86 (t, 2H, *J* = 4.3 Hz), 3.68 (q, 4H, *J* = 7.3 Hz), 3.30 (s, 3H), 1.46 (t, 6H, *J* = 7.3 Hz) ppm. ¹³C NMR (75 MHz, acetone-*d*₆, Figure S18b): δ = 121.3 (q), 109.2 (t), 105.6 (t), 68.1 (t), 66.6 (s), 60.8 (t), 58.4 (t), 48.6 (t), 8.2 (s) ppm. ¹⁹F NMR (565 MHz, acetone-*d*₆, Figure S18c): δ = -78.6 (s, 6F), -119.4 (m, 2F), -124.5 (m, 2F), -129.6 (br, 2F), -137.8 (d, 2F) ppm. IR (ATR, cm⁻¹): 2925, 1349 (S=O), 1170 (S=O), 1131, 1053, 513 (C-F). No reproducible CHN analysis results could be obtained for this compound.

4a: *N,N*-butylmethylpyrrolidinium hexafluorobutanoate

An aqueous saturated solution of potassium hydroxide was added dropwise to hexafluorobutanoic acid (15 g, 72 mmol) under stirring, until the pH slightly exceeded pH 7. To the resulting aqueous solution of potassium heptafluorobutanoate, 1-butyl-3-methylpyrrolidinium bromide was added (15.98 g, 72 mmol) and the solution was stirred for 30 minutes. No phase separation was observed. The water was carefully evaporated. Dichloromethane (100 mL) was added to the dry residue and the solution was placed in the fridge for 1 hour to precipitate KBr. Filtration on a glass filter (porosity 4) and evaporation of dichloromethane yielded a transparent oil which tested negative for bromides with AgNO₃. ¹H NMR (300 MHz, CDCl₃, Figure S19a): δ = 3.72 (m, 4H), 3.52 (m, 2H), 3.21 (s, 3H), 2.78 (m, 4H),

1.76 (m, 2H), 1.43 (m, 2H), 0.99 (t, 3H) ppm. ^{19}F NMR (565 MHz, CDCl_3 , Figure S19c): $\delta = -84.7$ (t, 3F), -121.0 (q, 2F), -130.6 (broad s, 2F) ppm. IR (ATR, cm^{-1}): 2968, 1686 (C=O), 1202 (C-O), 1110 (C-N), 528 (C-F). No reproducible CHN analysis results could be obtained for this compound.

4b: *N,N*-butylmethylpyrrolidinium heptadecafluorononaoate

Potassium heptadecafluorononaoate (10.0 g, 19.9 mmol) was dissolved in 100 mL of a 1:1 solution of ethanol and acetone. 1-Butyl-3-methylpyrrolidinium chloride (3.36 g, 18.92 mmol) in 20 mL of dichloromethane was added and the mixture was stirred at room temperature for 20 minutes. After this time, the formed KCl precipitate was filtered off on a glass filter and the solvents were evaporated. The residue was re-dissolved in dry dichloromethane and filtrated. Evaporation gave a slightly green transparent solid (m = 11.43 g, yield: 99.8%). ^1H NMR (300 MHz, CDCl_3 , Figure S20a): $\delta = 3.72$ (m, 4H), 3.51 (m, 2H), 3.20 (s, 3H), 2.26 (m, 4H), 1.74 (m, 2H), 1.43 (m, 2H), 0.98 (t, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , Figure S20b): cation peaks: $\delta = 64.4$ (s), 64.2 (s), 48.4 (s), 25.8 (s), 21.6 (s), 19.6 (s), 13.4 (s) ppm. ^{19}F NMR (565 MHz, CDCl_3 , Figure S20c): $\delta = -78.3$ (t, 3F), -80.8 (m), -117.1 (m), -126.8 (broad s, 2F) ppm. IR (ATR, cm^{-1}): 2976, 1679 (C=O), 1198 (C-O), 1147 (C-N), 527 (C-F). CHN, % (calculated): C: 34.88 (35.71), H: 3.76 (3.33), N: 2.30 (2.31).

Oxygen concentration measurements

The dissolved oxygen concentration was determined by combining the steady-state current on an ultramicroelectrode and the Cottrell equation on a macroelectrode. It was noticed that the fluorinated chains on the ionic liquids had a surfactant-like behavior while bubbling oxygen. This resulted in bubbles that were lasting longer compared to the commercial ionic liquids. As a result, the time until a stable measurement could be performed was 20 minutes after bubbling. The procedure was tested and the results are shown below for ionic liquid **2a**

as example for the procedure (Figure SS2). In Table S2 it can be seen that the values for the Cottrell measurements, directly after bubbling and after 10 minutes of resting periode, are deviating from the other values due to the surfactant-like behavior of the fluorinated chains on the ionic liquids. Therefore they cannot be used for the determination of the oxygen concentration in the ionic liquid and only the values from 20 to 50 minutes were used for further calculations.

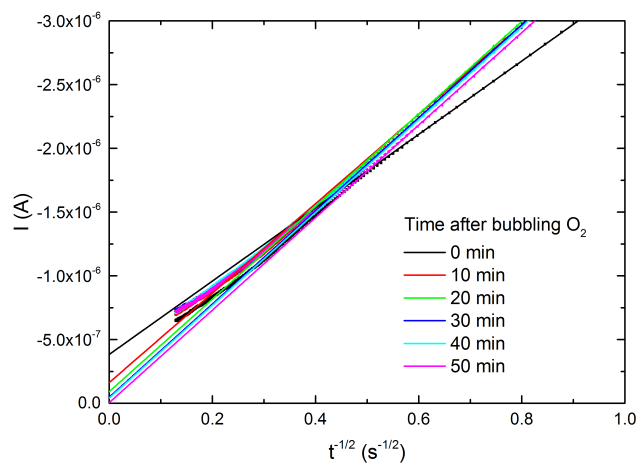
A potentiostatic signal was applied on a gold macroelectrode where the oxygen reduction reaction is in mass transport limitation. The current response can be describe by the Cottrell equation (Eq. (1)):

