Electronic Supporting Information

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

David Dupont†, Stijn Raiguel†, Koen Binnemans*†
1. Chemicals and materials

Chemicals for extraction and leaching experiments

NiO (97%), Y₂O₃ (99.99%), CrCl₃·6H₂O (98%), ZnCl₂ (98.5%), CuCl₂ anh. (99%), H₂SO₄ (96%), HCl (37%), 1,4-dioxane (99.9%), Al₂O₃ (99%), Cr₂O₃ (99%) and LaCl₃·7H₂O (99.99%) were purchased from Acros Organics (Geel, Belgium). La₂O₃ (99.99%), Fe₂O₃ (95%), TiO₂ (99%), GaCl₃ anh. (99.99%), NiCl₂ (98%), InCl₃ (97%), FeCl₃ (99%), YCl₃·6H₂O (99.9%), DyCl₃·6H₂O (99.9%), CoCl₂ (97%), MnO (99%) and LuCl₃·6H₂O (99.9%) were bought from Sigma-Aldrich (Diegem, Belgium). NdCl₃·6H₂O (99.9%) and Co₃O₄ (99.5%) were purchased from Strem Chemicals Inc. (Newburyport, USA), SnCl₂ (99%) from Merck (Overijse, Belgium) and WO₃ (99%) from ABCR Chemicals (Karlsruhe, Germany). CaCl₂·2H₂O (99.5%) and the 1000 mg·L⁻¹ gallium(III) and selenium(VI) standard solutions in HNO₃ (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 Aesar (Karlsruhe, Germany). A silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH (Germany). All chemicals were used as received without further purification.

Sc₂O₃ was kindly provided by Solvay (La Rochelle, France). ScCl₃·xH₂O was prepared by dissolving Sc₂O₃ 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.
Bistriflimic acid (80 wt% in H₂O) (99%) was purchased from IoLiTec (HeilBonn, 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* 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$_2$N 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

<table>
<thead>
<tr>
<th>IL abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>([\text{N}_{111}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Trimethylammoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{N}_{222}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Triethylammoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{N}_{333}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Tripropylammoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{N}_{444}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Tributylammoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{N}_{666}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Trihexylammoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{N}_{888}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Trioctylammoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{P}_{444}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Tributylphosphoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{P}_{666}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Trihexylphosphoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{P}_{888}\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Trioctylphosphoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
<tr>
<td>([\text{PPPh}_3\text{C}_3\text{SO}_3\text{H}])[\text{TF}_2\text{N}]</td>
<td>Triphenylphosphoniumpropanesulfonic acid bistriflimide(^{(a)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\)Bistriflimide = bis(trifluoromethylsulfonyl)imide
4. Synthesis of ionic liquids

4.1 [N\textsubscript{111}C\textsubscript{3}SO\textsubscript{3}H][Tf\textsubscript{2}N]

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\textsubscript{111}C\textsubscript{3}SO\textsubscript{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\textsubscript{2}N (0.115 mol, 32.33 g) was then added (as a 80 wt% solution in H\textsubscript{2}O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [N\textsubscript{111}C\textsubscript{3}SO\textsubscript{3}H][Tf\textsubscript{2}N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [N\textsubscript{111}C\textsubscript{3}SO\textsubscript{3}H][Tf\textsubscript{2}N]

\textsuperscript{1}H NMR (300 MHz, δ, D\textsubscript{2}O): 3.36 (2H, m, CH\textsubscript{2}), 3.02 (9H, s, 3 CH\textsubscript{3}), 2.86 (2H, t, 7.0 Hz, CH\textsubscript{2}), 2.13 (2H, m, CH\textsubscript{2}). \textsuperscript{13}C NMR (75 MHz, δ, CD\textsubscript{3}Cl): 125.51 (CF\textsubscript{3}), 121.28 (CF\textsubscript{3}), 117.04 (CF\textsubscript{3}), 112.27 (CF\textsubscript{3}), 64.64 (CH\textsubscript{2}), 52.73 (CH\textsubscript{3}), 47.17 (CH\textsubscript{2}), 18.44 (CH\textsubscript{2}). CHN analysis: (calculated for C\textsubscript{8}H\textsubscript{16}F\textsubscript{6}N\textsubscript{2}O\textsubscript{7}S\textsubscript{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⋅cm\textsuperscript{-3} (25 °C)

