

A Trialkyl Phosphine Oxide Functionalized Task Specific Ionic Liquid for Actinide Ion Complexation: Extraction and Spectroscopic studies[†]

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Electronic Supplementary Information

Synthesis of PO-TSIL

A solution of lithium bis(trifluoromethanesulfonyl)imide salt (2.7 mmol, 780 mg) in dry acetonitrile (1.5 ml) was added to the solution of [TSIL]OMs (2.6 mmol, 1.2 g) [ref no.] in acetonitrile (1.5 ml) under argon atmosphere and allowed to stir it for 12h. The reaction mixture was under reduced pressure to remove excess acetonitrile and the residue was extracted with ethyl acetate and water. The organic extract was concentrated under reduced pressure to give [TSIL]NTf₂ (1.64 g, 98.5%).

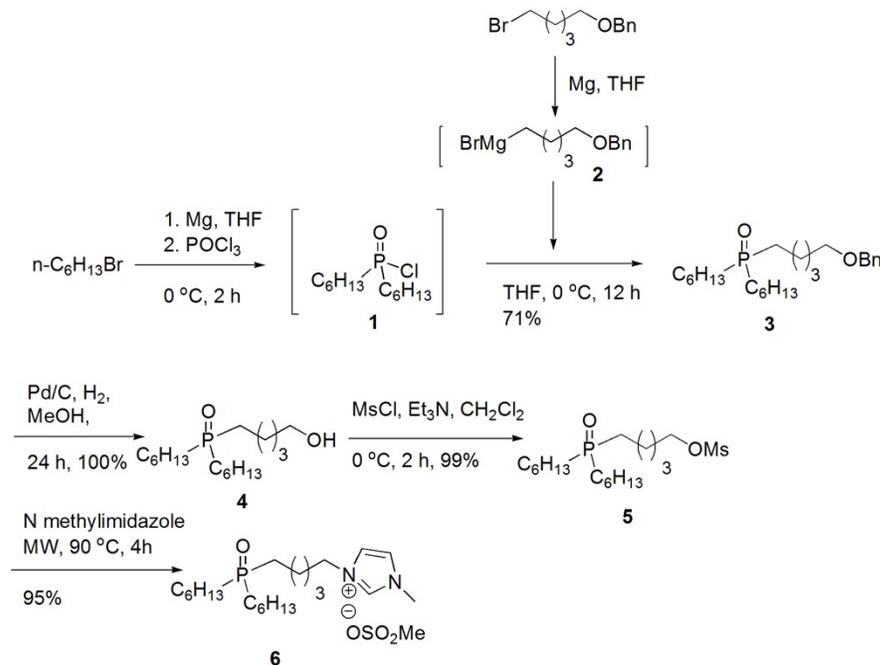
IR (film): 3156, 3028, 2939, 2863, 1573, 1467, 1351, 1194, 1136, 1058, 767 cm⁻¹;

¹H NMR (500 MHz, CDCl₃): δ 9.13 (1 H, s, Im, NCHN), 7.51 (1H, s, Im), 7.26 (1 H, s, Im), 4.26 (2 H, t, ³J_{HH} = 7.0 Hz, NCH₂), 3.94 (3 H, s, NCH₃), 2.01-1.87 (8 H, m, 4 × CH₂), 1.73-1.64 (2 H, m, CH₂), 1.59-1.48 (6 H, m, 3 × CH₂), 1.46-1.37 (4 H, m, 2 × CH₂), 1.34-1.26 (8 H, m, 4 × CH₂), 0.89 (6 H, t, ³J_{HH} = 6.5 Hz).

¹³C NMR (125 MHz, CDCl₃): δ 136.1, 123.5, 122.4, 119.7 (2 C, q, ¹J_{CF} = 319 Hz), 49.6, 36.1, 31.1 (2 C), 30.5 (2 C, d, ²J_{PC} = 13.6 Hz), 29.3, 27.2 (2 C, d, ¹J_{PC} = 65.0 Hz), 27.0 (1 C, d, ²J_{PC} = 22.0 Hz), 26.6 (1 C, d, ¹J_{PC} = 65.6 Hz), 22.3 (2 C), 21.4, 20.7, 13.8 (2 C).