$$I(t) = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad (1)$$

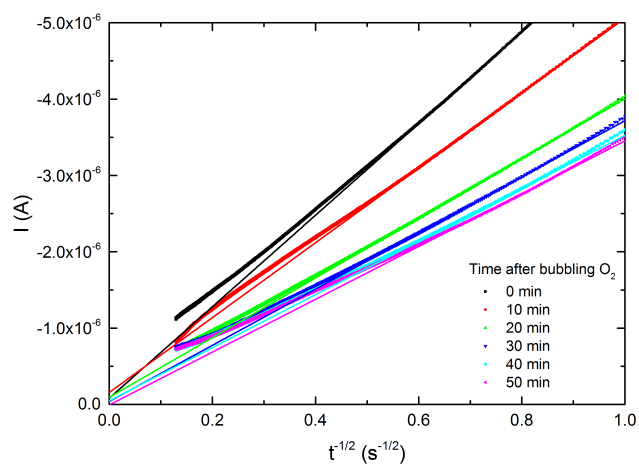
with n the number of electrons in the redox reaction ($= 1$), F the Faraday constant ($96485.3399 \text{ s} \cdot \text{A mol}^{-1}$), C the dissolved oxygen concentration (mol m^{-3}), D the diffusion coefficient of oxygen ($\text{m}^2 \text{ s}^{-1}$), A the disk electrode surface (m^2) and t the time (s). Via the slope analysis of the I vs. $t^{-1/2}$ plot a value can be determined for $C \cdot D^{1/2}$, which can be used as input in Eq. (2) of the steady-state current on a gold ultramicroelectrode:

$$I_{ss} = 4nFCDr \quad (2)$$

with r the disk radius of the ultramicroelectrode ($25 \mu \text{ m}$). By combining the two equations, the two unknown variables C and D can be determined. These measurements have been done for both the fluorinated and non-fluorinated, commercial ionic liquids. This way the effect of attaching a fluorinated chain can be evaluated indisputable. Because it was observed in literature that the value of the dissolved oxygen concentration differs for the same solvents when different measuring techniques were used (e.g. electrochemical, gravimetric or volumetric methods). The electrochemical data is presented for IL **1a** and **1b** in Table S4 and S5, for IL **2a** in Table S1 and S2, for IL **2b** in Table S1 and S3, for IL **3a** and **3b** in Table S6 and S7, and finally for IL **4a** and **4b** in Table S8 and S9.



(a) Experiment 1



(b) Experiment 2

Figure S2: Linear fit for the determination of the slope the Cottrell equation (Eq. 1). A potentiostatic signal of -1.65 V vs. Ag^+/Ag was applied, using IL **2a** as electrolyte, a gold macroelectrode ($\phi = 0.6$ mm) and a platinum counter electrode at room temperature.

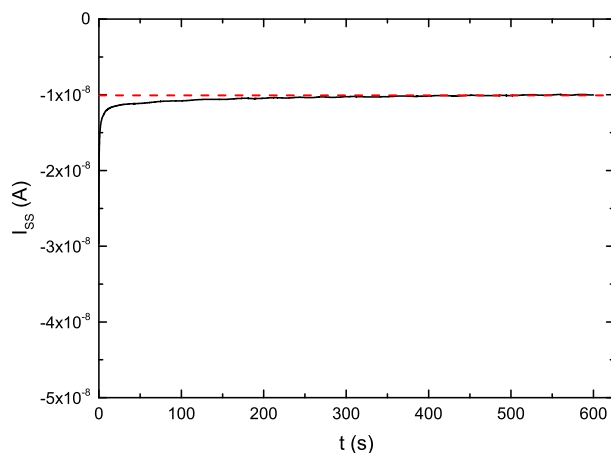


Figure S3: Steady state current on the ultramicroelectrode i_{ss} equation (Eq. 2). A potentiostatic signal of -1.65 V vs. Ag^+/Ag was applied, using IL **2a** as electrolyte, a gold ultramicroelectrode ($\phi = 25$ μm) as working electrode and a platinum counter electrode at room temperature.

Table S1: Steady-state current on a gold ultramicroelectrode ($\phi = 25$ μm) for ionic liquid **2a** and **2b**.

I_{SS} ($\times 10^{-9}$ A)	2a	2b
1	-13.4	-3.9
2	-10.1	-4.2
3	-8.9	-4.4
4	-10.1	-3.9
5	-10.0	-3.8
Average	-10.5 ± 1.5	-4.0 ± 0.3

Table S2: Slope of the linear fit of Cottrell on a gold macroelectrode ($\phi = 0.6$ mm) and the calculated dissolved oxygen concentration for ionic liquid **2a**.

Time after bubbling O_2 (min)	2a - exp1		2a - exp2	
	Slope ($\times 10^{-6}$ A s $^{-1/2}$)	C_{O_2} (mol m $^{-3}$)	Slope ($\times 10^{-6}$ A s $^{-1/2}$)	C_{O_2} (mol m $^{-3}$)
0	-2.88	16.1	-6.00	70.0
10	-3.51	23.9	-4.90	46.6
20	-3.63	25.3	-3.91	29.9
30	-3.65	25.8	-3.68	26.3
40	-3.64	25.7	-3.48	23.5
50	-3.63	25.6	-3.46	23.2
Average		25.6 ± 0.2		25.6 ± 3

Table S3: Slope of the linear fit of Cottrell on a gold macroelectrode ($\phi = 0.6$ mm) and the calculated dissolved oxygen concentration for ionic liquid **2b**.

Time after bubbling O ₂ (min)		2b	
	Slope ($\times 10^{-6}$ A s ^{-1/2})		C _{O₂} (mol m ⁻³)
20	-2.67		36.0
30	-2.55		32.8
40	-2.55		32.8
50	-2.59		33.9
Average			33.9 \pm 2

Table S4: Steady-state current on a gold ultramicroelectrode ($\phi = 25$ μ m) for ionic liquid **1a** and **1b**.

I _{SS} ($\times 10^{-9}$ A)	1a	1b
1	-6.6	-2.3
2	-6.4	-2.2
3	-6.4	-2.2
4	-6.3	-2.2
5	-6.4	-2.2
Average	-6.4 \pm 0.1	-2.2 \pm 0.1

Table S5: Slope of the linear fit of Cottrell on a gold macroelectrode ($\phi = 0.6$ mm) and the calculated dissolved oxygen concentration for ionic liquid **1a** and **1b**.

Time after bubbling O ₂ (min)		1a		1b	
	Slope ($\times 10^{-6}$ A s ^{-1/2})	C _{O₂} (mol m ⁻³)	Slope ($\times 10^{-6}$ A s ^{-1/2})	C _{O₂} (mol m ⁻³)	
20	-2.36	17.7	-1.76	28.2	
30	-2.27	16.4	-1.74	27.5	
40	-2.19	15.3	-1.58	22.7	
50	-2.16	14.8	-1.69	26.0	
Average		16.0 \pm 1.3		26.1 \pm 2.4	

Table S6: Steady-state current on a gold ultramicroelectrode ($\phi = 25 \mu\text{m}$) for ionic liquid **3a** and **3b**.

