

SUPPORTING INFORMATION

SOLVENT EXTRACTION OF U(VI) BY TASK SPECIFIC IONIC LIQUIDS BEARING PHOSPHORYL GROUPS

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General Experimental Information: ¹H and ¹³C NMR spectra were recorded by using Bruker AC-300 spectrometer, ³¹P NMR was recorded by using Bruker Avance serie 400 MHz spectrometer. CDCl₃ was used as NMR solvent. Chemical shifts are reported as δ values in ppm relative to TMS in CDCl₃ for ¹H NMR and to external standard 85% H₃PO₄ for ³¹P NMR. Mass spectra were measured by using a microTOF (Bruker Daltonic) mass spectrometer.

Synthesis:

TSIL 2:

To a solution of 3-dimethylamino-1-propylamine (2.23 g, 21.9 mmol) and triethylamine (5.54 g, 55.00 mmol) in diethylether (60 ml) was added dropwise a solution of dibutylchlorophosphate (5.0 g, 21.9 mmol) in diethylether (20 ml) at 5°C under vigorous stirring. The reaction mixture was stirred for 10 h at room temperature then triethylamine chloride was removed by filtration. Evaporation of the solvent yielded the product as colourless oil (5.81 g, 93%). To this solution of dibutyl (*N,N*-dimethylpropylamine) phosphate (5.81 g, 19.8 mmol) in diethylether (60 ml) was added a solution of methyl iodide (2.96 g, 19.8 mmol) in diethylether (20 ml) at 5°C under vigorous stirring. The reaction mixture was stirred for 3 h at room temperature. The precipitate was filtered, washed with diethyl ether (3×20 ml) and dried under reduced pressure yielding the product as a white solid (8.41 g, 91 %). A solution of *N*-lithiotrifluoromethanesulfonimide (8.52 g, 29.7 mmol) in deionised water (30 mL) was added to the aqueous solution of the functional tetraalkylammonium iodide (8.41 g, 19.2 mmol) and the suspension was stirred vigorously for 20 h at room temperature. The top aqueous layer was removed, the ionic liquid washed with deionised water (5×20 ml). The product was dried at 70°C *in vacuo* yielding the product as viscous pale yellow oil (15.3 g, 68.6 %).

¹H NMR: 0.82 (t, *J* = 7.2 Hz, 6H, CH₃(CH₂)₃O), 1.31 (q, 4H, *J* = 7.5 Hz CH₃CH₂(CH₂)₂O), 1.52 (q, *J* = 7.3 Hz, 4H, CH₃CH₂CH₂CH₂O), 1.95 (m, 2H, NHCH₂CH₂CH₂N(CH₃)₃), 2.94 (m, 2H, NHCH₂CH₂CH₂N(CH₃)₃), 3.08 (s, 9H, N(CH₃)₃), 3.41 (m, 2H, NHCH₂CH₂CH₂N(CH₃)₃), 3.86 (q, *J* = 7.0 Hz, 8H, OCH₂CH₂)
³¹P NMR: 10.06

¹³C NMR 13.50 (s, CH₃), 18.71, 24.95 (two singlets, CH₂), 32.31 (d, *J* = 6.2, CH₂CH₂N), 53.39 (N(CH₃)₃), 64.8 (CH₂N) 66.4 (d, *J* = 6.7, CH₂O), 118.3 (q, *J* = 320.4, CF₃)

HRMS (ESI) *m/z* (%): calcd for C₁₄H₃₄N₂O₃P (M⁺) 309.2302, found 309.2220

Anal. calcd for C₁₆H₃₄F₆N₃O₇PS₂: C, 32.60; H, 5.81; N, 7.13, found: C, 32.21; H, 5.99; N, 7.08

TSIL 3:

To a solution of *N,N*-dimethylethanolamine (5.84 g, 65.59 mmol) and triethylamine (7.3 g, 72.15 mmol) in diethylether (60 ml) was added dropwise a solution of dibutylchlorophosphate (15.0 g, 65.59 mmol) in diethylether (20 ml) at 5°C under vigorous stirring. The reaction mixture was stirred for 5 h at room temperature then triethylamine chloride was removed by filtration. Evaporation of the solvent yielded the product as colourless oil (15.01 g, 81%).

To a solution of dibutyl (*N,N*- dimethylethylamine) phosphate (15.03 g, 53.43 mmol) in diethylether (60 ml) was added a solution of iodide methyl (7.58 g, 53.43 mmol) in diethylether (20 ml) at 5°C under vigorous stirring. The reaction mixture was stirred at room temperature for 3 h. The precipitate was filtered, washed with diethyl ether (3×20 ml) and dried under reduced pressure during 4 h. yielding the product was obtained as a white solid (15.39 g, 68 %). The same procedure described above for **2** was used for metathesis. **3** was obtained as a pale yellow oil (9.10 g, 79 %) from tetraalkylammonium iodide salt (8.5 g, 20 mmol) and LiNTf₂ (6.9 g, 24 mmol).

