Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Sulfonic acid functionalized ionic liquids for the dissolution of metal oxides and solvent extraction of metal ions

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1. Chemicals and materials

Chemicals for extraction and leaching experiments

NiO (97%), Y_2O_3 (99.99%), $CrCl_3 \cdot 6H_2O$ (98%), $ZnCl_2$ (98.5%), $CuCl_2$ anh. (99%), H_2SO_4 (96%), HCl (37%), 1,4-dioxane (99.9%), Al_2O_3 (99%), Cr_2O_3 (99%) and $LaCl_3 \cdot 7H_2O$ (99.99%) were purchased from Acros Organics (Geel, Belgium). La_2O_3 (99.99%), Fe_2O_3 (95%), TiO_2 (99%), $GaCl_3$ anh. (99.99%), $NiCl_2$ (98%), $InCl_3$ (97%), $FeCl_3$ (99%), $YCl_3 \cdot 6H_2O$ (99.9%), $DyCl_3 \cdot 6H_2O$ (99.9%), $CoCl_2$ (97%), MnO (99%) and $LuCl_3 \cdot 6H_2O$ (99.9%) were bought from Sigma-Aldrich (Diegem, Belgium). $NdCl_3 \cdot 6H_2O$ (99.9%) and Co_3O_4 (99.5%) were purchased from Strem Chemicals Inc. (Newburyport, USA), $SnCl_2$ (99%) from Merck (Overijse, Belgium) and WO_3 (99%) from ABCR Chemicals (Karlsruhe, Germany). $CaCl_2 \cdot 2H_2O$ (99.5%) and the 1000 $mg \cdot L^{-1}$ gallium(III) and selenium(VI) standard solutions in HNO_3 (2−5 wt%) were obtained from Chem-Lab (Zedelgem, Belgium). Ethanol (Analytical reagent grade) was obtained from Fisher Scientific Limited (Loughborough, UK). CuO (99.9999%) and CoO (95%) were purchased from Alfa Aeser (Karlsruhe, Germany). A silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH (Germany). All chemicals were used as received without further purification.

Sc_2O_3 was kindly provided by Solvay (La Rochelle, France). $ScCl_3 \cdot xH_2O$ was prepared by dissolving Sc_2O_3 in an excess of hydrochloric acid (two equivalents). The mixture was dried on a rotary evaporator to remove the water together with the excess of hydrochloric acid. This step was repeated several times until a crystalline material was obtained, the purity was verified with TXRF analysis.

