

**Electronic Supplementary Information (ESI)**

**Isolation of molybdenum(VI) from simulated leachates of irradiated uranium-aluminum  
targets using diluted and undiluted sulfate ionic liquids**

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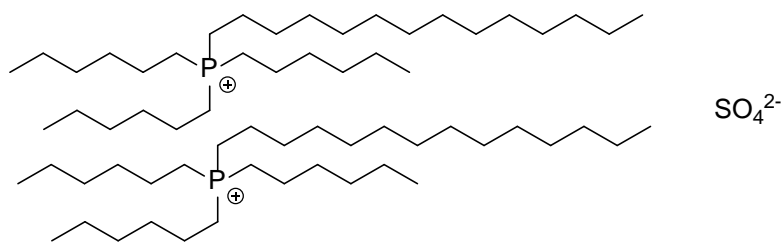
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## Synthesis and characterization

### Trihexyltetradecylphosphonium sulfate



Cyphos IL 101 (31.92 g, 61.47 mmol) was diluted to 100 mL with toluene, contacted once with 100 mL of 2 M NaHSO<sub>4</sub> and four times with 50 mL of 2 M NaHSO<sub>4</sub>. A contact time of 10 minutes was used for each step. Subsequently, the mixture was contacted once with 100 mL of 2 M NaOH and once with 50 mL of 2 M NaOH, using a contact time of 30 minutes per step. The organic layer was concentrated under reduced pressure and dried overnight using a Schlenk line at 80 °C, affording the title compound as a deliquescent yellow solid in a yield of 95% (31.11 g, 29.25 mmol).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ/ppm): 0.88 (t, 12H, 4 CH<sub>3</sub>), 1.17-1.36 (m, 32H, 16 CH<sub>2</sub>), 1.37-1.60 (m, 15H, β-CH<sub>2</sub>), 1.55 (m, 7H, α-CH<sub>2</sub>).

Deviations from theoretical integration values are a result of the presence of phosphine oxide impurities in commercial Cyphos® IL101 and the presence of residual water.

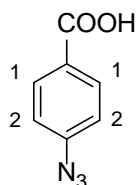
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 14.02 (C<sub>6</sub> CH<sub>3</sub>), 14.13 (C<sub>14</sub> CH<sub>3</sub>), 18.66, 19.09, 19.12, 22.19, 22.23, 22.42, 22.70, 29.25, 29.38, 29.62, 29.67, 29.69, 29.71, 30.49, 30.63, 30.80, 30.84, 30.94, 31.40 (C<sub>6</sub> α-CH<sub>2</sub>), 31.93 (C<sub>14</sub> α-CH<sub>2</sub>).

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, δ/ppm): 35.09 (phosphonium salt), 50.61 (phosphine oxide).

FTIR (v/cm<sup>-1</sup>): 2954, 2923, 2854 (aliphatic C-H stretch), 1465 (CH<sub>2</sub> deformation), 1079 (sulfate S=O stretch), 810, 721 (CH<sub>2</sub> rocking), 607 (sulfate bending mode).

ESI-MS calculated for C<sub>32</sub>H<sub>68</sub>P<sup>+</sup>: 483.51, found: 483.7.

### 4-Azidobenzoic acid

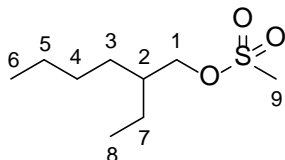


4-Azidobenzoic acid was prepared according to a literature procedure.<sup>1</sup> 4-Aminobenzoic acid (30.00 g, 219 mmol, 1 eq.) was suspended in 3 M H<sub>2</sub>SO<sub>4</sub> (400 mL) and cooled to -5 °C using a salt and ice bath. NaNO<sub>2</sub> (18.28 g, 265 mmol, 1.2 eq.) dissolved in water (40 mL) was added dropwise, after which the mixture was stirred for 40 min. Subsequently, methyl isobutyl ketone (150 mL) was poured into the mixture and NaN<sub>3</sub> (22.00 g, 338 mmol, 1.5 eq.) dissolved in water (80 mL) was added dropwise. The mixture was stirred for a further 90 min. The aqueous phase was then drained and the organic layer was washed with 50 mL of

water combined with 10 mL of brine. Evaporation of the solvent afforded 4-azidobenzoic acid as a light yellow powder in a yield of 96% (34.41 g, 211 mmol).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 7.22 (d,  $^3\text{J}=8.5$  Hz, 2H, H2), 7.96 (d,  $^3\text{J}=8.5$  Hz, 2H, H1).

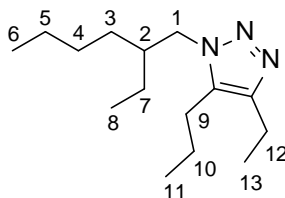
## 2-Ethylhexyl methanesulfonate



2-Ethylhexanol (39 mL, 0.25 mol, 1.0 eq) and methanesulfonyl chloride (21 mL, 0.28 mol, 1.1 eq.) were combined in a flask charged with 100 mL of toluene and cooled to 0 °C. Triethylamine (38 mL, 0.28 mol, 1.1 eq.) was added dropwise. A washing bottle filled with NaOH solution was used to trap HCl effervescence. The mixture was stirred at room temperature overnight and then filtered under vacuum. The filtrate was washed with 100 mL of saturated sodium bicarbonate solution for 3 h. The organic phase was then dried over magnesium sulfate and concentrated under reduced pressure to obtain 2-ethylhexyl methanesulfonate in a yield of 85% (44.32 g, 213 mmol).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.85-0.96 (2 t, 6H, H6+H8), 1.23-1.47 (m, 8H, H3+H4+H5+H7), 1.66 (quintet,  $^3\text{J}=6.0$  Hz, 1H, H2), 3.00 (s, 3H, H9), 4.13 (dd,  $^2\text{J}=1.5$  Hz,  $^3\text{J}=5.5$  Hz, 2H, H1).

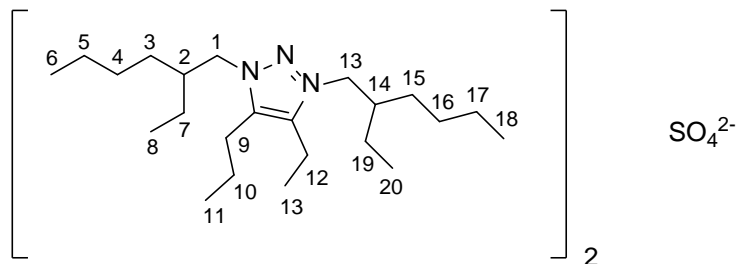
## 4-Ethyl-1-(2-ethylhexyl)-5-propyl-1,2,3-triazole



4-Ethyl-1-(2-ethylhexyl)-5-propyl-1,2,3-triazole and its derived ionic liquid were synthesized according to a previously published procedure.<sup>2</sup> 4-Heptanone (100 mL, 0.81 mol, 4.4 eq.), 2-ethylhexylamine (27 mL, 0.17 mol, 1.4 eq.) and azidobenzoic acid (19.42 g, 119 mmol, 1.0 eq.) were combined in a flask and stirred at 80 °C for 24 h with 5.0 g of 4 Å molecular sieves. The excess of the ketone was evaporated and the residue was suspended in 100 mL toluene. This suspension was then filtered under vacuum. The filtrate was washed 10%  $\text{NaH}_2\text{PO}_4$  solution (3x125 mL and 3x 50 mL). The organic layer was then washed four times with a mixture of 1 M  $\text{NH}_3$  (125 mL) and brine (25 mL). Concentration of the the organic phase under reduced pressure yields 4-ethyl-1-(2-ethylhexyl)-5-propyl-1,2,3-triazole. Yield: 66% (19.82 g, 78.8 mmol).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.82-0.93 (2t, 6H, H6+H8), 0.97 (t,  $^3\text{J}=7.5$  Hz, 3H, H11), 1.14-1.40 (m, 11H, H3+H4+H5+H7+H13), 1.56 (6-et,  $^3\text{J}=8.0$  Hz, 2H, H10), 1.93 (7-et, 1H, H2), 2.57 (t, 2H,  $^3\text{J}=8.0$  Hz, 2H, H9), 2.64 (q, 2H,  $^3\text{J}=7.5$  Hz, H12), 4.06 (d,  $^3\text{J}=7.5$  Hz, 2H, H1).