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

Degradation temperature: ≈ 275 °C
4.2 $[\text{N}_{222}\text{C}_3\text{SO}_3\text{H}][\text{Tf}_2\text{N}]$

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 $[\text{N}_{222}\text{C}_3\text{SO}_3]$ 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$_2$N (0.045 mol, 14.00 g) was then added (as a 80 wt% solution in H$_2$O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid $[\text{N}_{222}\text{C}_3\text{SO}_3\text{H}][\text{Tf}_2\text{N}]$, in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid $[\text{N}_{222}\text{C}_3\text{SO}_3\text{H}][\text{Tf}_2\text{N}]$

$^1$H NMR (300 MHz, δ, D$_2$O): 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$_2$O): 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$_6$N$_2$O$_7$S$_3$): 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\textsubscript{333}C\textsubscript{3}SO\textsubscript{3}H][\text{Tf}_2\text{N}]

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\textsubscript{333}C\textsubscript{3}SO\textsubscript{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\textsubscript{2}N (0.165 mol, 46.34 g) was then added (as a 80 wt% solution in H\textsubscript{2}O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [N\textsubscript{333}C\textsubscript{3}SO\textsubscript{3}H][\text{Tf}_2\text{N}], in quantitative yield. The product was dried using a Schlenk line.

**Ionic liquid [N\textsubscript{333}C\textsubscript{3}SO\textsubscript{3}H][\text{Tf}_2\text{N}]**

\(^1\text{H}\) NMR (300 MHz, \(\delta, \text{D}_2\text{O}\)): 3.28 (2H, m, CH\textsubscript{2}), 3.09 (6H, m, CH\textsubscript{2}), 2.84 (2H, t, 7.0 Hz, CH\textsubscript{2}), 2.03 (2H, m, CH\textsubscript{2}), 1.60 (6H, m, 3 CH\textsubscript{2}), 0.84 (9H, t, 7.0 Hz, 3 CH\textsubscript{3}). \(^{13}\text{C}\) NMR (75 MHz, \(\delta, \text{D}_2\text{O}\)): 125.54 (CF\textsubscript{3}), 121.34 (CF\textsubscript{3}), 117.11 (CF\textsubscript{3}), 112.86 (CF\textsubscript{3}), 59.94 (CH\textsubscript{2}), 57.44 (3 CH\textsubscript{2}), 47.18 (CH\textsubscript{2}), 17.33 (CH\textsubscript{2}), 14.76 (CH\textsubscript{2}), 9.69 (3 CH\textsubscript{3}). CHN analysis: (calculated for C\textsubscript{14}H\textsubscript{28}F\textsubscript{6}N\textsubscript{2}O\textsubscript{7}S\textsubscript{3}·2H\textsubscript{2}O): C 28.65% (28.86%), H 5.84% (5.54%), N 4.77% (4.81%).

Glass transition temperature (-37 °C)

Density: 1.42 g·cm\(^{-3}\) (25 °C)

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

Degradation temperature: \(\approx \) 275 °C
4.4 [N\text{444}C_3SO_3\text{H}][\text{Tf}_2\text{N}]

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\text{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\text{2}N (0.126 mol, 35.352 g) was then added (as a 80 wt% solution in H\text{2}O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [N\text{444}C_3SO_3\text{H}][\text{Tf}_2\text{N}], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [N\text{444}C_3SO_3\text{H}][\text{Tf}_2\text{N}]