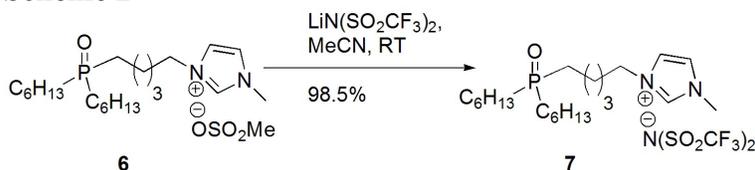
ESI-MS, m/z (rel.int.): 369 (100) [M-NTf₂]

Scheme 1



Then the desired TSIL- 7 was obtained by reacting IL 6 with lithium triflimide salt in dry acetonitrile following scheme 2.

Scheme 2



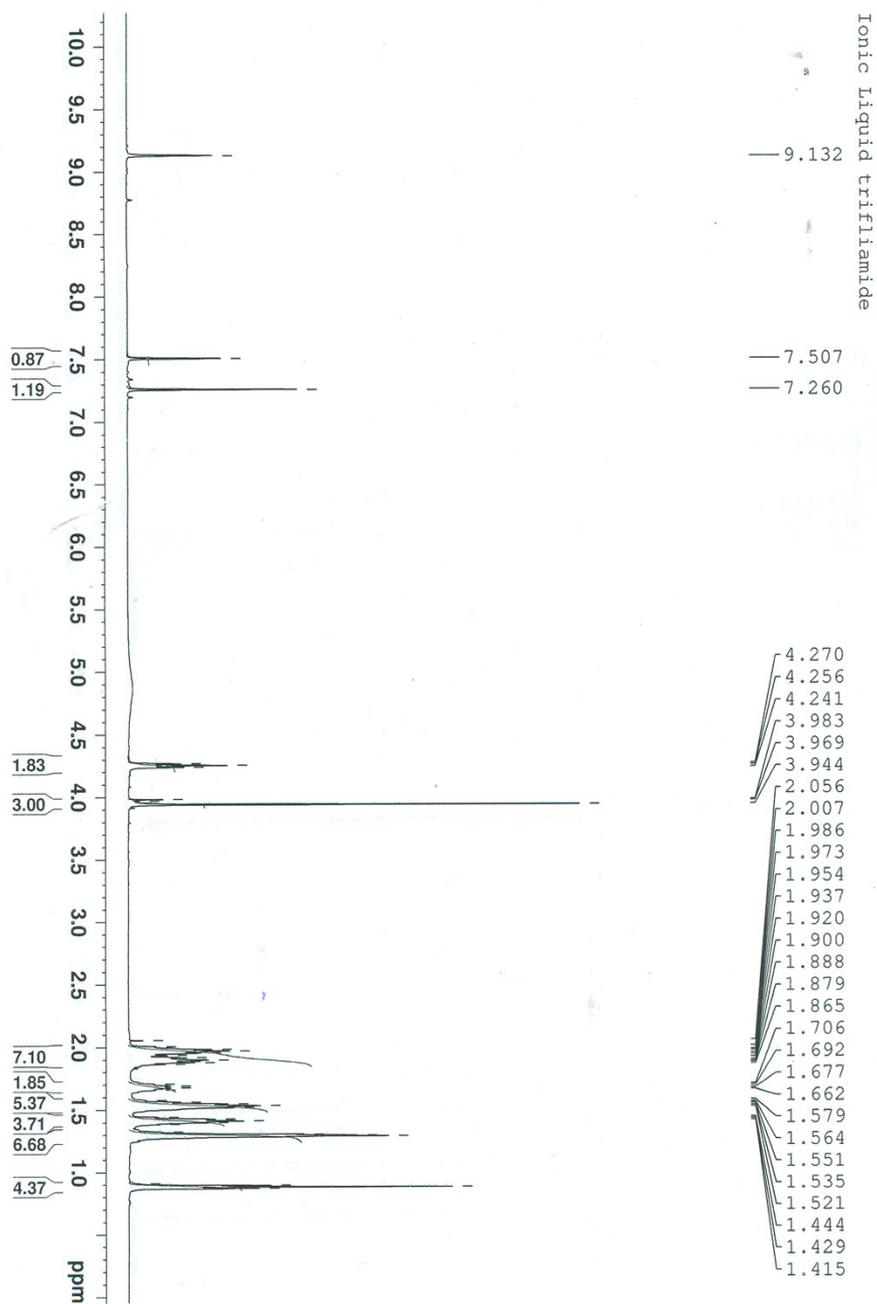


Fig. S1. ^1H NMR spectra of PO-TSIL obtained in CDCl_3

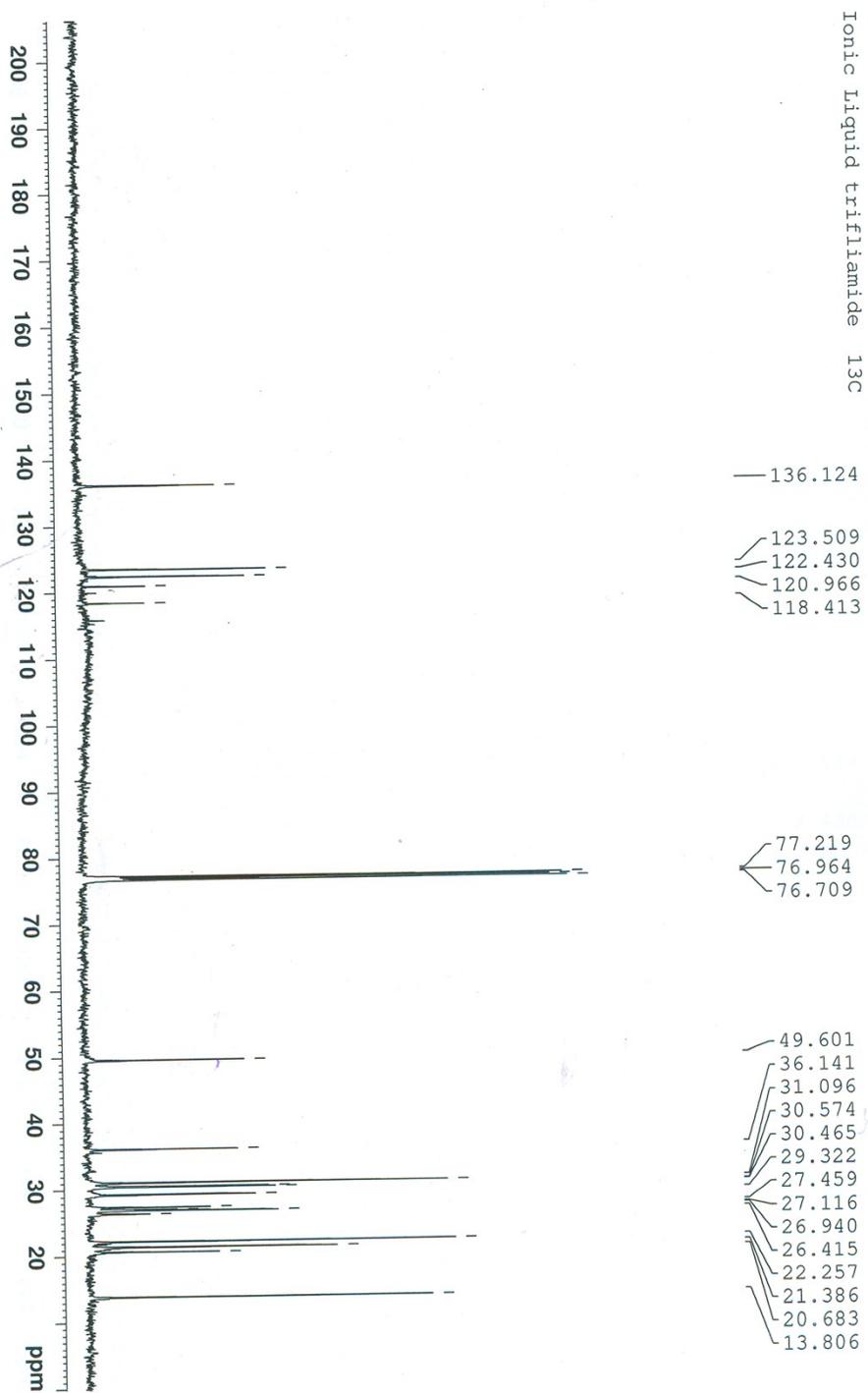


Fig. S2. ^{13}C NMR spectra of PO-TSIL obtained in CDCl_3

Kinetics of extraction:

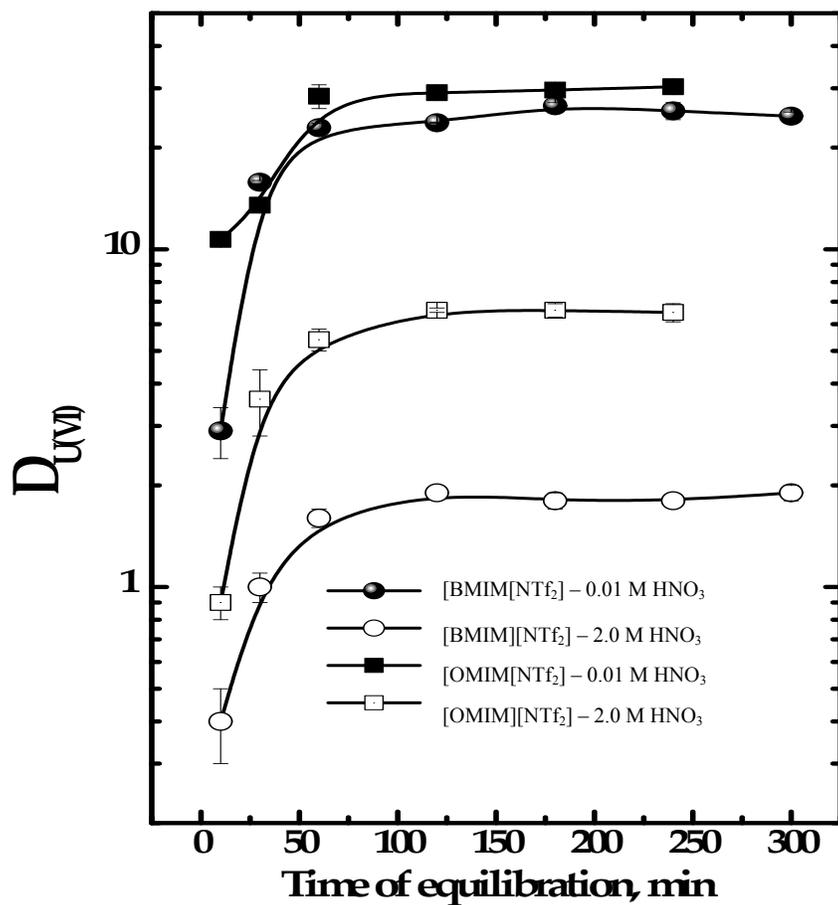


Fig. S3. Role of equilibration time on U(VI) extraction from 0.01 M and 2 M HNO₃ using both [BMIM]NTf₂ as well as [OMIM]NTf₂