#### 4-Ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate



2-Ethylhexyl methanesulfonate (17.10 g, 82.1 mmol, 1.1 eq.) and 4-ethyl-1-(2-ethylhexyl)-5-propyl-1,2,3-triazole (19.82 g, 78.8 mmol, 1.0 eq.) are combined in a flask. The mixture is stirred at 100 °C for 3 d. Deionized water (100 mL) is added and the aqueous phase is washed three times with 100 mL of heptane. A 100 mL portion of a 2 M NaHSO<sub>4</sub> solution is added and the aqueous phase is extracted with ethyl acetate (50 mL). The organic phase is contacted six times with 2 M NaHSO<sub>4</sub> (50 mL), twice with 2 M NaOH (100 mL) and once with 2 M NaOH (50 mL). Every step entailed a shaking time of 10 minutes. Evaporation of solvent affords the desired ionic liquid in a yield of 66% (21.39 g, 25.9 mmol).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ/ppm): 0.80-0.98 (m, 12H, H<sub>6</sub>+H<sub>8</sub>+H<sub>18</sub>+H<sub>20</sub>), 1.06 (t, <sup>3</sup>J=7.5 Hz, 3H, H<sub>11</sub>), 1.16-1.46 (m, 19H, H<sub>3</sub>+H<sub>4</sub>+H<sub>5</sub>+H<sub>7</sub>+H<sub>13</sub>+H<sub>15</sub>+H<sub>16</sub>+H<sub>17</sub>+H<sub>19</sub>), 1.68 (6-et, <sup>3</sup>J=8.5 Hz, 2H, H<sub>10</sub>), 2.00 (broad m, 2H, H<sub>2</sub>+H<sub>14</sub>), 2.93 (t, 2H, <sup>3</sup>J=8.5 Hz, 2H, H<sub>9</sub>), 3.03 (q, 2H, <sup>3</sup>J=7.5 Hz, H<sub>12</sub>), 4.42 & 4.48 (2 d, <sup>3</sup>J=7.5 Hz, 4H, H<sub>1</sub>+H<sub>13</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 10.33 (2 CH<sub>3</sub>), 13.02 (CH<sub>3</sub>), 13.95 (2 CH<sub>3</sub>), 14.05 (CH<sub>3</sub>), 16.76 (CH<sub>2</sub>) 22.11 (CH<sub>2</sub>), 22.85 (2 CH<sub>2</sub>), 23.56 (2 CH<sub>2</sub>) 25.01 (CH<sub>2</sub>), 28.34 (2 CH<sub>2</sub>), 30.27 (2 CH<sub>2</sub>), 39.33 (2 CH), 54.55 (N-CH<sub>2</sub>), 54.65 (N-CH<sub>3</sub>), 140.96 (sp<sup>2</sup> C), 142.53 (sp<sup>2</sup> C).

IR (ν/cm<sup>-1</sup>): 2959, 2930, 2873 (aliphatic C-H stretch), 1583, 1461, 1375 (ring breathing modes), 1109 (C-N stretch), 1064 (sulfate S=O stretch), 896, 729, 634, 610 (sulfate bending mode).

ESI-MS calculated for C<sub>32</sub>H<sub>68</sub>P<sup>+</sup>: 446.37, found: 364.4.

# <sup>1</sup>H NMR spectra

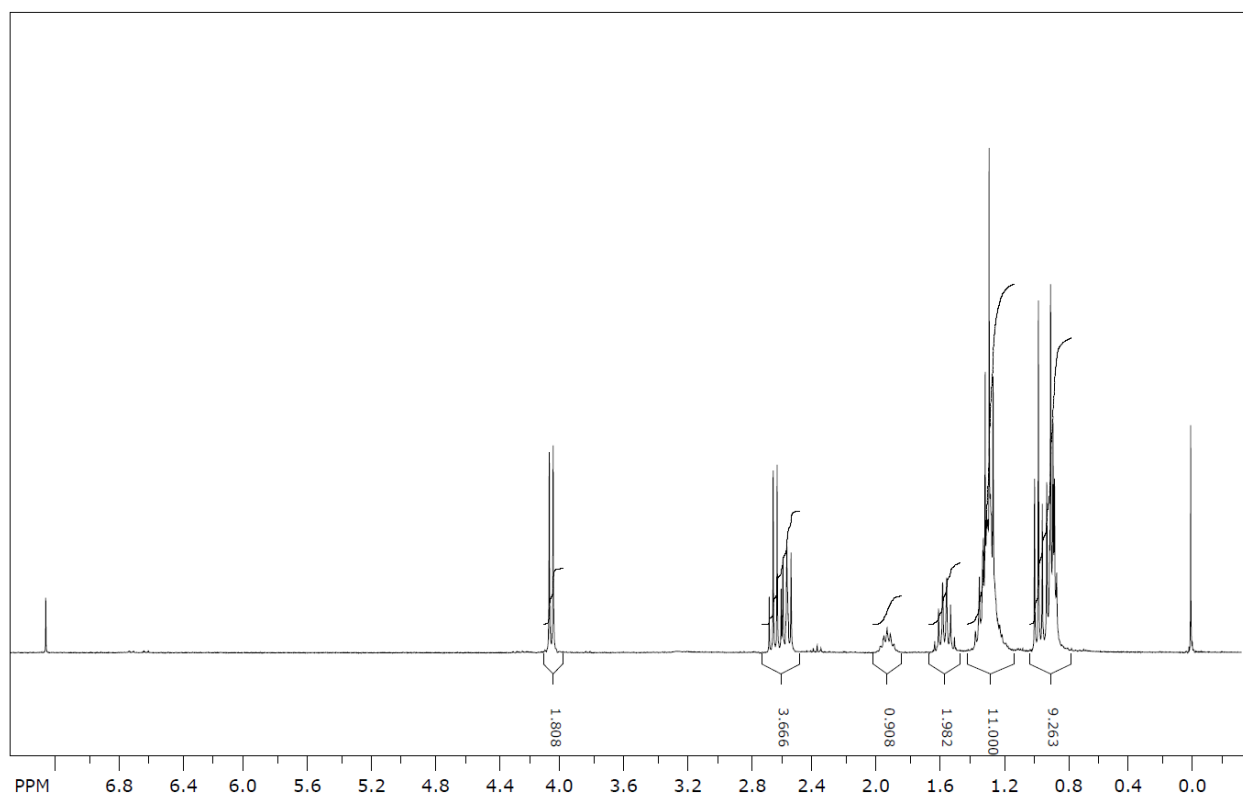


Figure S1: <sup>1</sup>H NMR spectrum of 4-ethyl-1-(2-ethylhexyl)-5-propyl-1,2,3-triazole in chloroform-d.