\text{1H NMR (300 MHz, } \delta, \text{D}_2\text{O): 3.28 (2H, m, CH}_2\text{), 3.13 (6H, m, CH}_2\text{), 2.84 (2H, t, 7.0 Hz, CH}_2\text{), 2.03 (2H, m, CH}_2\text{), 1.56 (6H, m, 3 CH}_2\text{), 1.26 (6H, m, 3 CH}_2\text{), 0.84 (9H, t, 7.5 Hz, 3 CH}_3\text{).}\text{ 13C NMR (75 MHz, } \delta, \text{D}_2\text{O): 13C NMR (75 MHz, } \delta, \text{D}_2\text{O): 125.81 (CF}_3\text{), 121.50 (CF}_3\text{), 117.27 (CF}_3\text{), 112.96 (CF}_3\text{), 58.24 (CH}_2\text{), 56.48 (3 CH}_2\text{), 47.15 (CH}_2\text{), 23.08 (CH}_2\text{), 19.00 (CH}_2\text{), 17.42 (CH}_2\text{), 12.71 (3 CH}_3\text{). CHN analysis: (calculated for C}_{17}H_{34}F_6N_2O_7S_3\cdot2H_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·cm\text{3} (25 °C)
Viscosity: > 15000 cP (30 °C) / 310 cP (80 °C)
Degradation temperature: \approx 275 °C
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 \( [N_{666}C_3SO_3H][Tf_2N] \)**

\[^1H\text{ NMR (300 MHz, } \delta, \text{ CD}_2\text{Cl}_2): 3.40 (2H, m, CH}_2\text{), 3.17 (8H, m, 4 CH}_2\text{), 2.20 (2H, m, CH}_2\text{), 1.66 (6H, m, 3 CH}_2\text{), 1.38 (18H, m, 9 CH}_2\text{), 0.94 (9H, t, 7.0 Hz, 3 CH}_3\text{).} \]

\[^{13}C\text{ NMR (75 MHz, } \delta, \text{ CD}_3\text{Cl): 125.91 (CF}_3\text{), 121.67 (CF}_3\text{), 122.07 (CF}_3\text{), 117.84 (CF}_3\text{), 58.98 (CH}_2\text{), 56.72 (CH}_2\text{), 47.38 (CH}_2\text{), 38.87 (CH}_2\text{), 30.87 (CH}_2\text{), 25.64 (CH}_2\text{), 22.54 (CH}_2\text{), 21.63 (CH}_2\text{), 17.32 (CH}_2\text{), 13.54 (CH}_2\text{).} \]

CHN analysis: (calculated for \( \text{C}_{23}\text{H}_{46}\text{F}_6\text{N}_{2}\text{O}_7\text{S}_3\cdot8\text{H}_2\text{O}): 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·cm\(^{-3}\) (25 °C)

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

Degradation temperature: \( \approx 270 °C \)
4.6 \([\text{N}_{888}\text{C}_3\text{SO}_3\text{H}]\text{[Tf}_2\text{N}]\)

Triocetylaine (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 \([\text{N}_{888}\text{C}_3\text{SO}_3]^{-}\) (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 \(\text{HTf}_2\text{N}\) (0.0399 mol, 11.22 g) was then added (as a 80 wt% solution in \(\text{H}_2\text{O}\)) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid \([\text{N}_{888}\text{C}_3\text{SO}_3\text{H}]\text{[Tf}_2\text{N}]\), in quantitative yield. The product was dried using a Schlenk line.

**Ionic liquid \([\text{N}_{888}\text{C}_3\text{SO}_3\text{H}]\text{[Tf}_2\text{N}]\)**

\(^1\text{H}\) NMR (300 MHz, \(\delta\), \(\text{CD}_2\text{Cl}_2\)): 3.39 (2H, m, \(\text{CH}_2\)), 3.16 (8H, m, 4 \(\text{CH}_2\)), 2.22 (2H, m, \(\text{CH}_2\)), 1.67 (6H, m, 3 \(\text{CH}_2\)), 1.35 (30H, m, 15 \(\text{CH}_2\)), 0.92 (9H, t, 7.0 Hz, 3 \(\text{CH}_3\)). \(^{13}\text{C}\) NMR (75 MHz, \(\delta\), \(\text{CD}_3\text{Cl}\)): 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 \(\text{C}_{29}\text{H}_{58}\text{F}_6\text{N}_2\text{O}_7\text{S}_3\cdot8\text{H}_2\text{O}\)): C 37.98% (38.65%), H 7.20% (8.28%), N 3.58% (3.11%).