I_{SS} ($\times 10^{-9}$ A)	3a	3b
1	-5.5	-3.2
2	-5.5	-1.7
3	-5.9	-0.9
4	-5.8	-1.4
5	-5.7	-1.2
Average	-5.7 ± 0.2	-1.7 ± 0.8

Table S7: Slope of the linear fit of Cottrell on a gold macroelectrode ($\phi = 0.6 \text{ mm}$) and the calculated dissolved oxygen concentration for ionic liquid **3a** and **3b**.

Time after bubbling O ₂ (min)	Slope ($\times 10^{-6}$ A s ^{-1/2})	3a C_{O_2} (mol m ⁻³)	Slope ($\times 10^{-6}$ A s ^{-1/2})	3b C_{O_2} (mol m ⁻³)
20	-2.26	18.2	-1.76	37.5
30	-2.09	15.6	-1.61	31.4
40	-2.06	15.2	-1.47	26.2
50	-2.01	14.4	-1.37	22.8
Average		15.9 ± 1.6		29.5 ± 6

Table S8: Steady-state current on a gold ultramicroelectrode ($\phi = 25 \mu\text{m}$) for ionic liquid **4a** and **4b**.

I_{SS} ($\times 10^{-9}$ A)	4a	4b
1	-6.7	-1.1
2	-5.8	-1.0
3	-5.4	-1.0
4	-5.3	-1.0
5	-5.6	-1.0
Average	-5.8 ± 0.6	-1.0 ± 0.1

Table S9: Slope of the linear fit of Cottrell on a gold macroelectrode ($\phi = 0.6$ mm) and the calculated dissolved oxygen concentration for ionic liquid **4a** and **4b**.

Time after bubbling O ₂ (min)	4a		4b	
	Slope ($\times 10^{-6}$ A s ^{-1/2})	C _{O₂} (mol m ⁻³)	Slope ($\times 10^{-6}$ A s ^{-1/2})	C _{O₂} (mol m ⁻³)
20	-1.74	10.7	-3.31	21.2
30	-1.67	9.9	-3.21	20.0
40	-1.61	9.2	-3.13	19.0
50	-1.56	8.6	-3.03	17.8
Average		9.6 \pm 0.9		19.5 \pm 1.4

Chemical and thermal stability of the fluorinated ionic liquids

The thermal stability and volatility of the fluorinated ionic liquids was evaluated via thermogravimetric analysis. No mass loss was observed at room temperature for 1 hour under a constant argon flow. Subsequently the temperature increased to 450 °C at a heating rate of 5 °C/min, again no mass loss was observed before the decomposition of the ionic liquid and thus the non-volatile property of the ionic liquids was confirmed (Figure S4–S7).

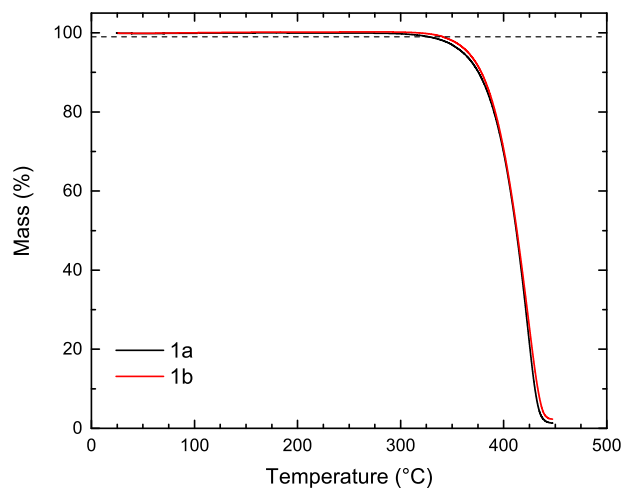


Figure S4: Thermogravimetric analysis of IL **1a** and **1b**. After 1 hour at 25 °C the temperature was increased until 450 °C at a heating rate of 5 °C/min under a constant argon flow.

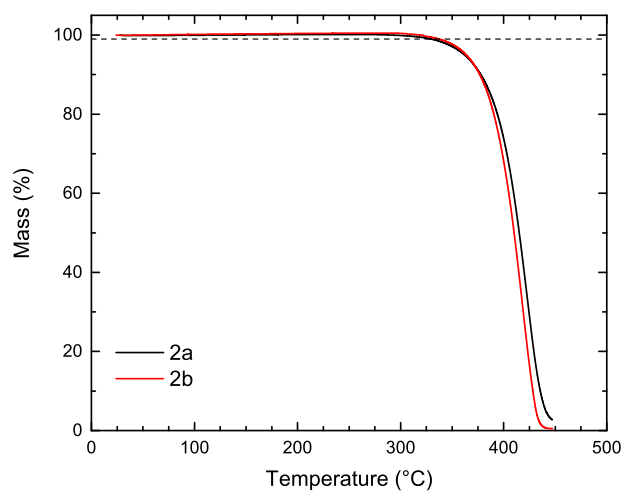


Figure S5: Thermogravimetric analysis of IL **2a** and **2b**. After 1 hour at 25 °C the temperature was increased until 450 °C at a heating rate of 5 °C/min under a constant argon flow.

The oxygen reduction reaction and oxygen evolution reaction was studied by cyclic voltammetry in all fluorinated ionic liquids (Figure S8–S11). The $O_2/O_2^{\cdot-}$ redox couple was reversible in all fluorinated ionic liquids even at a slow scan rate of 10 mV s⁻¹. This observation indicates that ionic liquids are stable against the superoxide radical at least within the time frame of the experiment. A good stability is crucial for the use of these ionic liquids in energy storage applications such as fuel cells and metal-air batteries.