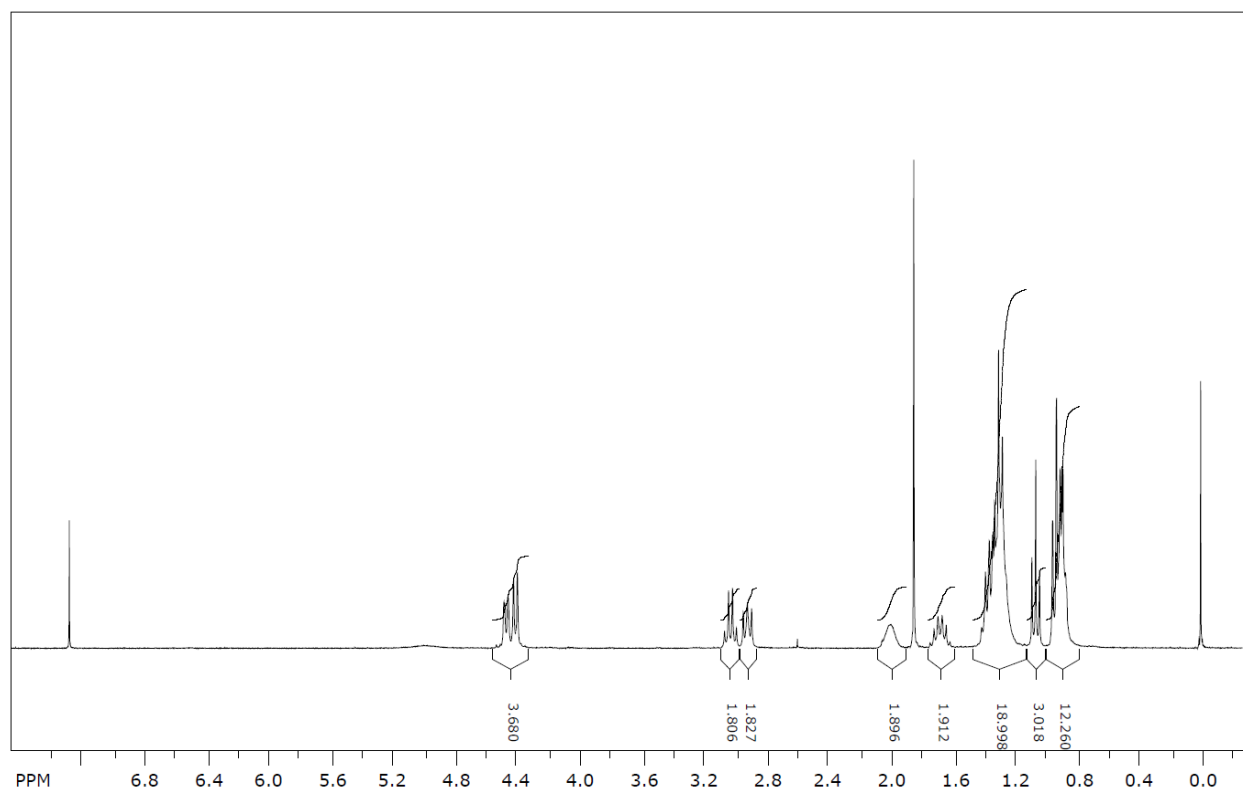


Figure S2:  $^1\text{H}$  NMR spectrum of 4-ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate in chloroform-*d*. Signals of water (approx. 1.8 ppm) and methylsulfonate (approx. 2.6 ppm) can also be observed.

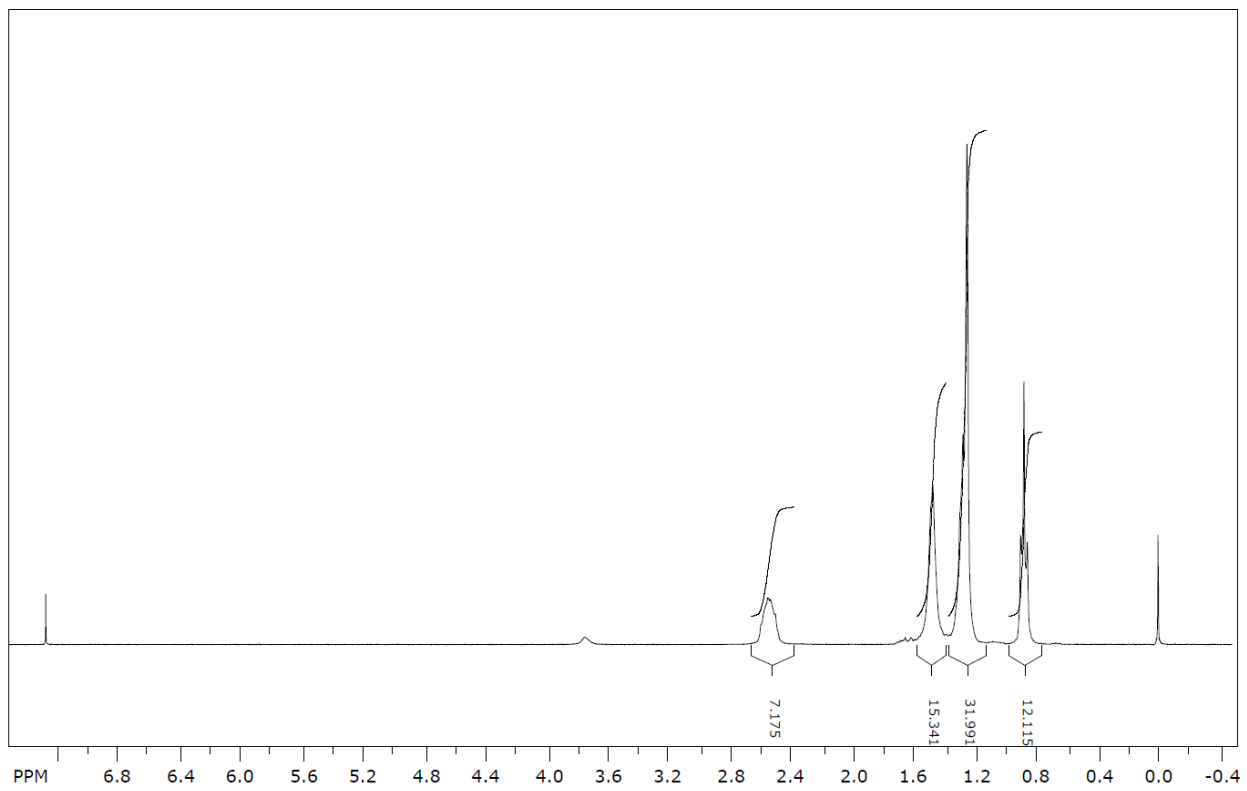


Figure S3:  $^1\text{H}$  NMR spectrum of trihexyltetradecylphosphonium sulfate in chloroform- $d$ .