Glass transition temperature (-61 °C)
Density: \(1.17 \text{ g cm}^{-3}\) (25 °C)
Viscosity 1703 cP (30 °C) / 125 cP (80 °C)
Degradation temperature: \(\approx 265 \text{ °C}\)
4.7 [PPh₃C₃SO₃H][Tf₂N]

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 [PPh₃C₃SO₃] 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 HTf₂N (0.0285 mol, 8.023 g) was then added (as a 80 wt% solution in H₂O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [PPh₃C₃SO₃H][Tf₂N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [PPh₃C₃SO₃H][Tf₂N]

¹H NMR (300 MHz, δ, D₂O): 7.59 (15H, m, 3 phenyl), 3.33 (2H, m, CH₃), 2.90 (2H, t, 7.0 Hz, CH₂), 1.96 (2H, m, CH₂). ¹³C NMR (75 MHz, δ, D₂O): 135.08 (phenyl), 133.49 (phenyl), 130.97 (phenyl), 121.01 (phenyl), 121.32 (CF₃), 118.02 (CF₃), 116.94 (CF₃), 113.81 (CF₃), 50.34 (CH₃), 20.28 (CH₂), 17.9 (CH₂). CHN analysis: (calculated for C₂₃H₂₂F₆NO₇PS₃·3H₂O): C 38.05% (38.39%), H 4.00% (3.92%), N 2.24% (1.95%).

Glass transition temperature (-39 °C)

Density: 1.50 g·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\(_2\) atmosphere) 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\(_2\)N (0.125 mol, 35.000 g) was then added (as a 80 wt% solution in H\(_2\)O) 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, \(\delta, \text{CD}_2\text{Cl}_2\)): 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, \(\delta, \text{CD}_2\text{Cl}_2\)):

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\(_6\)NO\(_7\)PS\(_3\)·3H\(_2\)O): C 30.12% (30.95%), H 5.96% (6.11%), N 2.47% (2.12%).

Glass transition temperature (-50 °C)

Density: 1.36 g·cm\(^{-3}\) (25 °C)

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

Degradation temperature: \(\approx\) 307 °C
4.9 [P$_{66}$C$_3$SO$_3$H][Tf$_2$N]

Trihexylphosphine (0.00579 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$_2$ atmosphere) to obtain the sulfonate zwitterion [P$_{66}$C$_3$SO$_3$] (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$_2$N (0.00597 mol, 1.68 g) was then added (as a 80 wt% solution in H$_2$O) to the sulfonate zwitterion and the mixture was stirred for 2 h at 50 °C to obtain the sulfonic acid functionalized ionic liquid [P$_{66}$C$_3$SO$_3$H][Tf$_2$N], in quantitative yield. The product was dried using a Schlenk line.

Ionic liquid [P$_{66}$C$_3$SO$_3$H][Tf$_2$N]

$^1$H NMR (300 MHz, δ, CD$_2$Cl$_2$): 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$_2$Cl$_2$): 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$_6$NO$_7$PS$_3$·3H$_2$O): C 37.14% (37.14%), H 6.74% (7.05%), N 2.12% (1.88%).

Glass transition temperature (-64 °C)

Density: 1.26 g·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]

Triocetylphosphine (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 atmosphere) 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). ^13C 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_3·3H_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·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, N₂ atmosphere).
6. Effect of water on the viscosity of the ILs

Increasing amounts of water were added to the ionic liquid $\text{[N}_{111}\text{C}_{3}\text{SO}_{3}\text{H}]\text{[Tf}_2\text{N]}$ to test the effect on the viscosity (50 °C) (Figure S 2).

![Graph showing the effect of water content on viscosity](image)

Figure S 2. Effect of the water content (wt%) on the viscosity of the ionic liquid $\text{[N}_{111}\text{C}_{3}\text{SO}_{3}\text{H}]\text{[Tf}_2\text{N]}$ at 50 °C.