Chemicals for ionic liquid synthesis

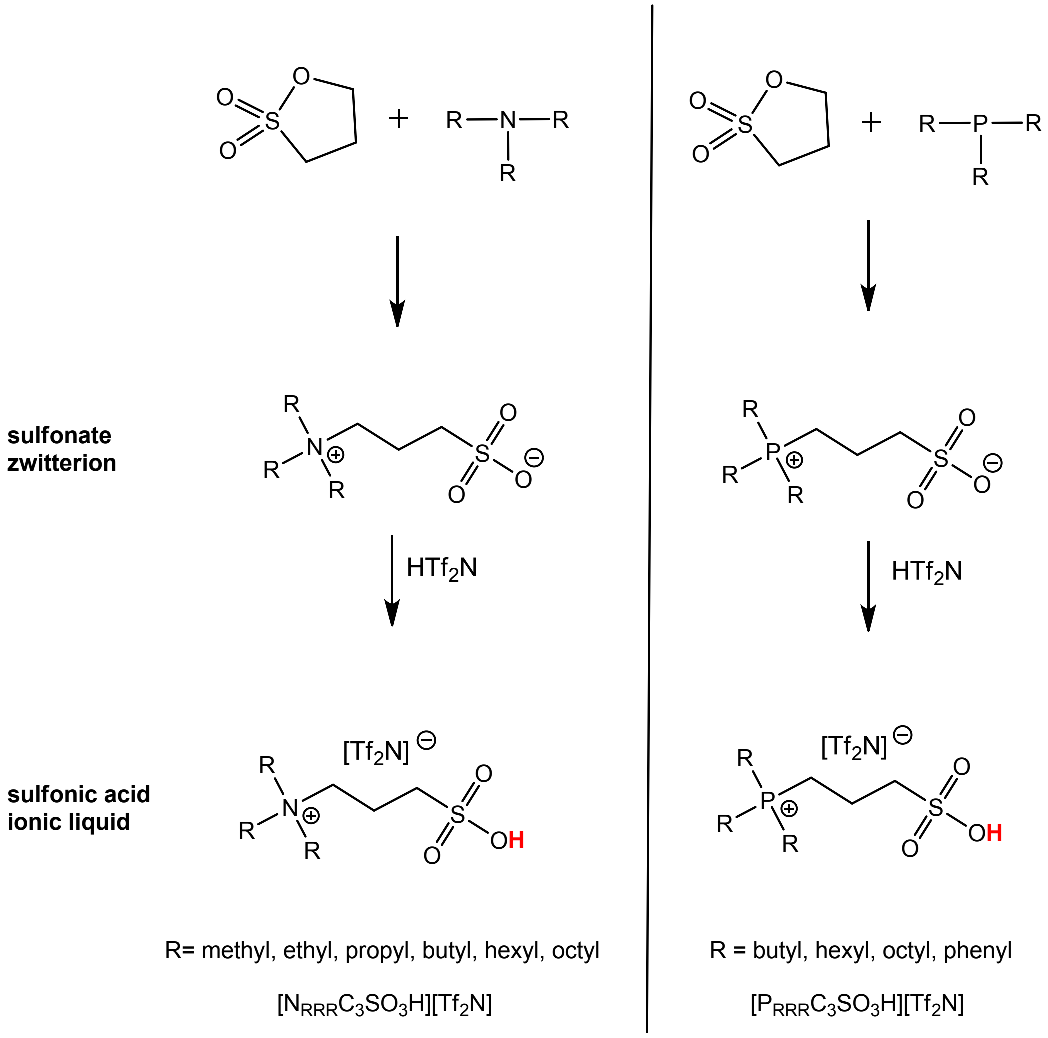
Bistriflimic acid (80 wt% in H_2O) (99%) was purchased from IoLiTec (HeilBronn, Germany). Triethylamine (99%), trioctylphosphine (90%) and trimethylamine (33% in EtOH) were purchased from Acros Organics (Geel, Belgium). Triphenyl phosphine (98.5%), 1,3-propanesultone (98%), tri-*n*-butylphosphine (97%), trioctylamine (98%), trihexylamine (96%), tributylamine (99%), tripropylamine (98%), ethylacetate (99.7%), toluene (99%) and diethylether (99.8%) were obtained from Sigma Aldrich (Diegem, Belgium). Trihexyl phosphine (95%) was bought from TCI (Zwijndrecht, Belgium). Acetonitrile (HPLC grade) and sodium hydroxide (97%) were obtained from Fisher Scientific Limited (Loughborough, UK).

2. Equipment and characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^{1}H, 75 MHz for ^{13}C). The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ^{1}H and ^{13}C. The coupling constants are given in Hertz. Solutions were made in D_2O, CD_2Cl_2 or CD_3Cl. The spectra were analyzed with SpinWorks software. The elemental analysis of carbon, hydrogen and nitrogen was performed on a CE-instruments EA-1110 elemental analyzer. The viscosity of the ionic liquids was measured using an automatic Brookfield plate cone viscometer, Model LVDV-II CP (Brookfield Engineering Laboratories, USA). Melting points were determined on a Mettler-Toledo DSC 1 (STAR^e system) instrument at a heating rate of 10 °C min^{-1} under a helium atmosphere. Thermogravimetric analysis (TGA) was done on a TA Instruments T500 thermogravimeter (heating rate: 5 °C min^{-1} from room temperature to 400 °C, under a nitrogen atmosphere). A TMS-200 thermoshaker (Nemus Life) was used to shake samples during extraction experiments and a Heraeus Megafuge 1.0 centrifuge was used to accelerate phase separation. Total reflection X-ray fluorescence (TXRF) analysis was performed with a Bruker S2 Picofox TXRF spectrometer equipped with a molybdenum source. For the sample preparation, plastic microtubes were filled with a small amount of sample (100 mg), internal standard (Ga(III) or Se(VI) solution) and water (800 μL). To measure the ionic liquid, a smaller sample was taken (25 mg) and dissolved in 1,4-dioxane/water (800 μL). The microtubes were then vigorously shaken on a vibrating plate (IKA MS 3 basic). Finally, a 1 μL drop of this solution was put on a quartz plate, previously treated with a silicone/isopropanol solution (Serva®) to avoid spreading of the sample droplet on the quartz plate. The quartz plates were then dried for 30 min at 60 °C prior to analysis. Each sample was measured for 5 min.