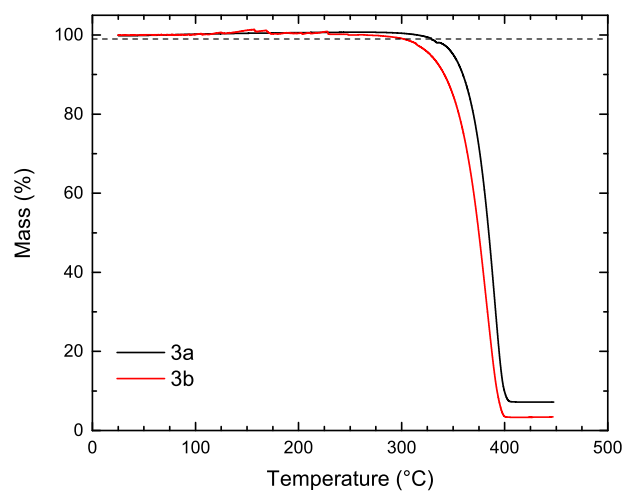


Figure S6: Thermogravimetric analysis of IL **3a** and **3b**. After 1 hour at 25 °C the temperature was increased until 450 °C at a heating rate of 5 °C/min under a constant argon flow.

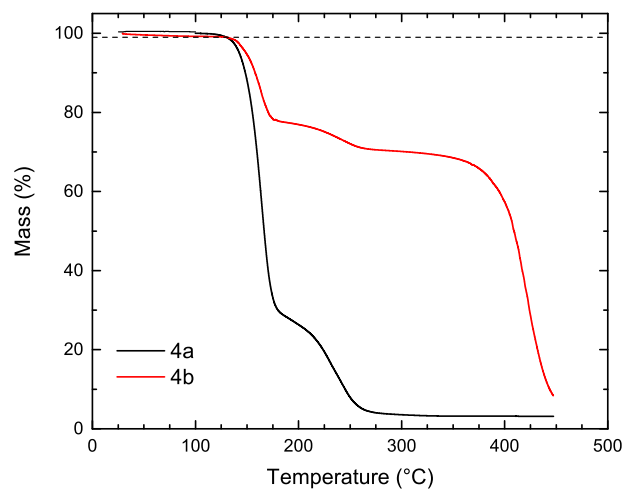
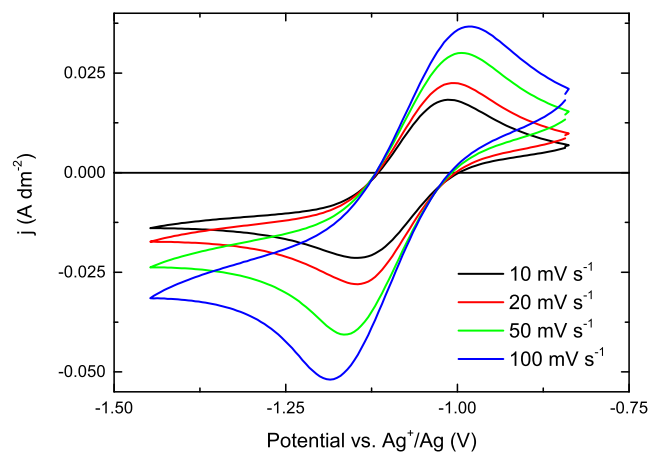
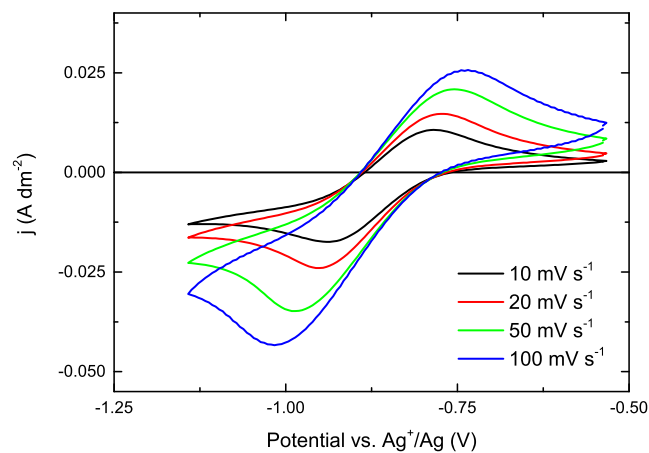


Figure S7: Thermogravimetric analysis of IL **4a** and **4b**. After 1 hour at 25 °C the temperature was increased until 450 °C at a heating rate of 5 °C/min under a constant argon flow.

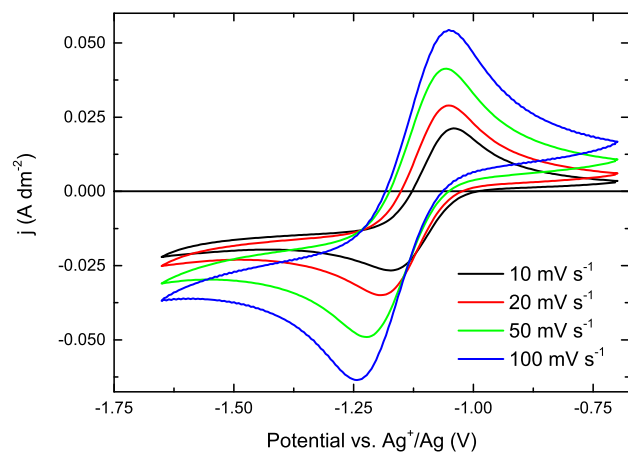


(a) IL **1a**

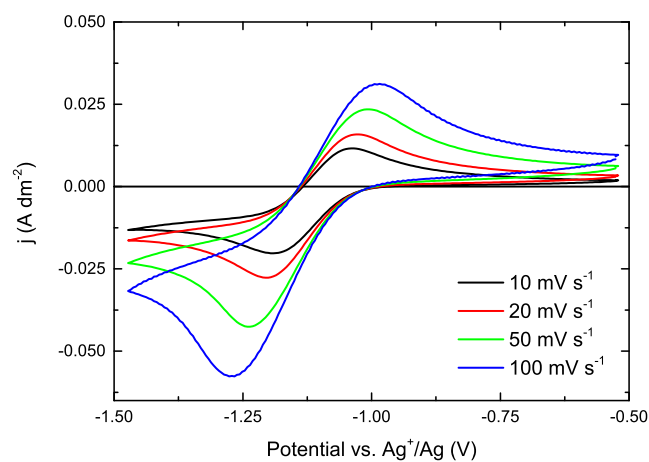


(b) IL **1b**

Figure S8: Cyclic voltammogram of the oxygen reduction reaction and oxygen evolution reaction in IL **1a** and **1b**. A gold macroelectrode ($\phi = 0.6$ mm) was used as working electrode and a platinum coil as reference electrode. A silver wire immersed in 0.01 M AgNO_3 and 0.1 M TBAP in acetonitrile was used as real reference electrode. The electrolyte was at room temperature.

