Electronic Supporting Information

Alkylsulfuric acid ionic liquids: a promising class of strongly acidic room-temperature ionic liquids

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1. Chemicals and materials

Chemicals for extraction and leaching experiments

NiO (97%), $ZnCl_2$ (98.5%), $CuCl_2$ anh. (99%), HCl (37%), Al_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%), $NiCl_2$ (98%), $InCl_3$ (97%), $YCl_3 \cdot 6H_2O$ (99.9%), $DyCl_3 \cdot 6H_2O$ (99.9%) and $CoCl_2$ (97%) 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). CaO (96%) was purchased from Riedel-de Haën AG (Seelze, Germany). The 1000 $mg \cdot L^{-1}$ gallium(III) standard solution in HNO_3 (2−5 wt%) was obtained from Chem-Lab (Zedelgem, Belgium). Ethanol (Analytical reagent grade) was obtained from Fisher Scientific Limited (Loughborough, UK). CuO (99.9999%) was 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.

Chemicals for ionic liquid synthesis

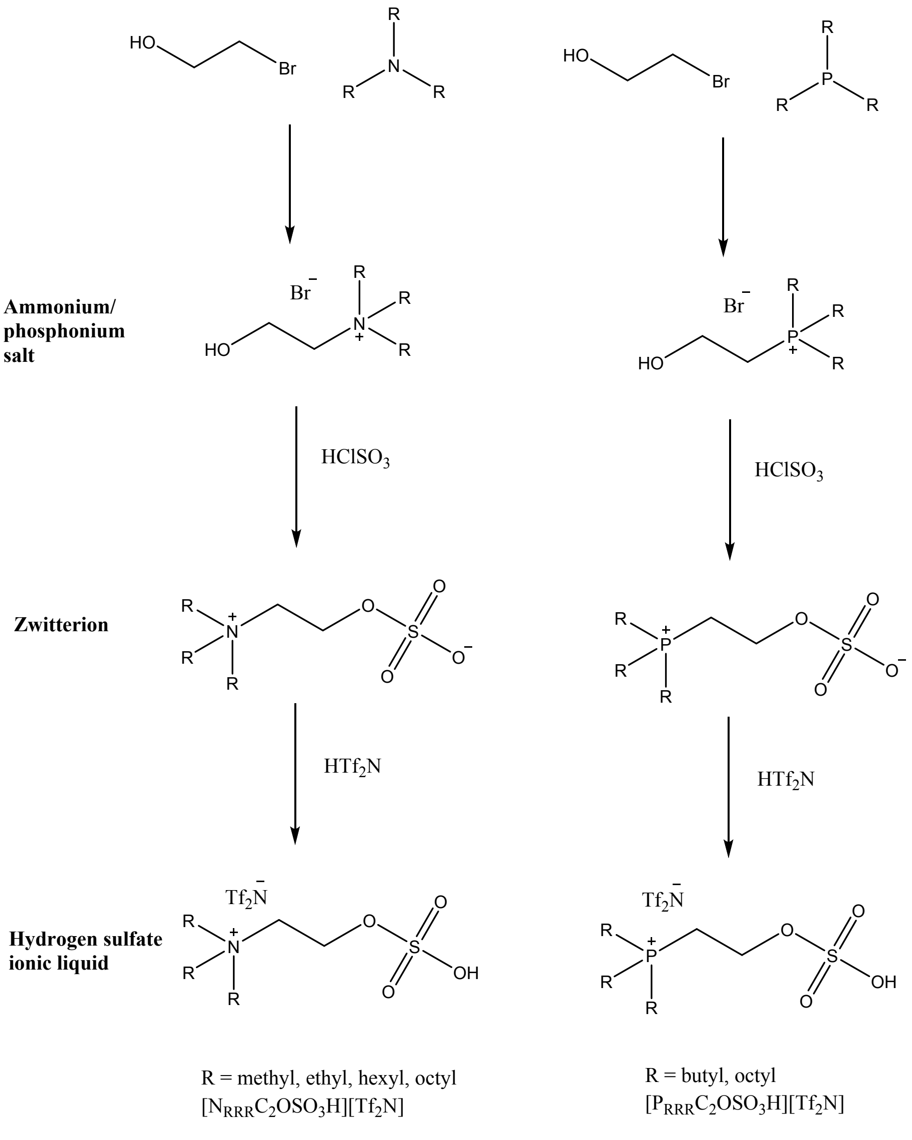
2-Bromoethanol (97%) was purchased from J&K Scientific (Beijing, China). Bistriflimic acid (80 wt% in H_2O) (99%) was purchased from IoLiTec (HeilBronn, Germany). Triethylamine (99%), choline chloride (99%), and trioctylphosphine (90%) purchased from Acros Organics (Geel, Belgium). Tri-*n*-butylphosphine (97%), trioctylamine (98%), trihexylamine (96%), chlorosulfonic acid (98%), ethylacetate (99.7%), toluene (99%), acetone (99.8, extra dry), and diethylether (99.8%) were obtained from Sigma-Aldrich (Diegem, Belgium). Trihexyl phosphine (95%) was bought from TCI (Zwijndrecht, Belgium). Acetonitrile (HPLC grade), Dichloromethane (99.8%), 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 300/400 spectrometer (operating at 300/400 MHz for ^{1}H, 75/100 MHz for ^{13}C, and 121/162 MHz for ^{31}P). The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ^{1}H and ^{13}C, and to 85% H_3PO_4 for ^{31}P. The coupling constants are given in Hertz. Solutions were made in D_2O, acetone-d_6 or CD_3Cl. 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. The viscosity of the ionic liquids was measured using an Anton-Paar rolling-ball viscometer Lovis 2000 M/ME. The density of the ionic liquids was determined using an Anton-Paar DMA 4500 M digital density meter. 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: 10 °C min^{-1} from room temperature to 500 °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) solution) and ethanol/water (800 µL). To measure the ionic liquid, a smaller sample was taken (75 mg) and dissolved in ethanol/water (800 µL). The microtubes were then vigorously shaken on a vibrating plate (IKA MS 3 basic). Finally, a 4 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 8 min.