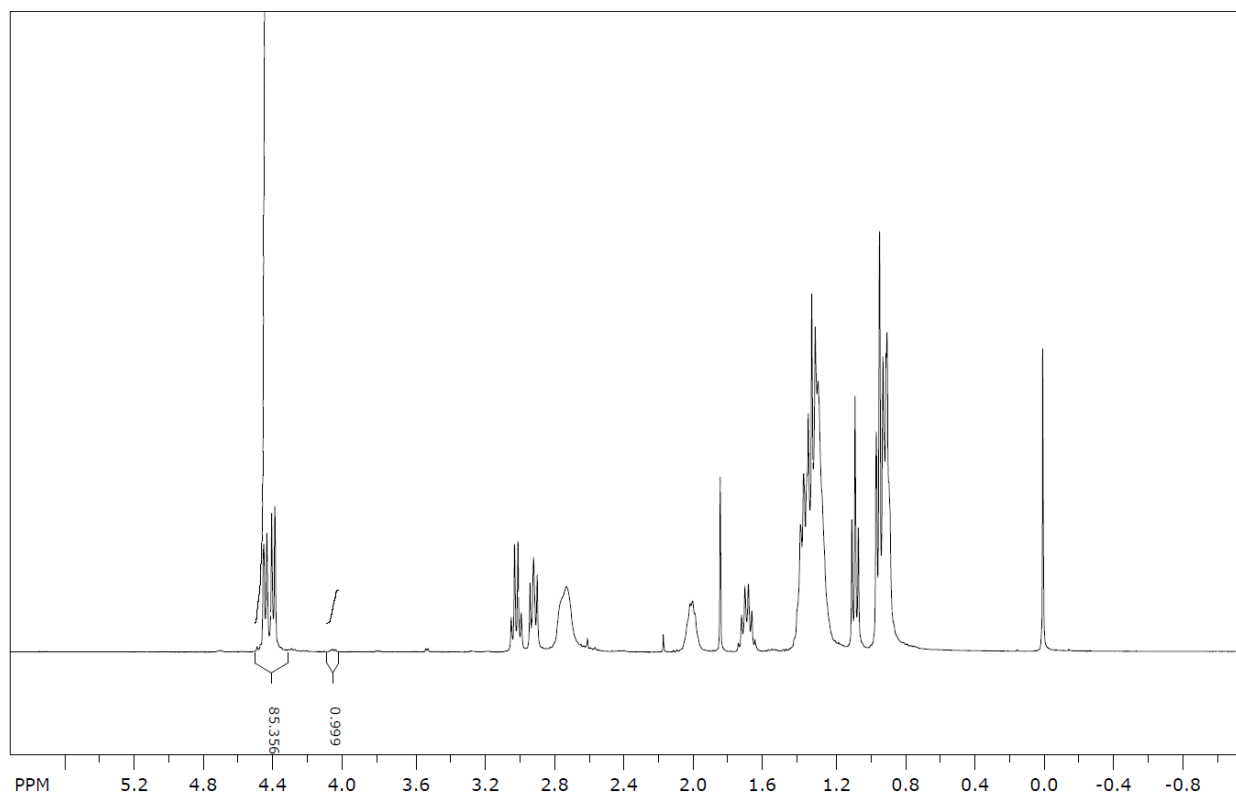


Figure S4: <sup>1</sup>H NMR spectrum of 4-ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate in chloroform-d after treatment with 2 mol/L NaOH at 60 °C for 10 d.



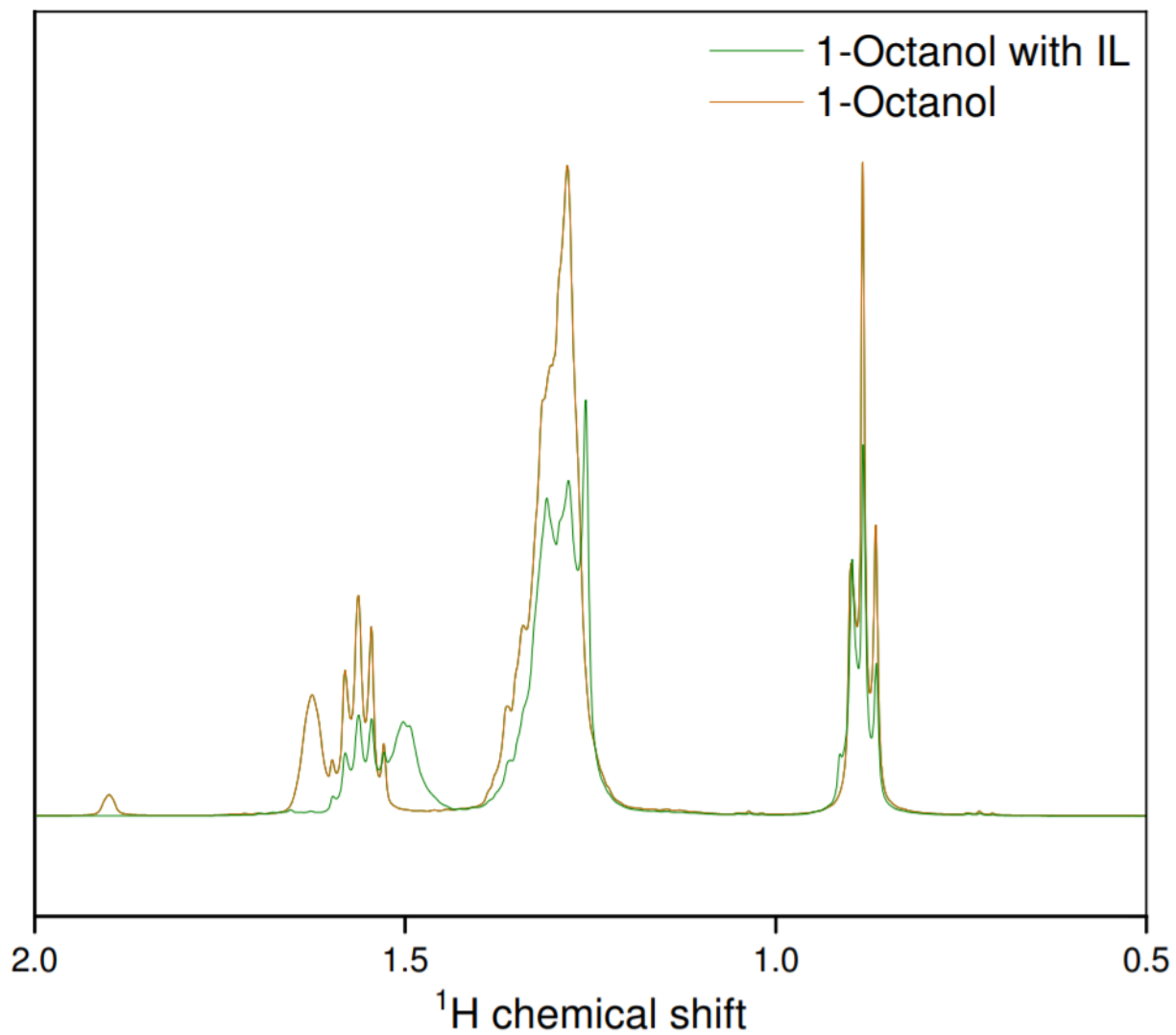


Figure S5:  $^1\text{H}$  NMR of 1-octanol with and without the addition of 60 wt% the ionic liquid  $[\text{P}_{66614}]_2[\text{SO}_4]$  (25 vol% chloroform-*d* added as lock reference).