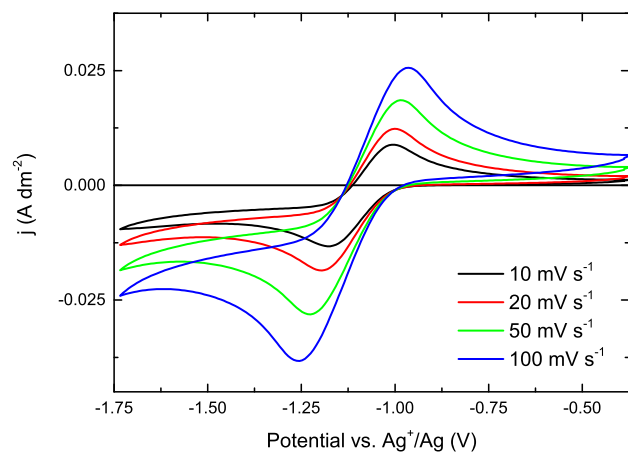


(a) IL **2a**

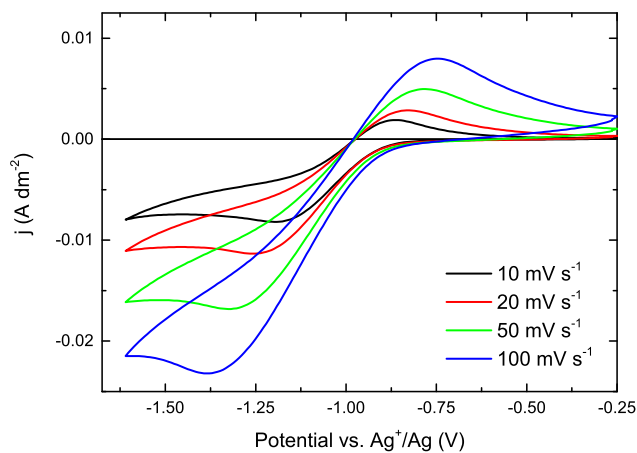


(b) IL **2b**

Figure S9: Cyclic voltammogram of the oxygen reduction reaction and oxygen evolution reaction in IL **2a** and **2b**. A gold macroelectrode ($\phi = 0.6$ mm) was used as working electrode and a platinum coil as reference electrode. A silver wire immersed in 0.01 M AgNO_3 and 0.1 M TBAP in acetonitrile was used as real reference electrode. The electrolyte was at room temperature.

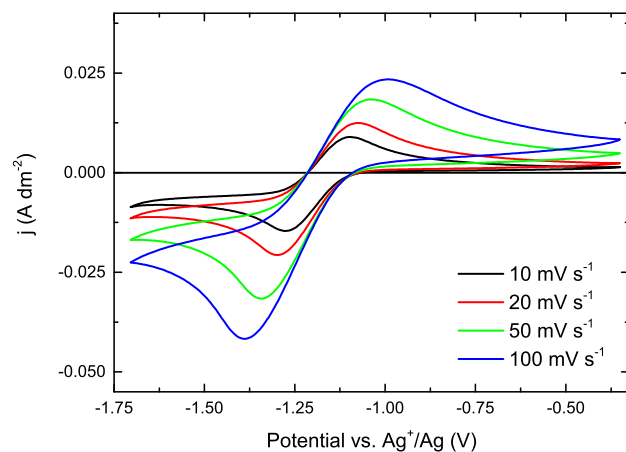


(a) IL **3a**

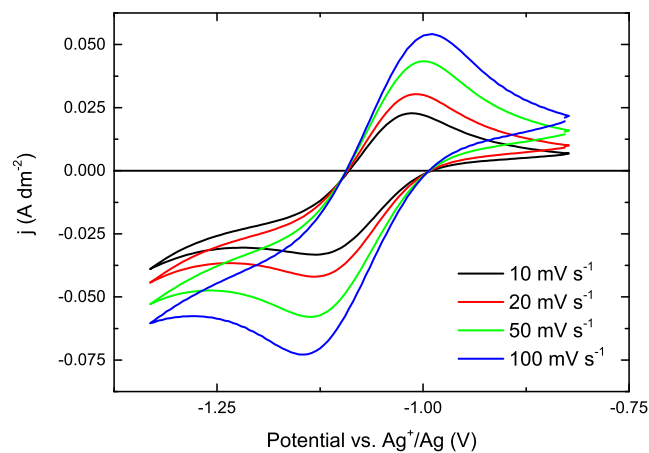


(b) IL **3b**

Figure S10: Cyclic voltammogram of the oxygen reduction reaction and oxygen evolution reaction in IL **3a** and **3b**. A gold macroelectrode ($\phi = 0.6$ mm) was used as working electrode and a platinum coil as reference electrode. A silver wire immersed in 0.01 M AgNO_3 and 0.1 M TBAP in acetonitrile was used as real reference electrode. The electrolyte was at room temperature.