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

The synthetic strategy was based on a 3-step reaction (Scheme S 1). First 2-bromoethanol was reacted with the appropriate trialkylamine or trialkylphoshine to obtain the ammonium/phosphonium salt. The ammonium/phosphonium salt was reacted with chlorosulfonic acid and base to obtain the hydrogen sulfate 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.



R = methyl, ethyl, hexyl, octyl
$[N_{RRR}C_2OSO_3H][Tf_2N]$

R = butyl, octyl
$[P_{RRR}C_2OSO_3H][Tf_2N]$

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

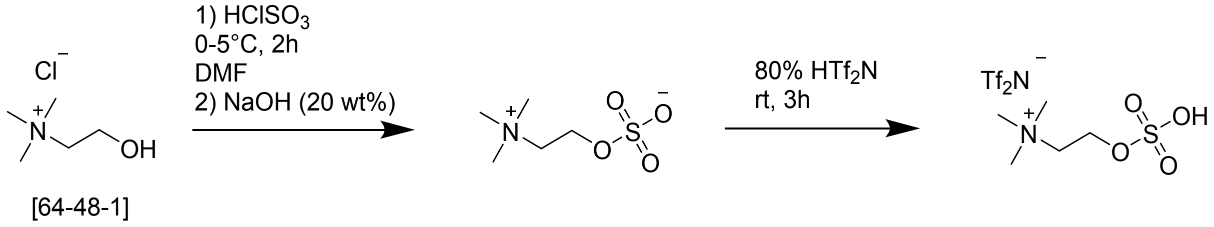
Table S 1. Overview of the ionic liquids synthesized in this work

Nr	IL abbreviation	Full name
1	$[N_{111}C_2OSO_3H][Tf_2N]$	Trimethylammoniumethane hydrogen sulfate bistriflimide$^{(a)}$
2	$[N_{222}C_2OSO_3H][Tf_2N]$	Triethylammoniumethane hydrogen sulfate bistriflimide$^{(a)}$
3	$[N_{666}C_2OSO_3H][Tf_2N]$	Trihexylammoniumethane hydrogen sulfate bistriflimide$^{(a)}$
4	$[N_{888}C_2OSO_3H][Tf_2N]$	Trioctylammoniumethane hydrogen sulfate bistriflimide$^{(a)}$
5	$[P_{444}C_2OSO_3H][Tf_2N]$	Tributylphosphoniummethane hydrogen sulfate bistriflimide$^{(a)}$
6	$[P_{888}C_2OSO_3H][Tf_2N]$	Trioctylphosphoniumethane hydrogen sulfate bistriflimide$^{(a)}$
7	$[N_{111}C_3OSO_3H][Tf_2N]$	Trimethylammoniumpropane hydrogen sulfate bistriflimide$^{(a)}$
8	$[N_{111}C_4OSO_3H][Tf_2N]$	Trimethylammoniumbutane hydrogen sulfate bistriflimide$^{(a)}$

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

4. Synthesis of ionic liquids

4.1 $[N_{111}C_2OSO_3H][Tf_2N]$



In a three-necked round bottom flask, equipped with stirring bar, choline chloride (20 g, 0.14 mol) was dissolved in 100 mL of DMF. The resulting mixture was stirred in an ice bath for 10 min. A solution of chlorosulfonic acid (20.03 g, 0.17 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 2 h at 0 °C. The produced HCl gas, was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%) and a white precipitate was formed. The solvent was removed under reduced pressure, yielding a mixture of the zwitterion $[N_{111}C_2OSO_3]$ and NaCl salts as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, the zwitterion $[N_{111}C_2OSO_3]$ zwitterion (26 g, 0.14 mol) was dissolved in 50 mL of water. An aqueous solution of bistriflimic acid (80 wt%) (59.85 g, 0.17 mol) was added dropwise at room temperature. The resulting mixture was stirred for 3 h. The solvent was removed under reduced pressure, yielding an light brown colored oil. The residue was stirred in 3 times in 100 mL dry acetone, the salts were filtered off, and the solvent removed under reduced pressure. The product was dried on a Schlenk line, and 42.43 g (overall yield 63%) of $[N_{111}C_2OSO_3H][Tf_2N]$ was obtained as a brown colored viscous oil.