# <sup>13</sup>C NMR spectra

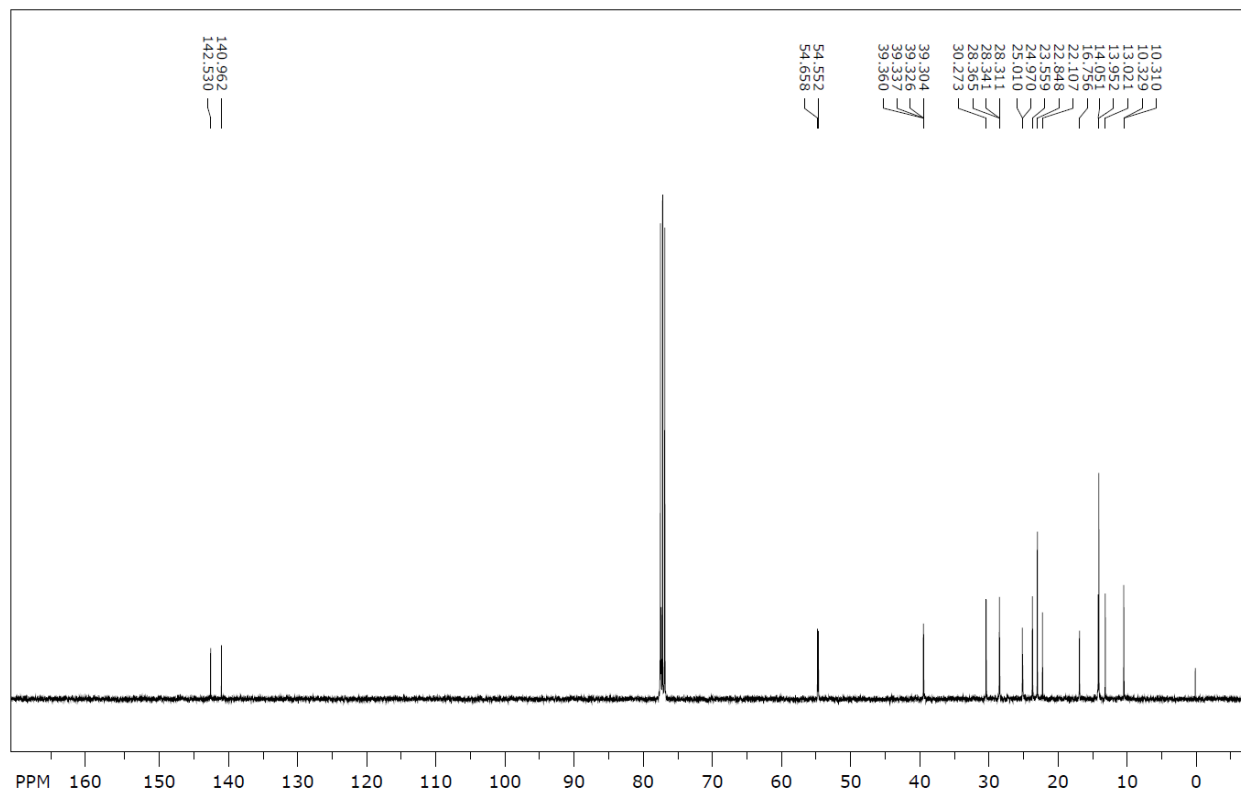


Figure S6: <sup>13</sup>C NMR spectrum of 4-ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate in chloroform-d.

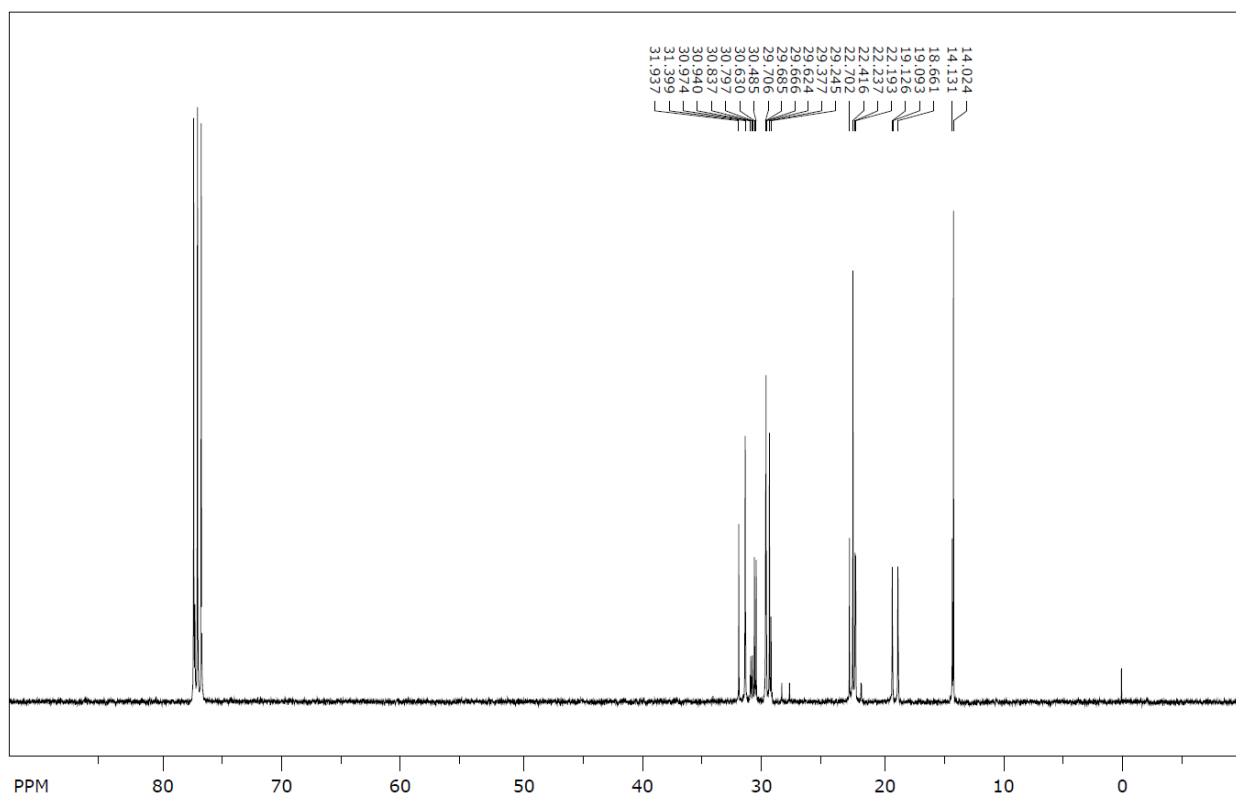


Figure S7:  $^{13}\text{C}$  NMR spectrum of trihexyltetradecylphosphonium sulfate in chloroform-*d*.