3. Overview of the synthetic strategy and the synthesized ionic liquids

The synthetic strategy for was based on a 2-step reaction (Scheme S 1). First 1,3-propanesultone was reacted with the appropriate trialkylamine or trialkylphoshine to obtain the sulfonate zwitterion. Then this zwitterion was reacted with the super acid HTf_2N to obtain the corresponding ionic liquid (IL). An overview of the synthesized ILs is given in Table S1.



Scheme S 1. Synthetic strategy for the synthesis of trialkylammonium- and trialkylphosphoniumpropanesulfonic acid bis(trifluoromethylsulfonyl)imide ionic liquids.

Table S1. Overview of the ionic liquids synthesized in this work

IL abbreviation	**Full name**
$[N_{111}C_3SO_3H][Tf_2N]$	Trimethylammoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[N_{222}C_3SO_3H][Tf_2N]$	Triethylammoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[N_{333}C_3SO_3H][Tf_2N]$	Tripropylammoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[N_{444}C_3SO_3H][Tf_2N]$	Tributylammoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[N_{666}C_3SO_3H][Tf_2N]$	Trihexylammoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[N_{888}C_3SO_3H][Tf_2N]$	Trioctylammoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[P_{444}C_3SO_3H][Tf_2N]$	Tributylphosphoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[P_{666}C_3SO_3H][Tf_2N]$	Trihexylphosphoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[P_{888}C_3SO_3H][Tf_2N]$	Trioctylphosphoniumpropanesulfonic acid bistriflimide$^{(a)}$
$[PPh_3C_3SO_3H][Tf_2N]$	Triphenylphosphoniumpropanesulfonic acid bistriflimide$^{(a)}$

$^{(a)}$Bistriflimide = bis(trifluoromethylsulfonyl)imide

4. Synthesis of ionic liquids

4.1 [$N_{111}C_3SO_3H$][Tf_2N]

1,3-Propanesultone (0.115 mol, 14.037 g) and trimethylamine (0.147 mol, 8.69 g) (as a 33% in ethanol solution) were dissolved in acetone at 0 °C. The solution was then stirred for 24 h at room temperature to obtain the sulfonate zwitterion [$N_{111}C_3SO_3$] as a white powder precipitate. The acetone and excess trimethylamine were removed using a rotary evaporator under reduced pressure. The yield was 100% (0.115 mol, 20.87 g). A stoichiometric amount of the super acid HTf_2N (0.115 mol, 32.33 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$N_{111}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$N_{111}C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, D_2O): 3.36 (2H, m, CH_2), 3.02 (9H, s, 3 CH_3), 2.86 (2H, t, 7.0 Hz, CH_2), 2.13 (2H, m, CH_2). ^{13}C NMR (75 MHz, δ, CD_3Cl): 125.51 (CF_3), 121.28 (CF_3), 117.04 (CF_3), 112.27 (CF_3), 64.64 (CH_2), 52.73 (CH_3), 47.17 (CH_2), 18.44 (CH_2). CHN analysis: (calculated for $C_8H_{16}F_6N_2O_7S_3$): C 20.06% (20.78%), H 3.94% (3.49%), N 5.87% (6.06%).

Glass transition temperature (-48 °C)

Density: 1.57 $g \cdot cm^{-3}$ (25 °C)

Viscosity 3230 cP (30 °C) / 180 cP (80 °C)

Degradation temperature: ≈ 275 °C

4.2 [$N_{222}C_3SO_3H$][Tf_2N]

Triethylamine (0.154 mol, 15.56 g) and 1,3-propanesultone (0.123 mol, 15.032 g) were dissolved in acetone at 0 °C. The solution was then stirred overnight at room temperature to obtain the sulfonate zwitterion [$N_{222}C_3SO_3$] as a white powder precipitate. The precipitate was filtered off and washed with acetone to remove the excess trimethylamine. The precipitate was then dried using a rotary evaporator under reduced pressure. The yield was 37% (0.045 mol, 10.050 g). A stoichiometric amount of the super acid HTf_2N (0.045 mol, 14.00 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$N_{222}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$N_{222}C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, D_2O): 3.20 (6H, m, 3 CH_2), 2.85 (2H, t, 7.5 Hz, CH_2), 2.01 (2H, m, CH_2), 1.15 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, D_2O): 125.55 (CF_3), 121.31 (CF_3), 117.03 (CF_3), 112.84 (CF_3), 54.61 (CH_2), 52.66 (CH_2), 47.18 (CH_2), 17.18 (CH_2), 6.54 (CH_3). CHN analysis: (calculated for $C_{11}H_{22}F_6N_2O_7S_3$): C 26.86% (26.19%), H 4.23% (4.40%), N 5.05% (5.55%).