Ionic liquid $[N_{111}C_2OSO_3H][Tf_2N]$

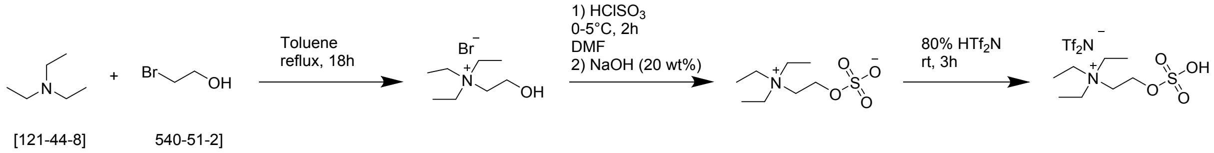
^1H NMR: (300 MHz, acetone-*d6*, δ/ppm): 9.78 (s, 1H, S-OH), 4.10 (m, 2H, CH_2-N), 3.62 (m, 2H, CH_2), 3.31 (s, 9H, 3 CH_3).

^{13}C NMR (75 MHz, acetone-*d6*, δ/ppm): 120.82 (CF_3, q, J= 318 Hz), 68.57 (CH_2), 56.85 (CH_2), 54.65 (CH_3).

ATR-FTIR: (ν/cm^{-1}): 3049, 2990, 2853 (C-H stretch), 1479 (C-H bending), 1345 (asymmetric O=S=O stretch), 1181 (CF_3 stretch), 1133 (symmetric O=S=O stretch), 1053 (S-N stretch), 612 (s, SO_2 bending), 571 (s, CF_3 bending), 513 (s, CF_3 bending).

Glass transition temperature (-28.3 °C)
Density: 1.57 g·cm^{-3} (25 °C)
Viscosity 323 cP (25 °C)

4.2 [$N_{222}C_2OSO_3H$][Tf_2N]



In a three-necked round bottom flask, equipped with stirring bar, triethylamine (4.05 g, 0.04 mol) was dissolved in toluene (40 mL). The resulting solution was heated at 90 °C, 2-bromoethanol (5.0 g, 0.04 mol) was added dropwise and the resulting mixture was stirred for 18 h at 110 °C. Afterwards the resulting mixture was cooled to room temperature. The precipitate was filtered, washed with acetone and dried under reduced pressure, yielding 8.77 (yield = 97%) of the ammonium salt as a white powder.

In a three-necked round bottom flask, equipped with stirring bar, the ammonium salt (1 g, 4 mmol) was dissolved in 50 mL of DMF. The resulting mixture was stirred in an ice bath for 10 min.. A solution of chlorosulfonic acid (515 mg, 5 mmol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 2 h at 0 °C. The produced HCl or HBr gas, was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%) and a white precipitate was formed. The solvent was removed under reduced pressure, yielding the zwitterion [$N_{222}C_2OSO_3$] and some NaCl and NaBr salts.

In a three-necked round bottom flask, equipped with stirring bar, the zwitterion [$N_{222}C_2OSO_3$] (0.99 g, 4 mmol) was dissolved in 10 mL water. An aqueous solution of bistriflimic acid (80 wt%) (1.865 g, 0.005 mol) was added dropwise at room temperature. The resulting mixture was stirred for 3 h. Afterwards, the solvent was removed under reduced pressure, yielding a yellow colored solid. The residue is stirred in 100 mL dry acetone to precipitate the salts. The precipitate was filtered off and the filtrate concencentrated under reduced pressure. The ionic liquid was dried on a Schlenk line at 60 °C, yielding 1.79 g (yield = 80%) of [$N_{222}C_2OSO_3H$][Tf_2N] as a brown colored viscous oil.

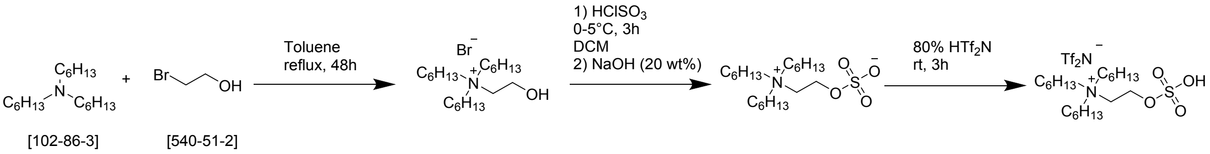
Ionic liquid [$N_{222}C_2OSO_3H$][Tf_2N]

^{1}H NMR: (300 MHz, DMSO-*d*$_6$, δ/ppm): 3.78 (m, 2H, CH_2-O-S), 3.29 (m, 8H, 4 CH_2-N), 1.19 (t, 9H, J= 7.0 Hz, 3 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 119.43 (CF_3, q, J= 320 Hz), 54.44 (CH_2), 52.66 (CH_2), 30.51 (CH_2), 7.04 (CH_3).