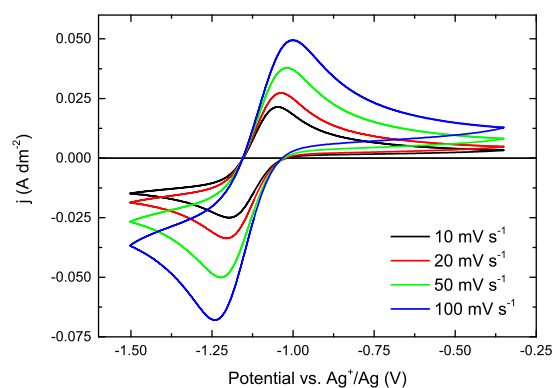


(a) IL **4a**

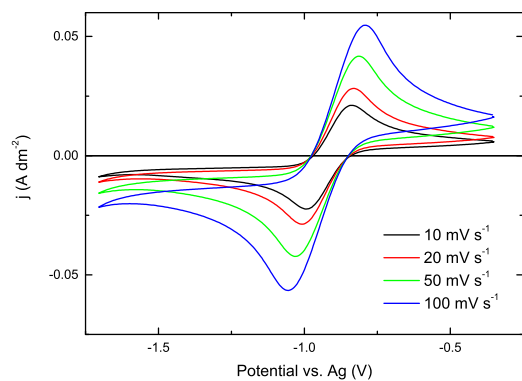


(b) IL **4b**

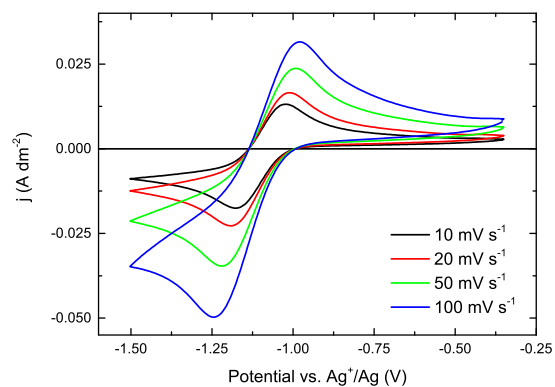
Figure S11: Cyclic voltammogram of the oxygen reduction reaction and oxygen evolution reaction in IL **4a** and **4b**. A gold macroelectrode ($\phi = 0.6$ mm) was used as working electrode and a platinum coil as reference electrode. A silver wire immersed in 0.01 M AgNO_3 and 0.1 M TBAP in acetonitrile was used as real reference electrode. The electrolyte IL **4a** was at 35 °C and IL **4b** was at room temperature.



(a) [BMPip][Tf₂N]



(b) [BMP][Tf₂N]



(c) [DEME][Tf₂N]

Figure S12: Cyclic voltammogram of the oxygen reduction reaction and oxygen evolution reaction in ionic liquids [BMPip][Tf₂N] (a), [BMP][Tf₂N] (b) and [DEME][Tf₂N] (c). A gold macroelectrode ($\phi = 0.6$ mm) was used as working electrode and a platinum coil as reference electrode. A silver wire immersed in 0.01 M AgNO₃ and 0.1 M TBAP in acetonitrile was used as real reference electrode. The electrolytes were at room temperature.

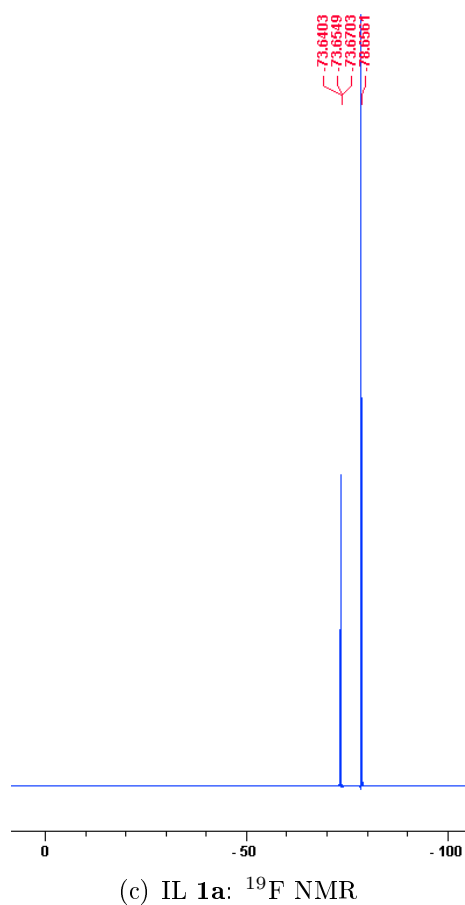
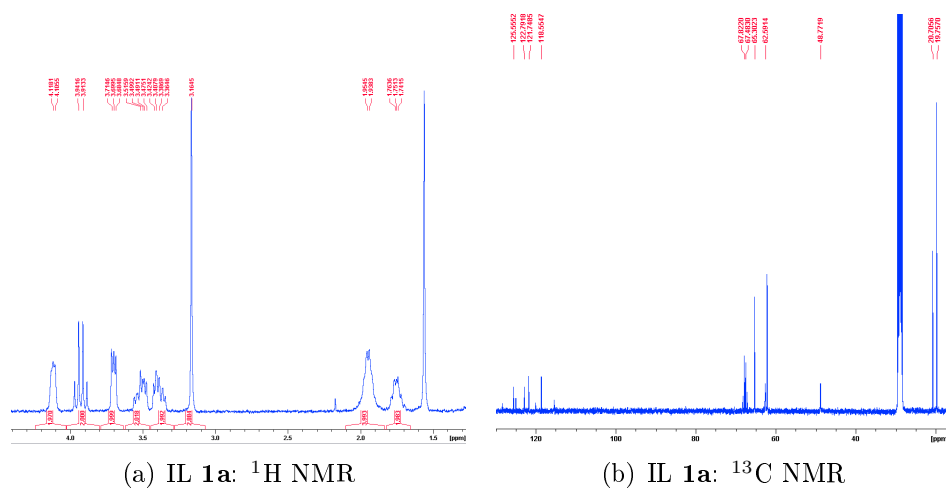


Figure S13: Nuclear magnetic resonance (NMR) spectra of IL **1a** for ^1H (300 MHz), ^{13}C (75 MHz) and ^{19}F (376 MHz) nuclei. The chemical shifts are noted in parts per million (ppm).