Glass transition temperature (-57 °C)

Density: 1.55 g·cm^{-3} (25 °C)

Viscosity 1463 cP (30 °C) / 79 cP (80 °C)

Degradation temperature: ≈ 275 °C

4.3 [$N_{333}C_3SO_3H$][Tf_2N]

Tripropylamine (0.173 mol, 24.85 g) and 1,3-propanesultone (0.163 mol, 19.918 g) were refluxed in acetonitrile for 24 h to obtain the sulfonate zwitterion [$N_{333}C_3SO_3$] (homogeneous solution). The acetonitrile was removed using a rotary evaporator under reduced pressure. The zwitterion was then washed with toluene and dried again using a rotary evaporator. The yield was 100% (0.163 mol, 43.33 g).

A stoichiometric amount of the super acid HTf_2N (0.165 mol, 46.34 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$N_{333}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$N_{333}C_3SO_3H$][Tf_2N]

^1H NMR (300 MHz, δ, D_2O): 3.28 (2H, m, CH_2), 3.09 (6H, m, CH_2), 2.84 (2H, t, 7.0 Hz, CH_2), 2.03 (2H, m, CH_2), 1.60 (6H, m, 3 CH_2), 0.84 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, D_2O): 125.54 (CF_3), 121.34 (CF_3), 117.11 (CF_3), 112.86 (CF_3), 59.94 (CH_2), 57.44 (3 CH_2), 47.18 (CH_2), 17.33 (CH_2), 14.76 (CH_2), 9.69 (3 CH_3). CHN analysis: (calculated for $C_{14}H_{28}F_6N_2O_7S_3 \cdot 2H_2O$): C 28.65% (28.86%), H 5.84% (5.54%), N 4.77% (4.81%).

Glass transition temperature (-37 °C)

Density: 1.42 $g \cdot cm^{-3}$ (25 °C)

Viscosity 10000 cP (30 °C) / 229 cP (80 °C)

Degradation temperature: ≈ 275 °C

4.4 [$N_{444}C_3SO_3H$][Tf_2N]

Tributylamine (0.126 mol, 23.34 g) and 1,3-propanesultone (0.123 mol, 15.00 g) were refluxed in acetonitrile for 72 h to obtain the sulfonate zwitterion [$N_{444}C_3SO_3$] (homogeneous solution). The acetonitrile was removed using a rotary evaporator under reduced pressure. The zwitterion was then washed with toluene and dried again using a rotary evaporator. The yield was 100% (0.123 mol, 37.821 g).

A stoichiometric amount of the super acid HTf_2N (0.126 mol, 35.352 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$N_{444}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$N_{444}C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, D_2O): 3.28 (2H, m, CH_2), 3.13 (6H, m, CH_2), 2.84 (2H, t, 7.0 Hz, CH_2), 2.03 (2H, m, CH_2), 1.56 (6H, m, 3 CH_2), 1.26 (6H, m, 3 CH_2), 0.84 (9H, t, 7.5 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, D_2O): ^{13}C NMR (75 MHz, δ, D_2O): 125.81 (CF_3), 121.50 (CF_3), 117.27 (CF_3), 112.96 (CF_3), 58.24 (CH_2), 56.48 (3 CH_2), 47.15 (CH_2), 23.08 (CH_2), 19.00 (CH_2), 17.42 (CH_2), 12.71 (3 CH_3). CHN analysis: (calculated for $C_{17}H_{34}F_6N_2O_7S_3 \cdot 2H_2O$): C 32.40% (32.69%), H 6.27% (6.13%), N 4.53% (4.48%).

Glass transition temperature (-40 °C)

Density: 1.35 $g \cdot cm^{-3}$ (25 °C)

Viscosity: > 15000 cP (30 °C) / 310 cP (80 °C)

Degradation temperature: ≈ 275 °C

4.5 [$N_{666}C_3SO_3H$][Tf_2N]

Trihexylamine (0.0619 mol, 16.674 g) and 1,3-propanesultone (0.0614 mol, 7.499 g) were refluxed in toluene for 24 h to obtain the sulfonate zwitterion [$N_{666}C_3SO_3$] (homogeneous solution). The toluene was removed using a rotary evaporator under reduced pressure and a waxy residue was obtained. This residue was washed by stirring with diethyl ether and then filtering the resulting suspension. The product was further purified by recrystallization from ethyl acetate at -32 °C. This produced a white solid product with a yield of 34% (0.0212 mol, 8.170 g). A stoichiometric amount of the super acid HTf_2N (0.021 mol, 5.910 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$N_{666}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$N_{666}C_3SO_3H$][Tf_2N]