ATR-FTIR: (ν/cm^{-1}): 3000, 2990, 2854 (C-H stretch), 1471 (C-H bending), 1347 (asymmetric O=S=O stretch), 1181 (CF_3 stretch), 1134 (symmetric O=S=O stretch), 1053 (S-N stretch), 613 (s, SO_2 bending), 571 (s, CF_3 bending), 512 (s, CF_3 bending).
Density: 1.46 g·cm^{-3} (25 °C)
Viscosity 377 cP (25 °C)

4.3 [$N_{666}C_2OSO_3H$][Tf_2N]



In a three-necked round bottom flask, equipped with stirring bar, trihexylamine (13.0 g, 0.048 mol) was dissolved in toluene (70 mL). The resulting solution was heated at 110 °C. 2-Bromoethanol (5.0 g, 0.04 mol) was added dropwise and the resulting mixture is stirred for 48 h at 110 °C. Afterwards the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was stirred two times in 200 mL diethyl ether overnight. The resulting residue was dissolved in 50 mL ethyl acetate and recrystallized in the freezer. The crystals were filtered off and dried under vacuum, yielding 4.76 g (yield = 30%) of the ammonium salt as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, the ammonium salt (1 g, 3 mmol) was dissolved in 20 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. A solution of chlorosulfonic acid (354 mg, 4 mmol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 3 h at 0 °C. The produced HCl or HBr gas, was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%). The the organic phase was washed with 20 mL water, dried over anhydr. Magnesium sulfate, filtered and concentrated under reduced pressure. The resulting residue was stirred in 200 mL diethyl ether overight. The formed precipitate was filtered off and dried under vacuum, yielding 0.90 g (yield = 90%) of the zwitterion $[N_{666}C_2OSO_3]$ as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, the zwitterion $[N_{666}C_2OSO_3]$ (0.90 g, 2.3 mmol) was dissolved in 20 mL toluene. An aqueous solution of bistriflimic acid (80 wt%) (1.0 g, 2.8 mmol) was added dropwise at room temperature. The resulting mixture was stirred for 3. Afterwards, the solvent was removed under reduced pressure, yielding 1.47 g (yield = 95%) of $[N_{666}C_2OSO_3H][Tf_2N]$ as a brown colored viscous oil.

Ionic liquid $[N_{666}C_2OSO_3H][Tf_2N]$

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 4.05 (m, 2H, CH_2-O-S), 3.42 (m, 2H, CH_2-N), 3.20 (m, 6H, 3 CH_2-N), 1.62 (m, 6H, 3 CH_2), 1.33 (m, 18H, 9 CH_2), 0.90 (t, 9H, J= 7.0 Hz, 3 CH_3).

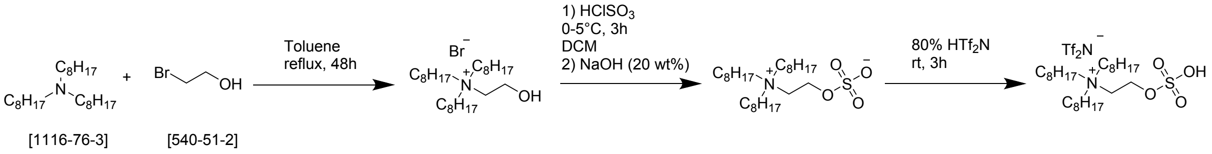
^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 122.77 (CF_3, q, J= 320 Hz), 60.20 (CH_2), 56.35 (CH_2), 31.66 (CH_2), 30.26 (CH_2), 26.42 (CH_2), 22.99 (CH_2), 22.33 (CH_2), 14.18 (CH_3).

ATR-FTIR: (ν/cm^{-1}): 2959, 2932, 2863 (C-H stretch), 1468 (C-H bending), 1347 (asymmetric O=S=O stretch), 1184 (CF_3 stretch), 1134 (symmetric O=S=O stretch), 1054 (S-N stretch), 615 (s, SO_2 bending), 571 (s, CF_3 bending), 513 (s, CF_3 bending).

Density: 1.30 g·cm^{-3} (25 °C)

Viscosity 1950 cP (25 °C)

4.4 $[N_{888}C_2OSO_3H][Tf_2N]$



In a three-necked round bottom flask, equipped with stirring bar, trioctylamine (17.0 g, 0.048 mol) was dissolved in toluene (75 mL). The resulting solution was heated at 110 °C. 2-Bromoethanol (5.0 g, 0.04 mol) was added dropwise and the resulting mixture was stirred for 48 h at 110 °C. Afterwards the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was stirred two times in 200 mL diethyl ether overnight. The resulting residue was dissolved in 50 mL ethyl acetate and recrystallized in the freezer. The crystals were filtered off and dried under vacuum, yielding 7.35 g (yield = 41 %) of the ammonium salt as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, the ammonium (1 g, 2 mmol) was dissolved in 20 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. A solution of chlorosulfonic acid (292 mg, 3 mmol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 3 h at 0 °C. The produced HCl or HBr gas, was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%). The the organic phase was washed with 20 mL water, dried over anhydr. Magnesium sulfate, filtered and concentrated under reduced pressure. The resulting residue was stirred in 200 mL diethyl ether overight. The formed precipitate was filtered off and dried under vacuum, yielding 0.90 g (yield = 90%) of the zwitterion [$N_{888}C_2OSO_3$] as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, the zwitterion [$N_{888}C_2OSO_3$] (0.90 g, 1.8 mmol) was dissolved in 20 mL toluene. An aqueous solution of bistriflimic acid (80 wt%) (0.79 g, 2.2 mmol) was added dropwise at room temperature. The resulting mixture was stirred for 3 h. Afterwards, the solvent was removed under reduced pressure, yielding 1.35 g (yield = 95%) of [$N_{888}C_2OSO_3H$][Tf_2N] as a brown colored viscous oil.