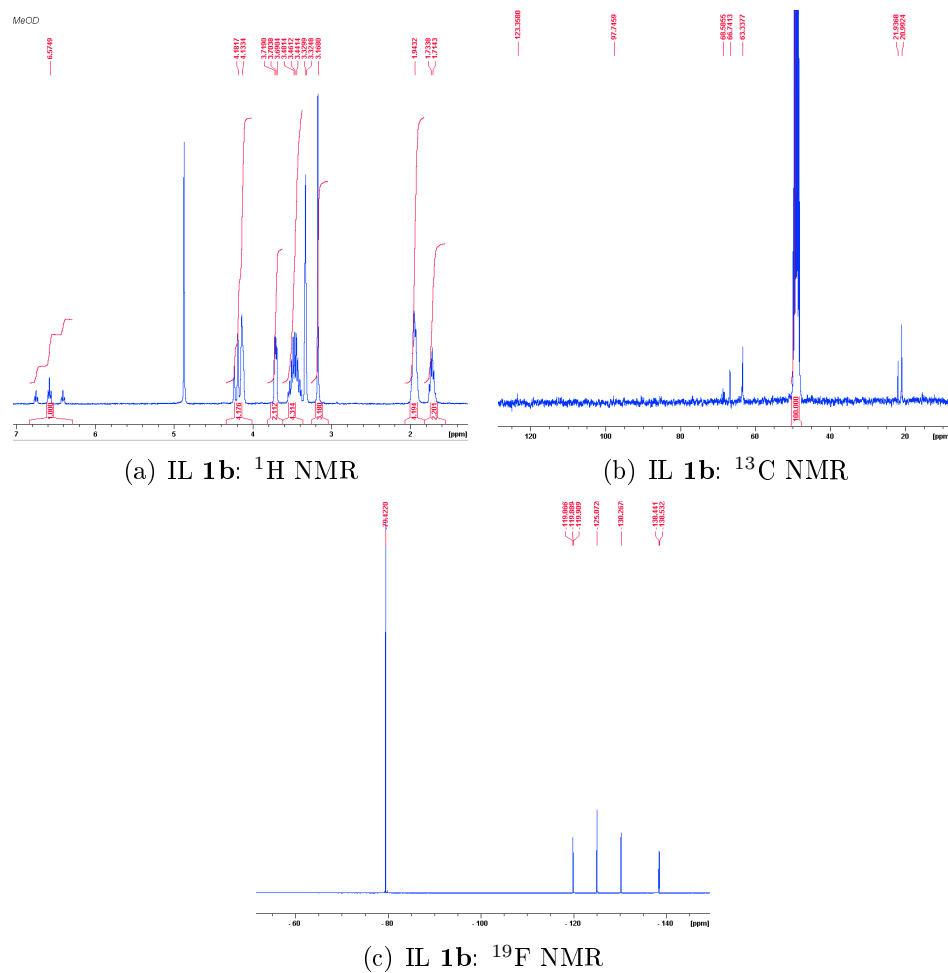


Figure S14: Nuclear magnetic resonance (NMR) spectra of IL **1b** for ^1H (300 MHz), ^{13}C (75 MHz) and ^{19}F (376 MHz) nuclei. The chemical shifts are noted in parts per million (ppm).

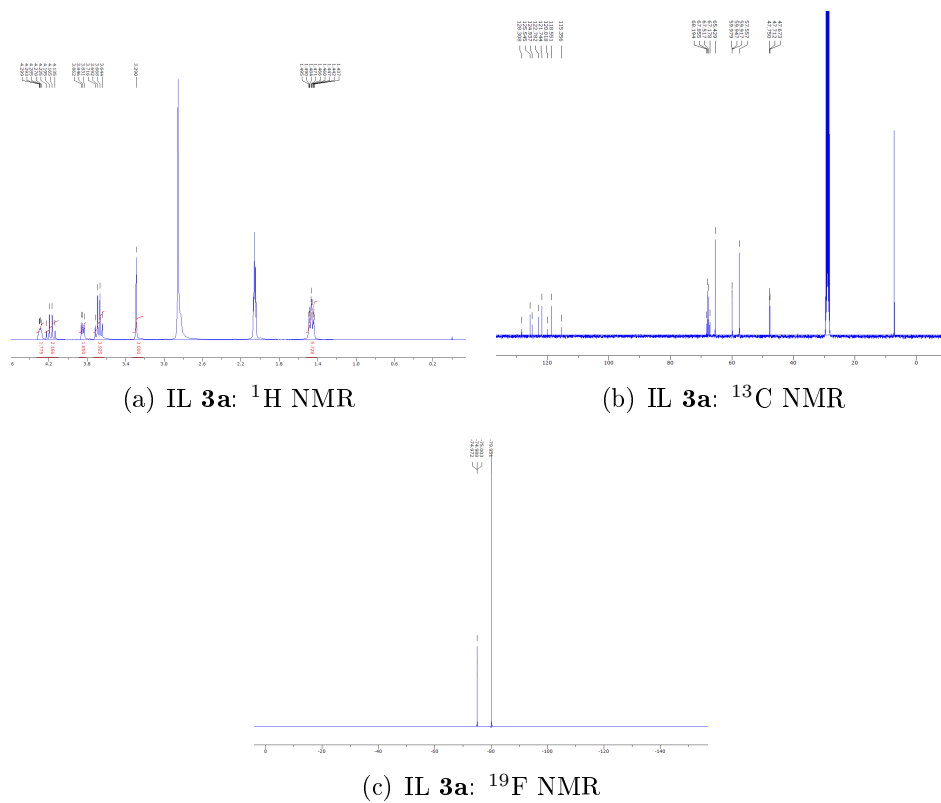


Figure S17: Nuclear magnetic resonance (NMR) spectra of IL **3a** for ^1H (300 MHz), ^{13}C (75 MHz) and ^{19}F (376 MHz) nuclei. The chemical shifts are noted in parts per million (ppm).