^1H NMR (300 MHz, δ, CD_2Cl_2): 3.40 (2H, m, CH_2), 3.17 (8H, m, 4 CH_2), 2.20 (2H, m, CH_2), 1.66 (6H, m, 3 CH_2), 1.38 (18H, m, 9 CH_2), 0.94 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, CD_3Cl): 125.91 (CF_3), 121.67 (CF_3), 122.07 (CF_3), 117.84 (CF_3), 58.98 (CH_2), 56.72 (CH_2), 47.38 (CH_2), 38.87 (CH_2), 30.87 (CH_2), 25.64 (CH_2), 22.54 (CH_2), 21.63 (CH_2), 17.32 (CH_2), 13.54 (CH_2). CHN analysis: (calculated for $C_{23}H_{46}F_6N_2O_7S_3 \cdot 8H_2O$): C 32.78% (33.82%), H 6.03% (7.65%), N 4.04% (3.43%). The slightly large than usual deviations are due to the lower purity of the trihexylamine starting product (96%) which contains amines with different alkyl chain lengths as impurities.

Glass transition temperature (-61 °C)

Density: 1.32 $g \cdot cm^{-3}$ (25 °C)

Viscosity 1347 cP (30 °C) / 111 cP (80 °C)

Degradation temperature: ≈ 270 °C

4.6 [$N_{888}C_3SO_3H$][Tf_2N]

Trioctylamine (0.0618 mol, 21.84 g) and 1,3-propanesultone (0.0614 mol, 7.449 g) were refluxed in toluene for 72 h to obtain the sulfonate zwitterion [$N_{888}C_3SO_3$] (homogeneous solution). The toluene was removed using a rotary evaporator under reduced pressure and a waxy residue was obtained. This residue was washed by stirring with diethyl ether and then filtering the resulting suspension. The resulting white powder product was collected with a yield of 54% (0.0329 mol, 15.649 g).

A stoichiometric amount of the super acid HTf_2N (0.0399 mol, 11.22 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$N_{888}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$N_{888}C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, CD_2Cl_2): 3.39 (2H, m, CH_2), 3.16 (8H, m, 4 CH_2), 2.22 (2H, m, CH_2), 1.67 (6H, m, 3 CH_2), 1.35 (30H, m, 15 CH_2), 0.92 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, CD_3Cl): 125.86.09 (CF_3), 121.66 (CF_3), 117.42 (CF_3), 113.12 (CF_3), 58.93 (CH_2), 59.05 (CH_2), 56.64 (CH_2), 53.40 (CH_2), 47.59 (CH_2), 31.56 (CH_2), 30.78 (CH_2), 28.77 (CH_2), 26.43 (CH_2), 25.98 (CH_2), 23.47 (CH_2), 22.46 (CH_2), 21.62 (CH_2), 17.27 (CH_2), 13.86 (CH_3). CHN analysis: (calculated for $C_{29}H_{58}F_6N_2O_7S_3 \cdot 8H_2O$): C 37.98% (38.65%), H 7.20% (8.28%), N 3.58% (3.11%).

Glass transition temperature (-61 °C)

Density: 1.17 g·cm^{-3} (25 °C)

Viscosity 1703 cP (30 °C) / 125 cP (80 °C)

Degradation temperature: ≈ 265 °C

4.7 [$PPh_3C_3SO_3H$][Tf_2N]

Triphenylphosphine (0.0615 mol, 16.134 g) and 1,3-propanesultone (0.0615 mol, 7.517 g) were refluxed in toluene for 24 h to obtain the sulfonate zwitterion [$PPh_3C_3SO_3$] as an orange precipitate. The precipitate was washed with toluene and dried using a rotary evaporator. The resulting orange powder product was collected with a yield of 43% (0.0265 mol, 10.196 g).

A stoichiometric amount of the super acid HTf_2N (0.0285 mol, 8.023 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$PPh_3C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$PPh_3C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, D_2O): 7.59 (15H, m, 3 phenyl), 3.33 (2H, m, CH_3), 2.90 (2H, t, 7.0 Hz, CH_2), 1.96 (2H, m, CH_2). ^{13}C NMR (75 MHz, δ, D_2O): 135.08 (phenyl), 133.49 (phenyl), 130.97 (phenyl), 121.01 (phenyl), 121.32 (CF_3), 118.02 (CF_3), 116.94 (CF_3), 113.81 (CF_3), 50.34 (CH_3), 20.28 (CH_2), 17.9 (CH_2). CHN analysis: (calculated for $C_{23}H_{22}F_6NO_7PS_3 \cdot 3H_2O$): C 38.05% (38.39%), H 4.00% (3.92%), N 2.24% (1.95%).