Ionic liquid [$N_{888}C_2OSO_3H$][Tf_2N]

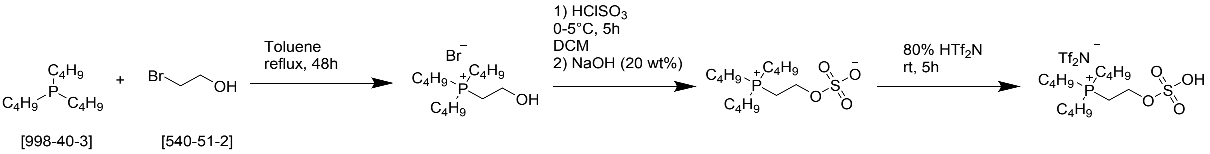
^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 4.02 (m, 2H, CH_2-O-S), 3.42 (m, 2H, CH_2-N), 3.23 (m, 6H, 3 CH_2-N), 1.62 (m, 6H, 3 CH_2), 1.30 (m, 30H, 15 CH_2), 0.88 (t, 9H, J= 7.0 Hz, 3 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 120.97 (CF_3, q, J= 320 Hz), 60.20 (CH_2), 56.21 (CH_2), 36.70 (CH_2), 34.39 (CH_2), 32.18 (CH_2), 29.96 (CH_2), 26.93 (CH_2), 23.26 (CH_2), 22.44 (CH_2), 14.38 (CH_3).

ATR-FTIR: (v/cm^{-1}): 2964, 2929, 2860 (C-H stretch), 1457 (C-H bending), 1346 (asymmetric O=S=O stretch), 1185 (CF_3 stretch), 1134 (symmetric O=S=O stretch), 1055 (S-N stretch), 615 (s, SO_2 bending), 571 (s, CF_3 bending), 513 (s, CF_3 bending).

Density: 1.28 g·cm^{-3} (25 °C)
Viscosity: 1538 cP (25 °C)

4.5 [$P_{444}C_2OSO_3H$][Tf_2N]



In a three-necked round bottom flask, equipped with stirring bar and nitrogen inlet, tributylphosphine (16.35 g, 0.08 mol) and 2-bromoethanol (10.0 g, 0.08 mol) were dissolved in toluene (75 mL). The resulting solution was heated at 110 °C, and stirred for 48 h. Afterwards the mixture was cooled to room temperature, and the solvent removed under reduced pressure. The residue is washed four times with 200 mL diethyl ether and 2 times with 100 mL *n*-heptane. This yields 16.23 g (yield = 62%) of the phosphonium salt as an orange colored oil.

In a three-necked round bottom flask, equipped with stirring bar, the phosphonium salt (16.0 g, 0.05 mol) was dissolved in 40 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. A solution of chlorosulfonic acid (5.93 g, 0.06 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 5 h at 0 °C. The produced HCl or HBr gas, was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%) and a white precipitate was formed. The precipitate (NaBr and NaCl salts) was filtered off. The filtrate is washed two times with 40 mL water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. This yields 12.31 g (yield = 76%) of the zwitterion [$P_{444}C_2OSO_3$] as an orange colored oil.

In a three-necked round bottom flask, equipped with stirring bar, the zwitterion [$P_{444}C_2OSO_3$] (12.0 g, 0.037 mol) was added. An aqueous solution of bistriflimic acid (80 wt%) (14.77 g, 0.042 mol) was added dropwise at room temperature. The resulting mixture was stirred for 5 h. Afterwards, the solvent was removed under reduced pressure. The ionic liquid was dried on a Schlenk line at 60 °C, yielding 20.10 g (yield = 90%) of [$P_{444}C_2OSO_3H$][Tf_2N] as a brown colored viscous oil.

Ionic liquid [$P_{444}C_2OSO_3H$][Tf_2N]

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 4.23 (m, 2H, CH_2-O), 2.54 (m, 2H, CH_2-N), 2.16 (m, 6H, 3 CH_2-N), 1.50 (m, 12H, 6 CH_2), 0.96 (t, 9H, J= 7.0 Hz, 3 CH_3).

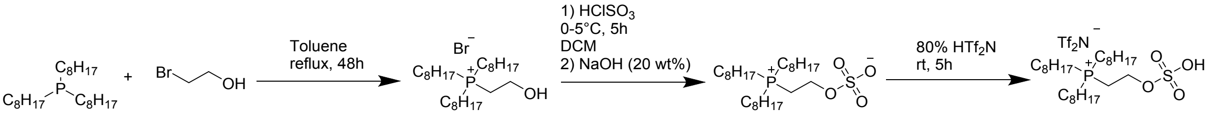
^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 119.27 (CF_3, q, J= 320 Hz), 55.8 (CH_2), 23.67 (CH_2), 23.29 (CH_2), 19.12 (CH_2), 18.65 (CH_2), 13.05 (CH_3).

^{1}P NMR (162 MHz, acetone-d_6, δ/ppm) 33.46

ATR-FTIR: (ν/cm^{-1}): 2966, 2939, 2879 (C-H stretch), 1437 (C-H bending), 1347 (asymmetric O=S=O stretch), 1187 (CF_3 stretch), 1131(symmetric O=S=O stretch), 1055 (S-N stretch), 608 (s, SO_2 bending), 570 (s, CF_3 bending), 511 (s, CF_3 bending).