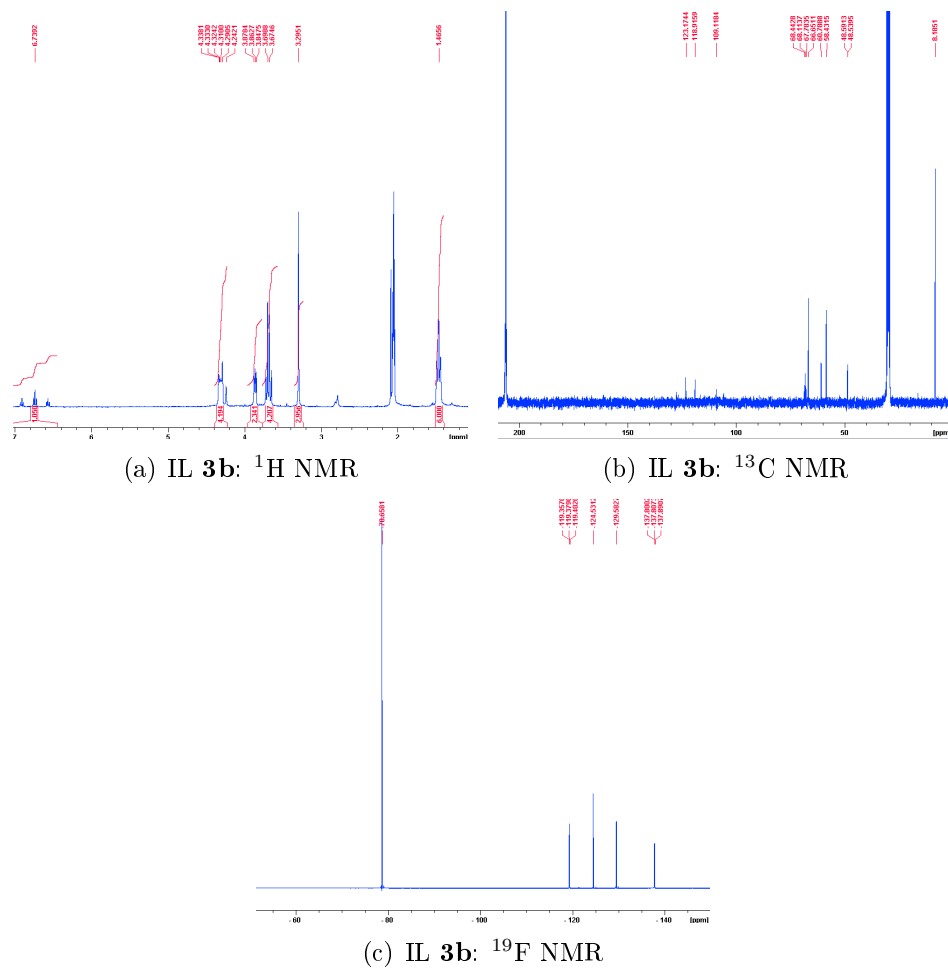


Figure S18: Nuclear magnetic resonance (NMR) spectra of IL **3b** for ^1H (300 MHz), ^{13}C (75 MHz) and ^{19}F (376 MHz) nuclei. The chemical shifts are noted in parts per million (ppm).

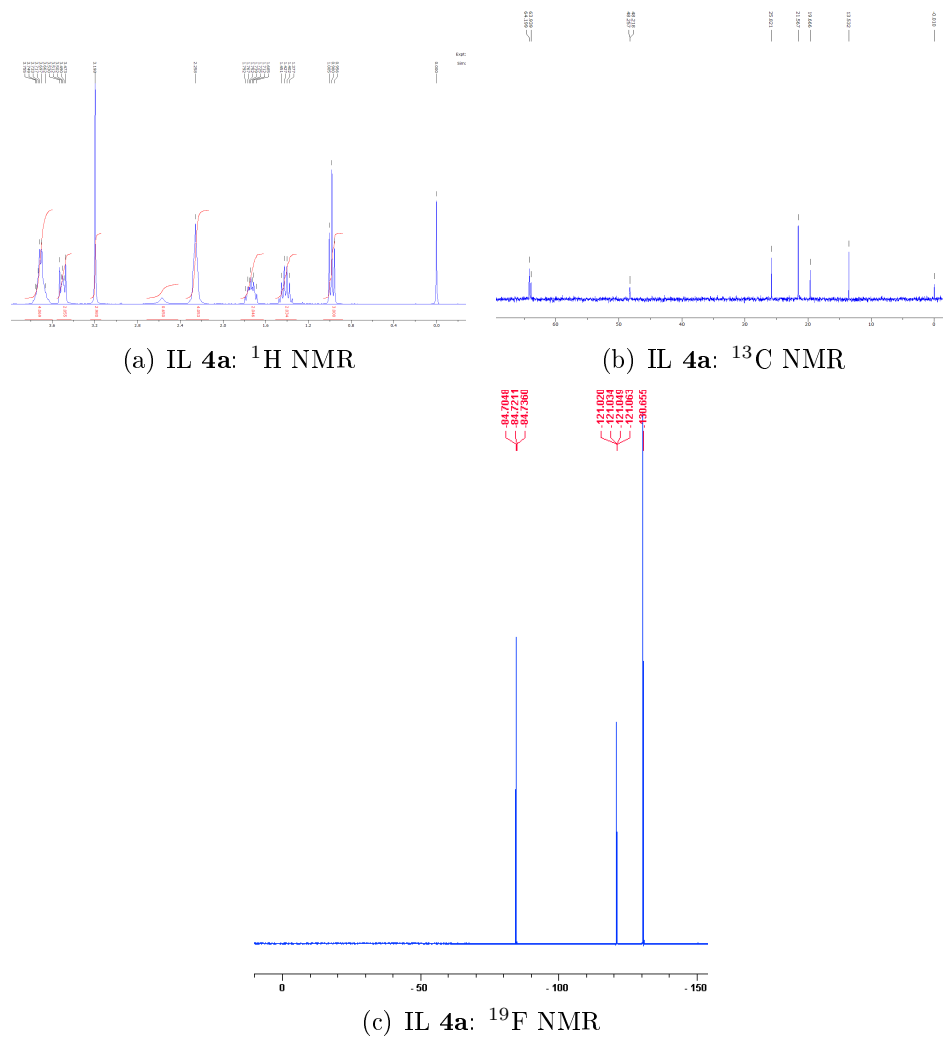


Figure S19: Nuclear magnetic resonance (NMR) spectra of IL **4a** for ^1H (300 MHz), ^{13}C (75 MHz) and ^{19}F (376 MHz) nuclei. The chemical shifts are noted in parts per million (ppm).

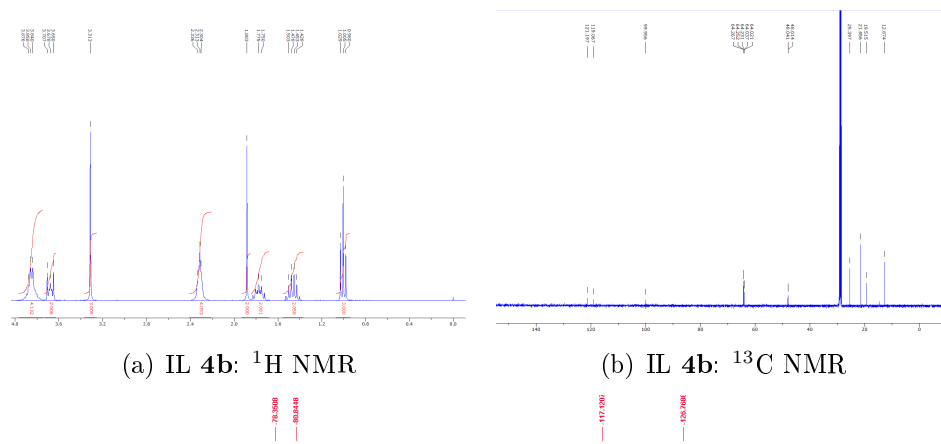


Figure S20: Nuclear magnetic resonance (NMR) spectra of IL **4b** for ^1H (300 MHz), ^{13}C (75 MHz) and ^{19}F (376 MHz) nuclei. The chemical shifts are noted in parts per million (ppm).

References

- (1) Kim, J.; Singh, R. P.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 2960–2966.