Glass transition temperature (-39 °C)

Density: 1.50 $g \cdot cm^{-3}$ (25 °C)

Viscosity > 20000 cP (30 °C) / 482 cP (80 °C)

Degradation temperature: ≈ 319 °C

4.8 [$P_{444}C_3SO_3H$][Tf_2N]

Tributylphosphine (0.124 mol, 25.10 g) and 1,3-propanesultone (0.121 mol, 14.798 g) were refluxed in acetonitrile for 72 h (N_2 atmopshere) to obtain the sulfonate zwitterion [$P_{444}C_3SO_3$] (homogeneous solution). The acetonitrile was removed using a rotary evaporator under reduced pressure. The resulting (liquid) zwitterion was washed by stirring with diethyl ether and then decanting the resulting suspension. The resulting (liquid) product was collected with a yield of 100% (0.121 mol, 39.280 g).

A stoichiometric amount of the super acid HTf_2N (0.125 mol, 35.000 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$P_{444}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$P_{444}C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, CD_2Cl_2): 3.31 (2H, t, 7.0 Hz, CH_2), 2.39 (2H, m, CH_2), 2.13 (8H, m, 4 CH_2), 1.54 (12H, m, 6 CH_2), 1.00 (9H, t, 7.0 Hz 3 CH_3). ^{13}C NMR (75 MHz, δ, CD_2Cl_2): 126.34 (CF_3), 122.11 (CF_3), 117.87 (CF_3), 113.63 (CF_3), 51.46 (CH_2), 51.23 (CH_2), 32.82 (CH_2), 24.24 (CH_2), 23.98 (CH_2), 23.61 (CH_2), 18.85 (CH_2), 18.26 (CH_2), 17.51 (CH_2), 17.08 (CH_2), 13.24 (CH_3). CHN analysis: (calculated for $C_{17}H_{34}F_6NO_7PS_3 \cdot 3H_2O$): C 30.12% (30.95%), H 5.96% (6.11%), N 2.47% (2.12%).

Glass transition temperature (-50 °C)

Density: 1.36 $g \cdot cm^{-3}$ (25 °C)

Viscosity 1888 cP (30 °C) / 119 cP (80 °C)

Degradation temperature: ≈ 307 °C

4.9 [$P_{666}C_3SO_3H$][Tf_2N]

Trihexylphosphine (00579 mol, 1.66 g) and 1,3-propanesultone (0.00589 mol, 0.720 g) were refluxed in toluene (90 °C) for 72 h (under N_2 atmopshere) to obtain the sulfonate zwitterion [$P_{666}C_3SO_3$] (homogeneous solution). The toluene was removed using a rotary evaporator under reduced pressure. This produced a liquid product with a yield of 95% (0.00558 mol, 2.278 g). A stoichiometric amount of the super acid HTf_2N (0.00597 mol, 1.68 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$P_{666}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$P_{666}C_3SO_3H$][Tf_2N]

^{1}H NMR (300 MHz, δ, CD_2Cl_2): 3.30 (2H, t, 7.0 Hz, CH_2), 2.40 (2H, m, CH_2), 2.14 (8H, m, 4 CH_2), 1.53 (12H, m, 6 CH_2), 1.37 (12H, m, 6 CH_2), 0.94 (9H, t, 7.0 Hz 3 CH_3). ^{13}C NMR (75 MHz, δ, CD_2Cl_2): 126.45 (CF_3), 121.16 (CF_3), 117.90 (CF_3), 113.63 (CF_3), 51.53 (CH_2), 51.30 (CH_2), 44.58 (CH_2), 31.29 (CH_2), 31.18 (CH_2), 30.50 (CH_2), 30.36 (CH_2), 24.72 (CH_2), 24.07 (CH_2), 23.82 (CH_2), 22.65 (CH_2), 21.71 (CH_2), 21.02 (CH_2), 19.21 (CH_2), 18.58 (CH_2), 18.25 (CH_2), 17.62 (CH_2), 17.17 (CH_2), 13.99 (CH_3). CHN analysis: (calculated for $C_{23}H_{46}F_6NO_7PS_3 \cdot 3H_2O$): C 37.14% (37.14%), H 6.74% (7.05%), N 2.12% (1.88%).