Density: 1.40 g·cm^{-3} (25 °C)
Viscosity 738 cP (25 °C)

4.6 [$P_{888}C_2OSO_3H$][Tf_2N]



[998-40-3] [540-51-2]

In a three-necked round bottom flask, equipped with stirring bar and nitrogen inlet, trioctylphosphine (17.80 g, 0.048 mol) and 2-bromoethanol (5.0 g, 0.04 mol) were dissolved in toluene (75 mL). The resulting solution was heated at 110 °C and stirred for 48 h. Afterwards the mixture was cooled to room temperature, and the solvent removed under reduced pressure. After washing in 200 mL diethyl ether and two times in 100 mL *n*-heptane overnight, the residue was dissolved in 50 mL ethyl acetate and recrystallized in the freezer. The crystals were filtered off immediately and dried under vacuum, yielding 14.09 g (yield = 71%) of the phosphonium salt as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, the phosphonium salt (14.0 g, 0.028 mol) was dissolved in 40 mL DCM. The resulting mixture was stirred in an ice bath for 10 min. A solution of chlorosulfonic acid (3.99 g, 0.034 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 5 h at 0 °C. The produced HCl or HBr gas, was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%) and a white precipitate was formed. The precipitate (NaBr and NaCl salts) was filtered off. The filtrate is washed two times with 40 mL water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. This yields 11.17 g (yield = 80%) of the zwitterion [$P_{888}C_2OSO_3$] as a white solid (yield = 87%).

In a three-necked round bottom flask, equipped with stirring bar, the zwitterion [$P_{888}C_2OSO_3$] (11.00 g, 0.025 mol) was dissolved in 40 mL toluene. An aqueous solution of bistriflimic acid (80 wt%) (10.538 g, 0.030 mol) was added dropwise at room temperature. The resulting mixture was stirred for 5 h. Afterwards, the solvent was removed under reduced pressure. The ionic liquid was dried on a Schlenk line at 60 °C, yielding 15.4 g (yield = 95%) of [$P_{888}C_2OSO_3H$][Tf_2N] as a brown colored viscous oil.

Ionic liquid [$P_{888}C_2OSO_3H$][Tf_2N]

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 4.05 (m, 2H, CH_2-O-S), 4.55 (m, 2H, CH_2-N), 2.41 (m, 6H, 3 CH_2-N), 1.48 (m, 12H, 6 CH_2), 1.28 (m, 24H, 12 CH_2), 0.88 (t, 9H, J= 7.0 Hz, 3 CH_3).

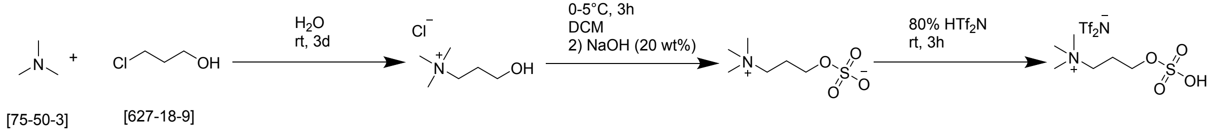
^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 119.26 (CF_3, q, J= 320 Hz), 31.58 (CH_2), 30.65 (CH_2), 30.46 (CH_2), 28.85 (CH_2), 28.67 (CH_2), 22.55 (CH_2), 21.46 (CH_2), 19.54 (CH_2), 18.93 (CH_2), 14.00 (CH_2).

^{31}P NMR (162 MHz, acetone-d_6, δ/ppm): 33.89

ATR-FTIR: (ν/cm^{-1}): 2955, 2928, 2859 (C-H stretch), 1462 (C-H bending), 1347 (asymmetric O=S=O stretch), 1188 (CF_3 stretch), 1133 (symmetric O=S=O stretch), 1056 (S-N stretch), 616 (s, SO_2 bending), 571 (s, CF_3 bending), 512 (s, CF_3 bending).

Density: 1.23 g·cm^{-3} (25 °C)
Viscosity 1332 cP (25 °C)

4.7 [$N_{111}C_3OSO_3H$][Tf_2N]



To a three-necked round bottom flask, equipped with stirring bar, an aqueous solution of trimethylamine (50 wt%) (12.50 g, 0.11 mol) was added. 3-Chloropropan-1-ol (10 g, 0.11 mol) was added dropwise and the resulting mixture was stirred for 3 days at room temperature. The solvent was removed under reduced pressure, yielding 12.61 g (yield = 78%) of trimethylhydroxypropylammonium chloride as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, trimethylhydroxypropylammonium chloride (12 g, 0.078 mol) was dissolved in 30 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. Chlorosulfonic acid (10.92 g, 0.094 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 3 h at 0 °C. The produced HCl gas was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%) and a white precipitate was formed. The solvent was removed under reduced pressure, yielding a white solid. The solvent was removed under reduced pressure, yielding a mixture of the zwitterion $[N_{111}C_3OSO_3]$ and NaCl salts as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, $[N_{111}C_3OSO_3]$ (15.40 g, 0.078 mol) was dissolved in 20 mL of water. An aqueous solution of bis(trifluoromethylsulfonyl)imide acid (80 wt%) (27.45 g, 0.078 mol) was added dropwise at room temperature. The resulting mixture was stirred for 3 h. The solvent was removed under reduced pressure, yielding a brown colored residue. The residue was stirred in 3 times in 100 mL of dry acetone, the salts were filtered off, and the solvent removed under reduced pressure. The product was dried on a Schlenk line, and 17.60 g (yield = 47%) of $[N_{111}C_3OSO_3H][Tf_2N]$ was obtained as a brown colored viscous oil.