## $^{31}\text{P}$ NMR spectra

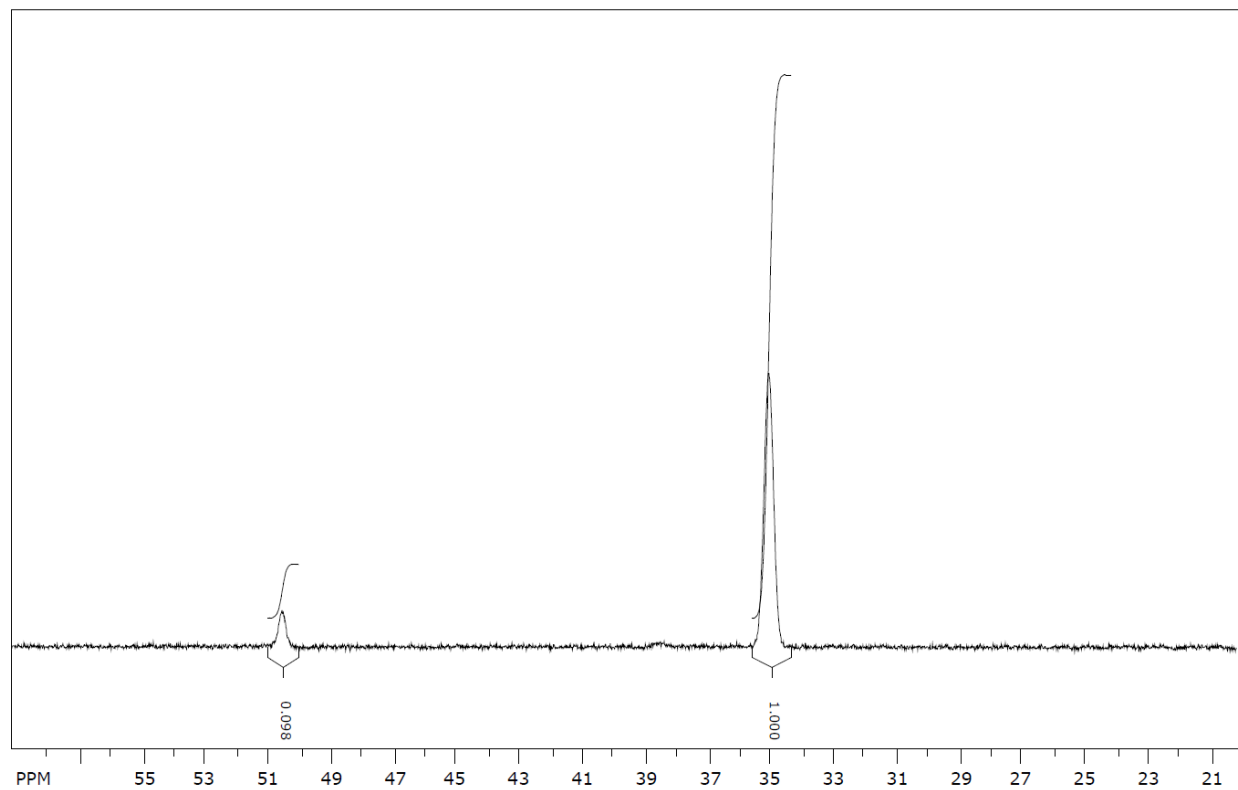


Figure S8:  $^{31}\text{P}$  NMR spectrum of trihexyltetradecylphosphonium sulfate in chloroform-*d*.

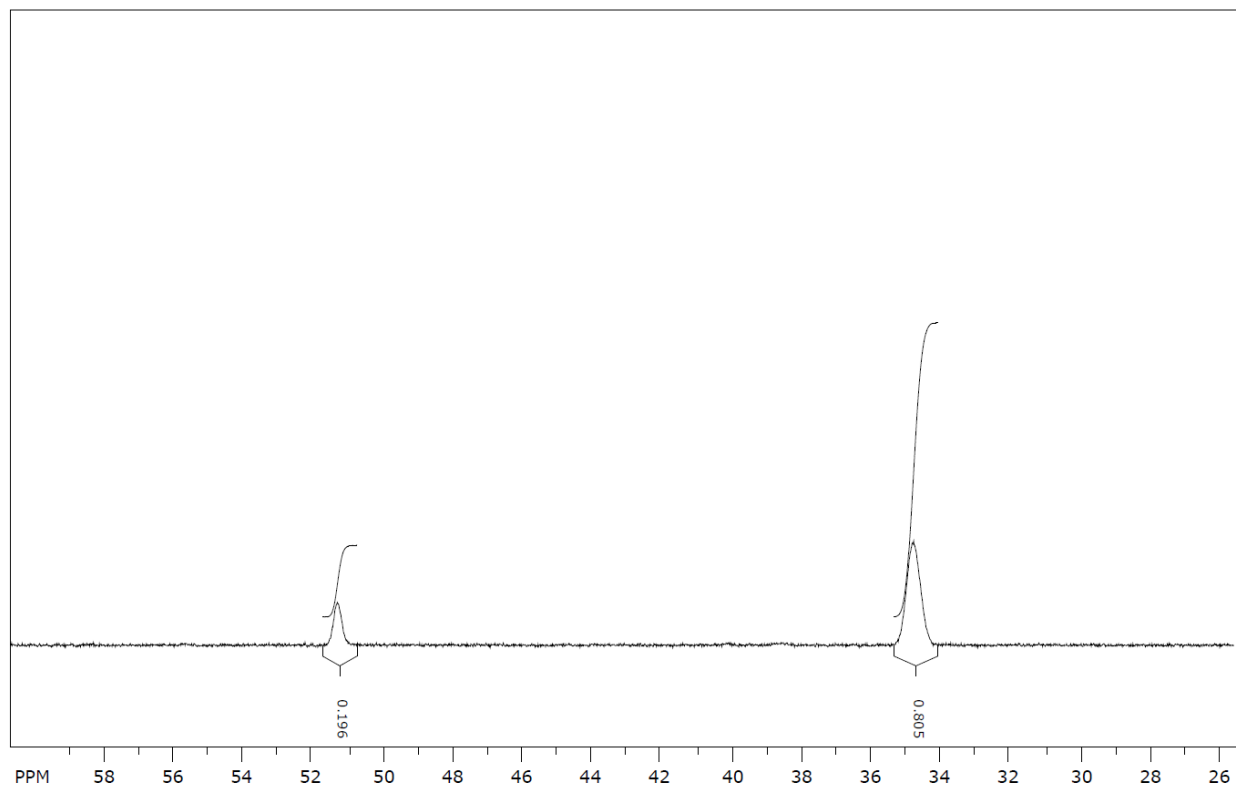


Figure S9:  $^{31}\text{P}$  NMR spectrum of trihexyltetradecylphosphonium sulfate in chloroform-d after contact with 2 mol/L NaOH at 30 °C for 10 days.