Glass transition temperature (-64 °C)

Density: 1.26 $g \cdot cm^{-3}$ (25 °C)

Viscosity 621 cP (30 °C) / 62 cP (80 °C)

Degradation temperature: ≈ 300 °C

4.10 [$P_{888}C_3SO_3H$][Tf_2N]

Trioctylphosphine (0.0626 mol, 23.21 g) and 1,3-propanesultone (0.0615 mol, 7.510 g) were refluxed in toluene (90 °C) for 72 h (under N_2 atmopshere) to obtain the sulfonate zwitterion [$P_{888}C_3SO_3$] (precipitate). The toluene was removed using a rotary evaporator under reduced pressure and the zwitterion powder was washed with diethyl ether. The resulting white powder product was collected with a yield of 90% (0.0552 mol, 27.182 g).

A stoichiometric amount of the super acid HTf_2N (0.0622 mol, 17.478 g) was then added (as a 80 wt% solution in H_2O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [$P_{888}C_3SO_3H$][Tf_2N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [$P_{888}C_3SO_3H$][Tf_2N]

^1H NMR (300 MHz, δ, CD_2Cl_2): 3.35 (2H, t, 7.0 Hz, CH_2), 2.39 (2H, m, CH_2), 2.13 (8H, m, 4 CH_2), 1.53 (12H, m, 6 CH_2), 1.33 (24H, m, 12 CH_2), 0.93 (9H, t, 7.0 Hz 3 CH_3). ^{13}C NMR (75 MHz, δ, CD_2Cl_2): 126.34 (CF_3), 122.01 (CF_3), 117.86 (CF_3), 113.63 (CF_3), 51.59 (CH_2), 51.37 (CH_2), 32.03 (CH_2), 31.04 (CH_2), 30.83 (CH_2), 29.28 (CH_2), 29.04 (CH_2), 22.95 (CH_2), 21.76 (CH_2), 19.19 (CH_2), 18.57 (CH_2), 18.25 (CH_2), 17.62 (CH_2), 17.13 (CH_2), 14.18 (CH_3). CHN analysis: (calculated for $C_{29}H_{58}F_6NO_7PS_3\cdot 3H_2O$): C 41.55% (42.07%), H 7.40% (7.79%), N 2.01% (1.69%).

Glass transition temperature (-56 °C)

Density: 1.20 $g\cdot cm^{-3}$ (25 °C)

Viscosity 1916 cP (30 °C) / 116 cP (80 °C)

Degradation temperature: ≈ 320 °C

5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out to determine the thermal stability of the different ionic liquids (Figure S **1**). The measurements were done on a TA Instruments T500 thermogravimeter (heating rate: 5 °C min^{-1} from room temperature to 400 °C, in a nitrogen atmosphere). Most of the ILs still contain around 5-10 wt% of hydration water even after extensive drying. This is also reflected in the molar equivalents of water that were determined by CHN analysis.