Ionic liquid $[N_{111}C_3OSO_3H][Tf_2N]$

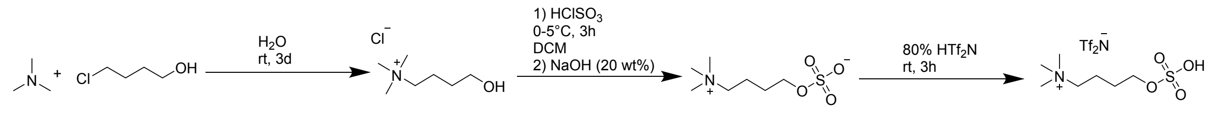
^{1}H NMR: (300 MHz, acetone-*d*$_6$, δ/ppm): 9.60 (s, 1H, S-OH), 3.75 (t, 2H, J= 6 Hz, CH_2-O), 3.58 (m, 2H, CH_2-N), 3.28 (s, 9H, 3 CH_3), 2.10 (m, 2H, CH_2).

^{13}C NMR (75 MHz, acetone-*d*$_6$, δ/ppm): 120.81 (CF_3, q, J= 321 Hz), 65.42 (CH_2), 59.01 (CH_2), 53.61 (CH_3), 26.67 (CH_2).

ATR-FTIR: (ν/cm-1): 3049, 2972, 2904 (C-H stretch), 1481 (C-H bending), 1343 (asymmetric O=S=O stretch), 1180 (CF_3 stretch), 1131 (symmetric O=S=O stretch), 1050 (S-N stretch), 611 (SO_2 bending), 571 (CF_3 bending), 513 (CF_3 bending).

Density: 1.59 g·cm^{-3} (25 °C)
Viscosity 1337 cP (25 °C)

4.8 $[N_{111}C_4OSO_3H][Tf_2N]$



[75-50-3] [33036-62-3]

To a three-necked round bottom flask, equipped with stirring bar, an aqueous solution of trimethylamine (50 wt%) (10.88 g, 0.092 mol) was added. A 85 wt% solution of 4-Chlorobutan-1-ol (11.76 g, 0.092 mol) was added dropwise and the resulting mixture was stirred for 3 days at room temperature. The solvent was removed under reduced pressure, yielding 6.89 g (yield = 45%) of trimethylhydroxybutylammonium chloride as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, trimethylhydroxybutylammonium chloride (6.0 g, 0.036 mol) was dissolved in 20 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. Chlorosulfonic acid (5.0 g, 0.043 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 3 h at 0 °C. The produced HCl gas was properly trapped. The solution was adjusted to circa pH 10 with aq. sodium hydroxide solution (20 wt%) and a white precipitate was formed. The solvent was removed under reduced pressure, yielding a mixture of the zwitterion $[N_{111}C_4OSO_3]$ and NaCl salts as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, trimethylammoniumbutanesulfuric acid zwitterion (7.56 g, 0.036 mol) was dissolved in 20 mL of water. An aqueous solution of bis(trifluoromethylsulfonyl)imide acid (80 wt%) (12.58 g, 0.036 mol) was added dropwise at room temperature. The resulting mixture was stirred for 3 h. The solvent was removed under reduced pressure, yielding a brown colored residue. The residue was stirred in 3 times in 100 mL of dry acetone, the salts were filtered off, and the solvent removed under reduced pressure. The product was dried on a Schlenk line, and 7.23 g (yield = 41%) of $[N_{111}C_4OSO_3H][Tf_2N]$ was obtained as a brown colored viscous oil.

Ionic liquid $[N_{111}C_4OSO_3H][Tf_2N]$

^{1}H NMR: (300 MHz, acetone-*d*$_6$, δ/ppm): ^{1}H NMR: (300 MHz, acetone-*d*$_6$, δ/ppm): 9.90 (s, 1H, S-OH), 3.69 (t, 2H, J= 6 Hz, CH_2-O), 3.55 (m, 2H, CH_2-N), 3.30 (s, 9H, 3 CH_3), 1.99 (m, 2H, CH_2), 1.65 (m, 2H, CH_2).

^{13}C NMR (75 MHz, acetone-d_6, δ/ppm): 120.82 (CF_3, q, J= 319 Hz), 67.26 (CH_2), 61.72 (CH_2), 53.49 (CH_3), 20.23 (CH_2).

ATR-FTIR: (v/cm-1): 3055, 2963, 2900 (C-H stretch), 1491 (C-H bending), 1355 (asymmetric O=S=O stretch), 1181 (CF_3 stretch), 1127 (symmetric O=S=O stretch), 1055 (S-N stretch), 609 (SO_2 bending), 573 (CF_3 bending), 518 (CF_3 bending).