¹H NMR: 0.79 (t, *J* = 7.2 Hz, 6H, CH₃(CH₂)₃O), 1.24 (q, 4H, *J* = 7.3 Hz CH₃CH₂(CH₂)₂O), 1.58 (q, *J* = 7.3 Hz, 4H, CH₃CH₂CH₂CH₂O), 3.08 (s, 9H, N(CH₃)₃), 3.52 (m, 2H, PCH₂), 3.3.93 (q, *J* = 7.0 Hz, 8H, OCH₂CH₂), 4.26 (m, 2H, POCH₂CH₂N)

³¹P NMR: 0.61

¹³C NMR 13.3 (s, CH₃), 18.4 (s, CH₂), 32.0 (d, *J* = 6.2, CH₂CH₂O), 54.2 (s, N(CH₃)₃), 60.7 (s, CH₂N) 68.3 (d, *J* = 6.7, CH₂O), 118.4 (q, *J* = 320.4, CF₃)

HRMS (ESI) *m/z* (%): calcd for C₁₃H₃₁NO₄P (M⁺) 296.1985, found 296.1967

Anal. calcd for C₁₅H₃₁F₆N₂O₈PS₂: C, 31.25; H, 5.42; N, 4.86, found: C, 30.81; H, 5.52; N, 4.77

TSIL 5:

To a solution of diethyl vinylphosphonate (11.79 g, 53.5 mmol) in ethanol (50 ml) was added diethylamine (7.83 g, 107.0 mmol). The mixture was stirred for 72 h and then concentrated to dryness; the residue was taken up in 30 ml of diethyl ether and ethyl iodide (50.93 g, 56.0 mmol) was added. After stirring one night, the precipitate was filtered and washed twice with diethyl ether (15 ml). The product was isolated as a yellow powder (16.63 g, 69.2 %). The same procedure as described above for **2** was used for metathesis. **5** was obtained as a pale yellow oil (15.3 g, 68.6 %) from tetraalkylammonium iodide salt (16.63 g, 370 mmol) and LiNTf₂ (11.59 g, 400 mmol).

¹H NMR: 0.96 (t, *J* = 7.2 Hz, 6H, CH₃CH₂N), 1.33 (t, *J* = 7.2 Hz, 9H, CH₃(CH₂)₃O), 1.37 (m, 4H, CH₃CH₂(CH₂)₂O), 1.71 (q, *J* = 7.3 Hz, 4H, CH₃CH₂CH₂CH₂O), 1.98 (m, 2H, PCH₂CH₂), 3.12 (q, *J* = 7.1 Hz, 8H, CH₂N), 3.89 (q, *J* = 7.0, 4H, OCH₂)

³¹P NMR: 24.7

¹³C NMR: 13.1, 13.4 (two singlets, CH₃), 18.3 (d, $J = 138.5$, O=PCH₂), 20.1 (s, CH₂), 32.4 (d, $J = 6.2$, CH₂CH₂O), 53.0 (s, N(CH₂)₄), 66.6 (d, $J = 6.7$, CH₂O), 118.3 (q, $J = 320.4$, CF₃)
HRMS (ESI) m/z (%): calcd for C₁₆H₃₇NO₃P (M⁺) 322.2506, found 322.2387
Anal. calcd for C₁₈H₃₇F₆N₂O₇PS₂: C, 35.88; H, 6.19; N, 4.65, found: C, 35.79; H, 6.07; N, 4.63

Extraction:

Extraction was performed by mixing 0.8 mL of the RTIL phase and 0.8 mL of the aqueous phase followed by vortexing (5 min) and centrifugation (5000 rpm) to equilibrate the phases. Extraction were performed in duplicate for each TSIL by shaking equal volumes of pre-equilibrated organic phase and aqueous phase on a vibrating mixer at room temperature for 3 hours. Phases were separated by centrifugation; uptake of uranium by ionic liquid phase was measured by determining the remaining ²³⁸U in the aqueous solutions with inductively coupled plasma mass spectroscopy (ICP-MS).

The distribution coefficients D_U for extraction of ²³⁸U are defined as $D_U = (C_i - C_f) / C_f$ where C_i and C_f represent the initial and final concentrations of ²³⁸U in the aqueous phase.

Each experiment was done in duplicate and the results agreed to within 5%.