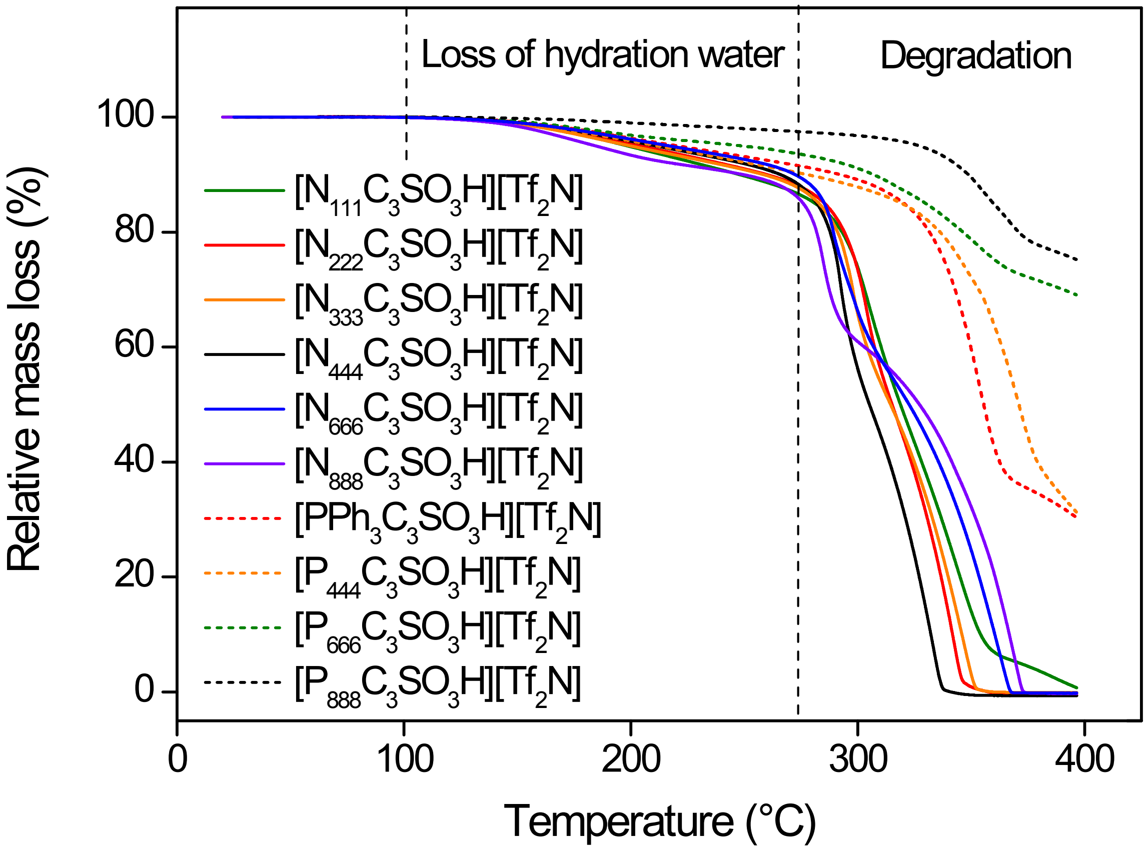


Figure S 1. Thermogravimetric analysis for the different synthesized ionic liquids (5 °C/min, N_2 atmosphere).

6. Effect of water on the viscosity of the ILs

Increasing amounts of water were added to the ionic liquid [$N_{111}C_3SO_3H$][Tf_2N] to test the effect on the viscosity (50 °C) (Figure S **2**).

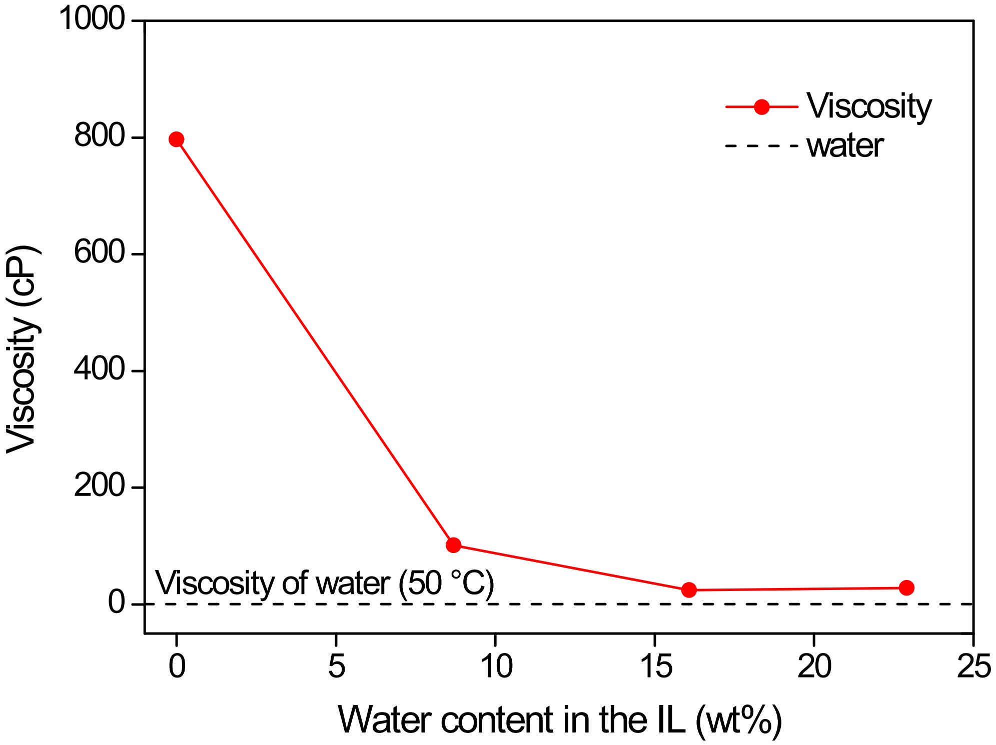


Figure S 2. Effect of the water content (wt%) on the viscosity of the ionic liquid [$N_{111}C_3SO_3H$][Tf_2N] at 50 °C.