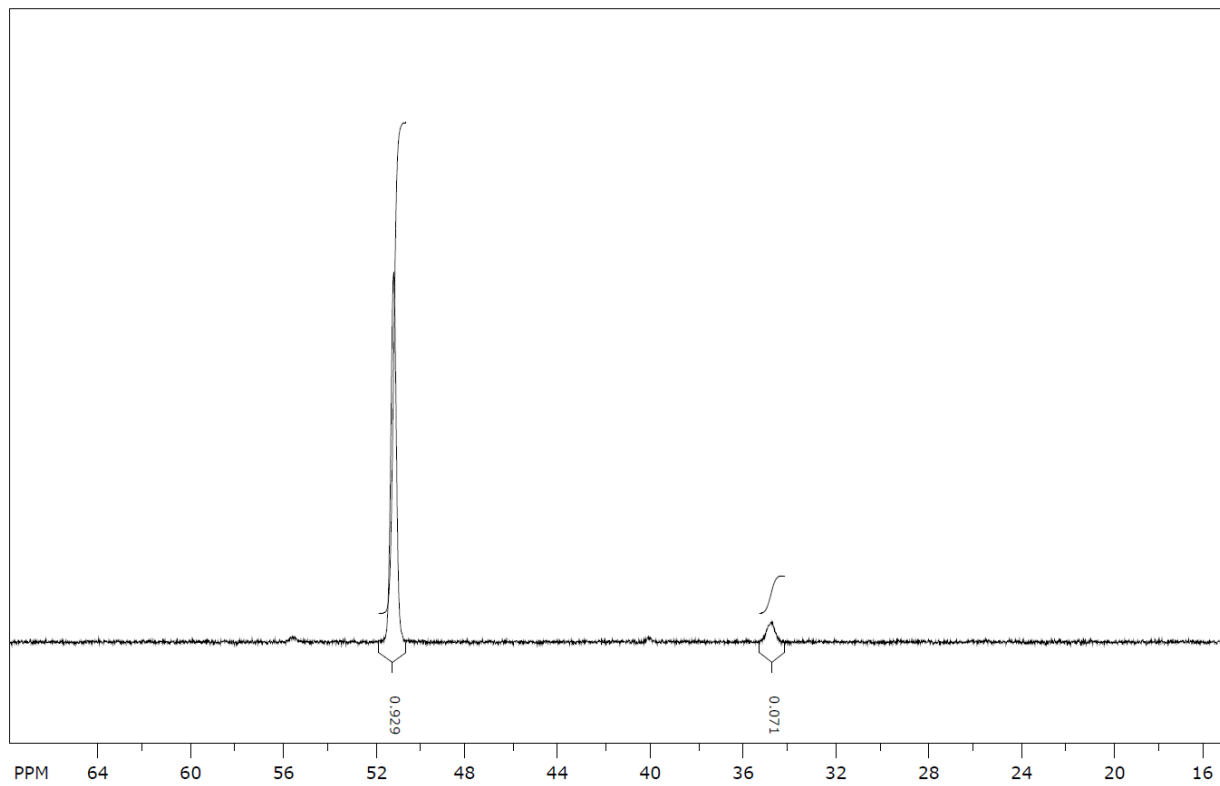


Figure S10:  $^{31}\text{P}$  NMR spectrum of trihexyltetradecylphosphonium sulfate in chloroform-*d* after contact with 2 mol/L NaOH at 60 °C for 10 days.

## FT-IR spectra

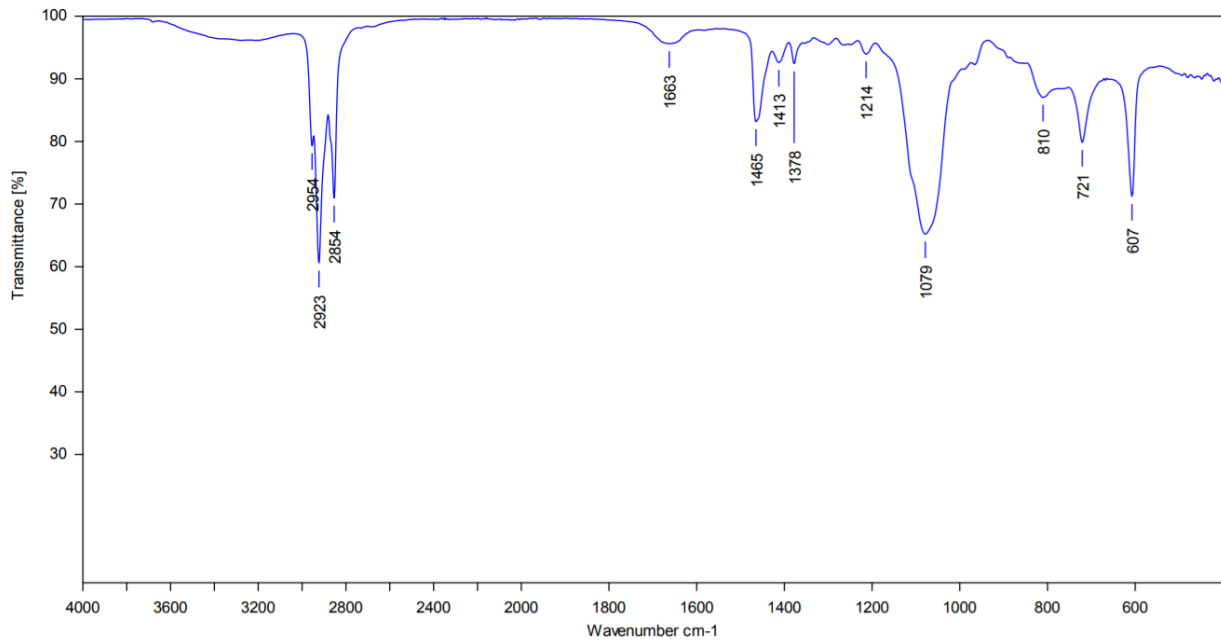


Figure S11: FT-IR spectrum of trihexyltetradecylphosphonium sulfate.

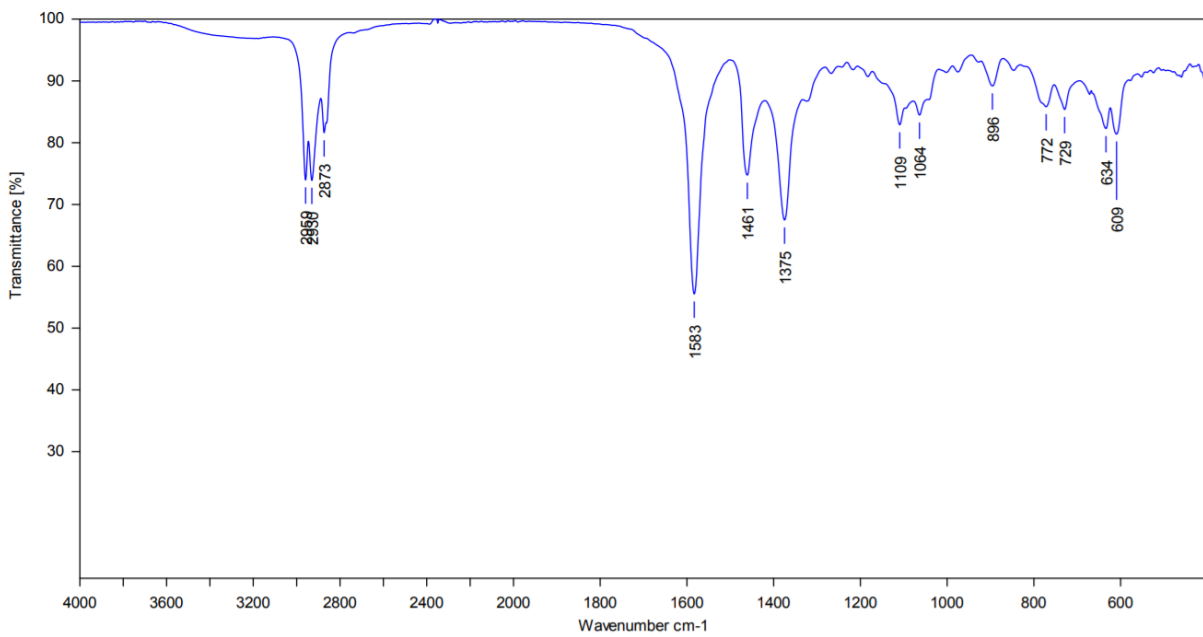


Figure S12: FT-IR NMR spectrum of 4-ethyl-1,3-bis(2-ethylhexyl)-5-propyl-1,2,3-triazolium sulfate.

## **Determination of phase volume after stripping**

The density of the organic phase before and after stripping was determined using an Anton-Paar Lovis 2000M/ME combined viscometer/densitometer. These were determined to be 0.92516 g/mL before stripping and 0.92585 g/mL after stripping.