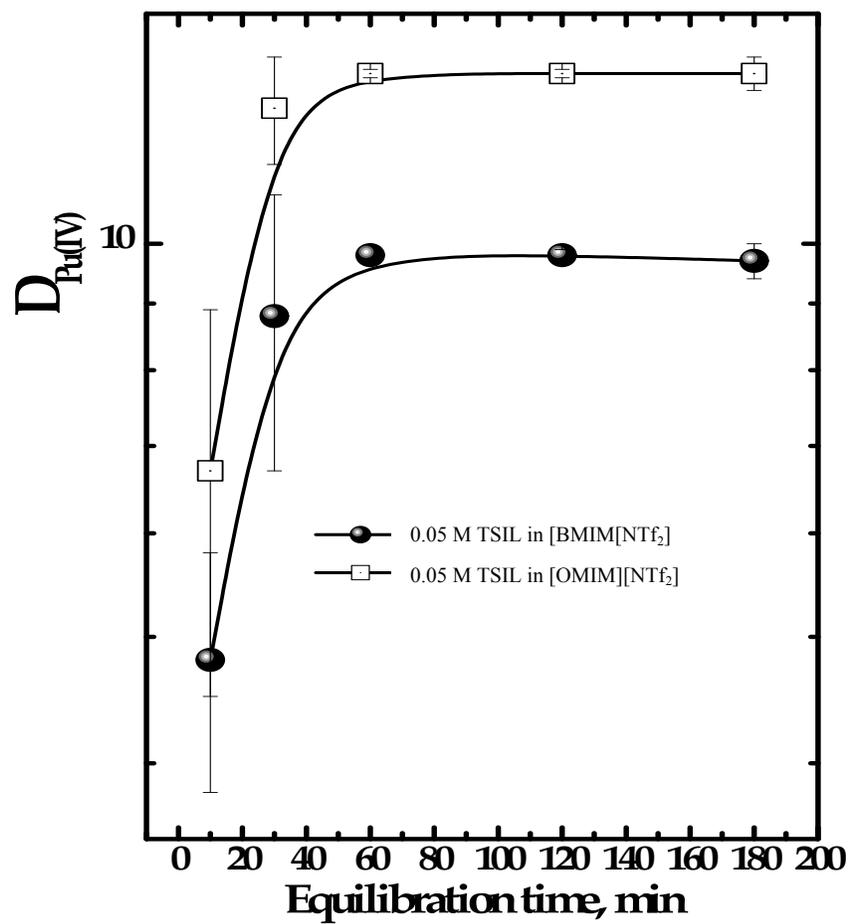


Fig. S4. Role of equilibration time on U(VI) extraction from 2 M HNO₃ using both [BMIM]NTf₂ as well as [OMIM]NTf₂

Nature of the extracted species by slope analysis method

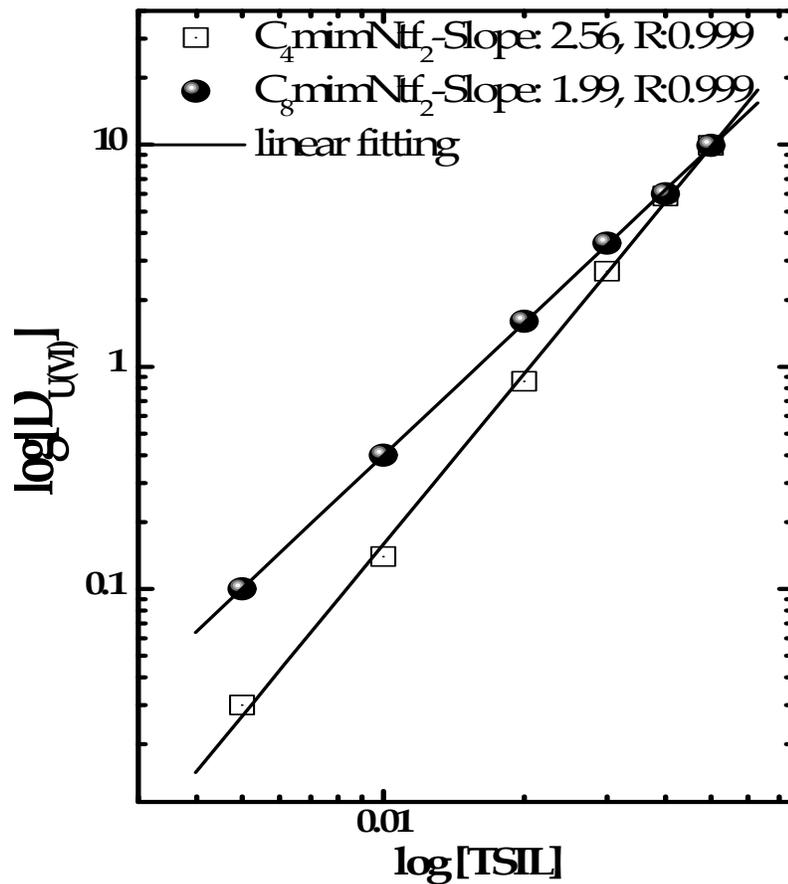


Fig. S5. Plots of $\log D_U$ vs $\log [\text{Ligand}]$ to ascertain the extracted species. Aqueous phase: 2 M HNO_3 using both $[\text{BMIM}]\text{NTf}_2$ as well as $[\text{OMIM}]\text{NTf}_2$