Density: 1.54 $g \cdot cm^{-3}$ (25 °C)
Viscosity 1258 cP (25 °C)

5. Characterization and properties of the ionic liquids

IL 1 $[N_{111}C_2OSO_3H][Tf_2N]$ is partially miscible with water and can be salted out using NaCl or Na_2SO_4 thus forming a biphasic system with thermomorphic behaviour. The temperature at which the biphasic system becomes homogeneous is called the cloud point temperature and depends on the salt concentration (Table S2)

Table S2. Influence of salt concentration in the aqueous phase on the cloud point temperature (°C) of $[N_{111}C_2OSO_3H][Tf_2N]$.[a]

Salt	0 M	0.2 M	0.5 M	1.0 M	1.5 M	2.0 M
NaCl	+	+	+	30 °C	48 °C	−
Na_2SO_4	+	32 °C	48 °C	80 °C	−	−

[a] Homogeneous system (+): fully miscible with water in range 20−100 °C. Biphasic system (−): immiscible with water in range 20−100 °C.

Stability of the ionic liquid

The thermal stability of the ionic liquids was tested by thermogravimetric analysis (TGA) under nitrogen atmosphere (Figure S 1). The samples were heated to 500 °C (10 °C / min). Between 150 and 200 °C the strongly coordinated water is removed which could not be removed by a rotary evaporator. Then around 330 °C, the degradation of the IL occurs.

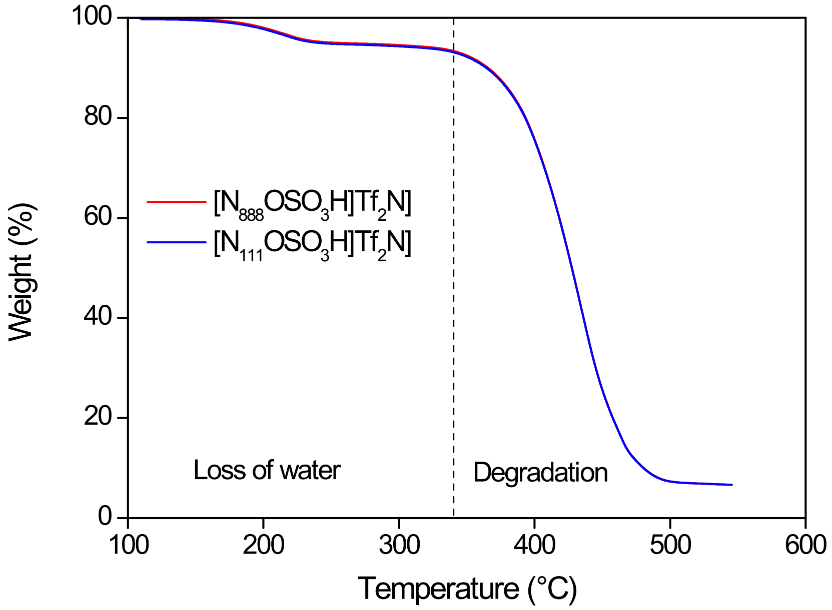


Figure S 1. TGA results for $[N_{111}OSO_3H][Tf_2N]$ and $[N_{888}OSO_3H][Tf_2N]$.

Furthermore, the stability of the ionic liquids was tested in water with an open air atmosphere. Table S3 gives an overview of the decomposition resistance of the pure ionic liquid and ionic liquid / water mixtures upon heating over prolonged amounts of time (24 h). The decomposition was quantified using NMR but no signs of degradation could be observed in these conditions, thus confirming the stability of these alkylsulfuric acid ILs.

Table S3. Decomposition (%) of $[N_{111}(CH_2)_2OSO_3][Tf_2N]$ in the absence and in the presence of water (NMR) at different temperatures over a 24 h interval.

	20 °C	**50 °C**	**80 °C**	**120 °C**	**150 °C**
Pure IL	< 1%	< 1%	< 1 %	< 1%	< 1%
IL/H_2O (1:1 wt/wt)	< 1%	< 1%	< 1%	ND[(a)]	ND[(a)]

(a) *ND: Could not be determined in water.*

Dissolution of metal oxides

The ability of the alkylsulfuric acid IL [$N_{111}C_2OSO_3H$][Tf_2N] to dissolve metal oxides is compared with the analogue carboxyl-functionalized IL [$N_{111}C_1COOH$][Tf_2N] (= [Hbet][Tf_2N]),[1] and sulfonic acid IL [$N_{111}C_3SO_3H$][Tf_2N],[2] which have an approximate pK_a of 2, -1.5 and -3.5, respectively (Table S4).[3] The increased acidity of the sulfonic acid and alkylsulfuric acid ILs allows the dissolution of more inert oxides (e.g. Fe_2O_3 and Co_3O_4).

Table S4. Dissolution of different metal oxides in [$N_{111}C_2OSO_3H$][Tf_2N], compared with literature results for [$N_{111}C_1COOH$][Tf_2N] (= [Hbet][Tf_2N]),[1] and [$N_{111}C_3SO_3H$][Tf_2N].[2] The samples consisted of a 10:1 molar ratio of IL to metal and a small amount of water was added to the IL (20 wt%). The samples were then stirred for 24 h at 80 °C and analyzed by TXRF.

IL	R-COOH IL[1,4]	R-SO_3H IL[2]	R-OSO_3H IL
pK_a	**2**	**-2**	**-3.5**
CaO	+	+	+
CuO	+	+	+
NiO	+	+	+
La_2O_3	+	+	+
Nd_2O_3	+	+	+
Co_3O_4	−	+	+
Fe_2O_3	−	+	+
Al_2O_3	−	−	−

Fast dissolution (< 1 h) (+), partial dissolution (±), very slow or no dissolution (> 24 h) (−)

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