Subsequently, the water content before and after stripping was measured. This was performed on a Mettler-Toledo C30S coulometric Karl Fischer titrator for the organic phase before stripping. The water content of the organic phase after stripping was measured on a Mettler-Toledo V30S volumetric Karl Fischer titrator, equipped with Stromboli oven at 80 °C, as hydrogen carbonate anions are incompatible with Karl-Fischer titrant and sensitive to temperatures above 80 °C. The following values were found: 26.56 wt% (before stripping) and 21.12% (after stripping).

The ratio of the phase volumes after stripping could be determined by assuming a constant amount of ionic liquid before and after stripping. The mass of the phases could then be determined by multiplying by the molecular weight and adding the experimentally determined mass fraction of water. Finally, the masses could be converted to volumes using the experimentally determined densities.



### Extraction by 50 vol% [EhEhT<sub>23</sub>]<sub>2</sub>[SO<sub>4</sub>] in 1-octanol

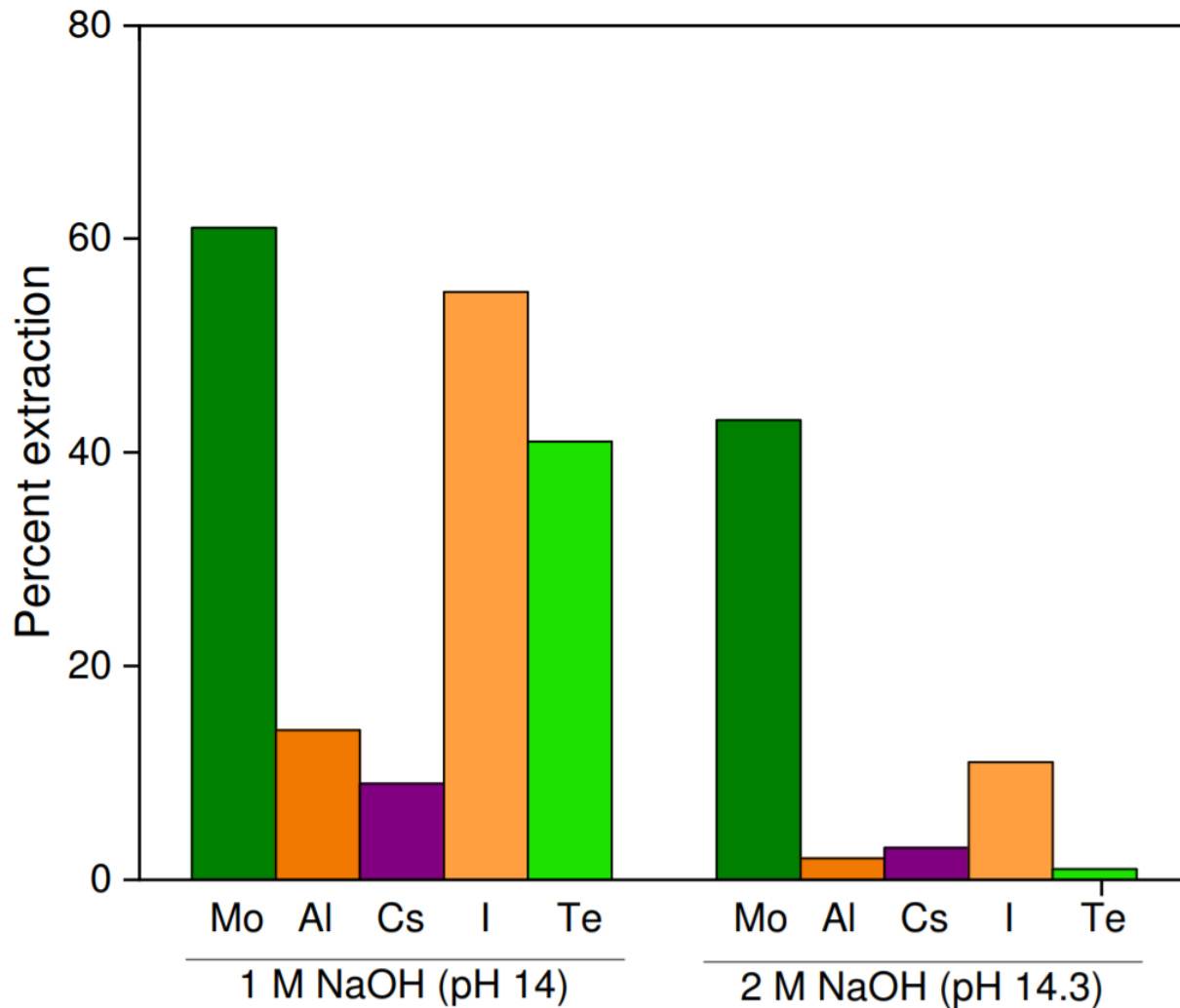


Figure S13: Variation of the percentages extraction of Mo, Te, I, Al and Cs as a function of the initial aqueous pH. Elements were present in 1000 ppm concentrations as their hydroxides or highest valence sodium salts. The organic phase was 50 vol% [EhEhT<sub>23</sub>]<sub>2</sub>[SO<sub>4</sub>] diluted in 1-octanol, presaturated with water containing an appropriate concentration of NaOH. A phase ratio of 2:1 (aqueous to organic) was used at 30 °C.

## Stripping with concentrated sulfate solutions

The loaded organic phases used in these experiments were prepared in an identical fashion to those used for bicarbonate stripping experiments. The organic phases were contacted with the sulfate solutions for 30 minutes at 30 °C while shaking at 3000 rpm. An aqueous-to-organic phase ratio of 2:1 was used. The degree of stripping was determined by measuring the organic phase concentration of molybdenum before and after stripping.

Table S1: Stripping of molybdenum from loaded<sup>a</sup> organic phases using saturated aqueous solutions of sulfate salts in a 2:1 aqueous-to-organic phase volume ratio.

Extractant	Stripping agent (saturated solution at 25 °C)	%S	D
[C101] <sub>2</sub> [SO <sub>4</sub> ] in 1-octanol (1:1 mixture)	Li <sub>2</sub> SO <sub>4</sub>	37	3.39
	MgSO <sub>4</sub> <sup>b</sup>	31	4.48
[C101] <sub>2</sub> [SO <sub>4</sub> ] neat	Li <sub>2</sub> SO <sub>4</sub>	13	12.95
	MgSO <sub>4</sub> <sup>b</sup>	32	4.16
[EhEhT <sub>23</sub> ] <sub>2</sub> [SO <sub>4</sub> ] in 1-octanol (30 vol%)	Li <sub>2</sub> SO <sub>4</sub>	47	2.28
	MgSO <sub>4</sub> <sup>B</sup>	53	1.75

<sup>a</sup> Loading conditions: aq:org = 2, 1000 ppm Mo as Na<sub>2</sub>MoO<sub>4</sub>, 2.00 mol L<sup>-1</sup> NaOH.

<sup>b</sup> A small amount of precipitate developed, presumably Mg(OH)<sub>2</sub>.

## References

- [1] X. Wu, L. Hu, *Bioorg. Med. Chem.* 2016, 24, 2697–2706.
- [2] S. Raiguel, J. Thomas, K. Binnemans and W. Dehaen, *Eur. J. Org. Chem.*, 2018, **35**, 4850-4856.