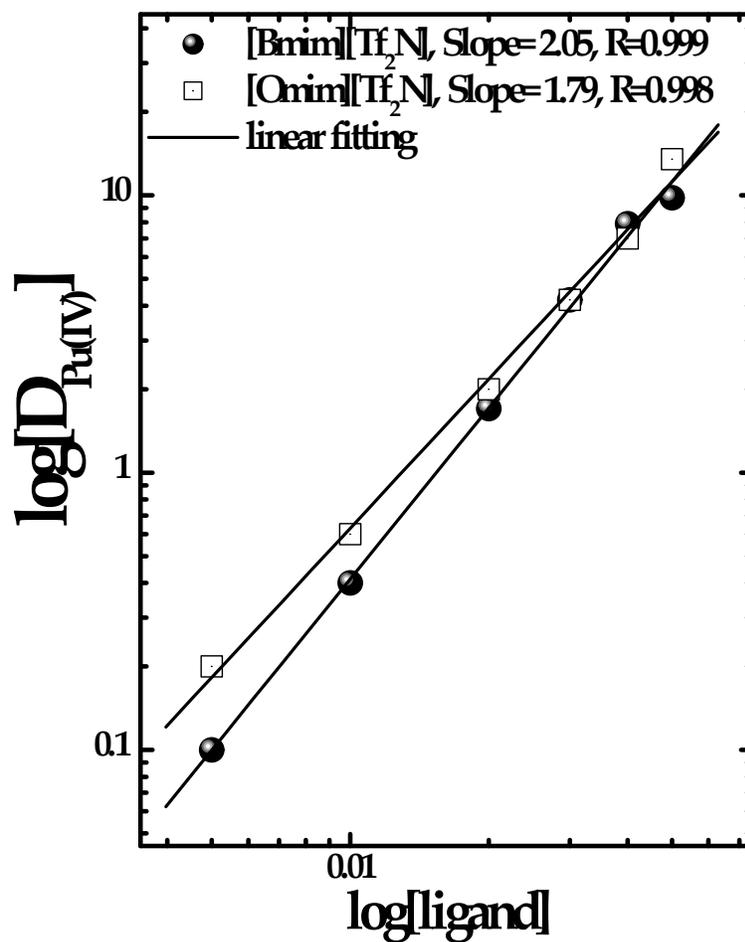


Fig. S6. Plots of $\log D_{\text{Pu}}$ vs $\log [\text{Ligand}]$ to ascertain the extracted species. Aqueous phase: 2 M HNO_3 using both $[\text{BMIM}]\text{NTf}_2$ as well as $[\text{OMIM}]\text{NTf}_2$

Stripping studies

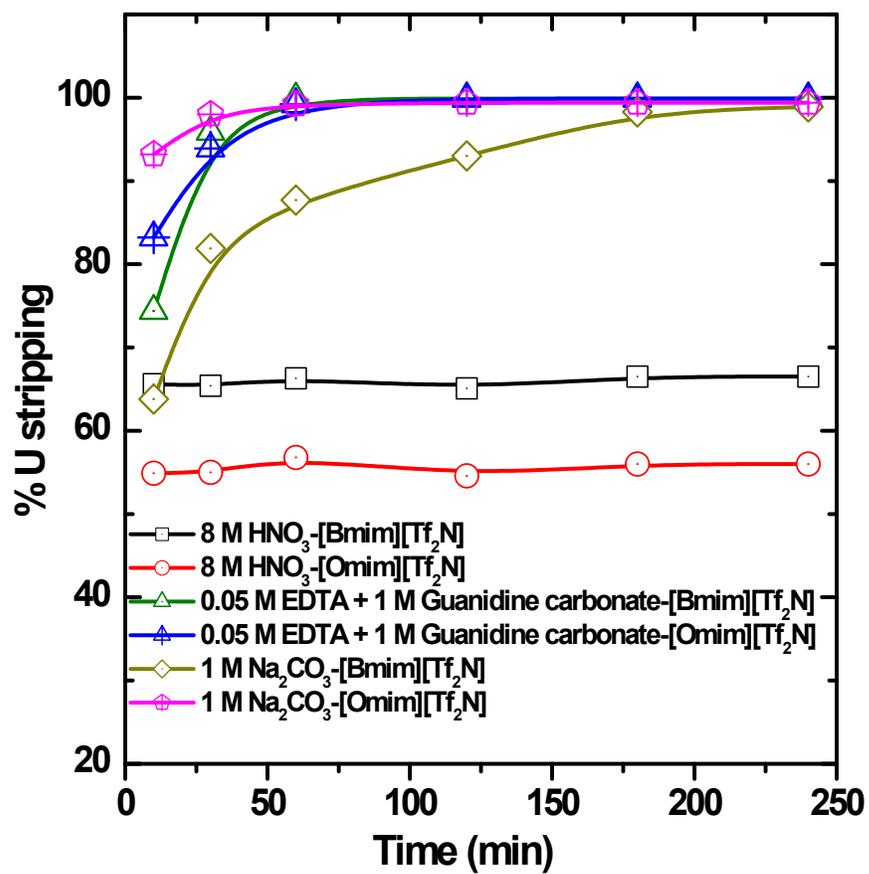


Fig. S7. Role of equilibration time on U(VI) stripping from under varying conditions.

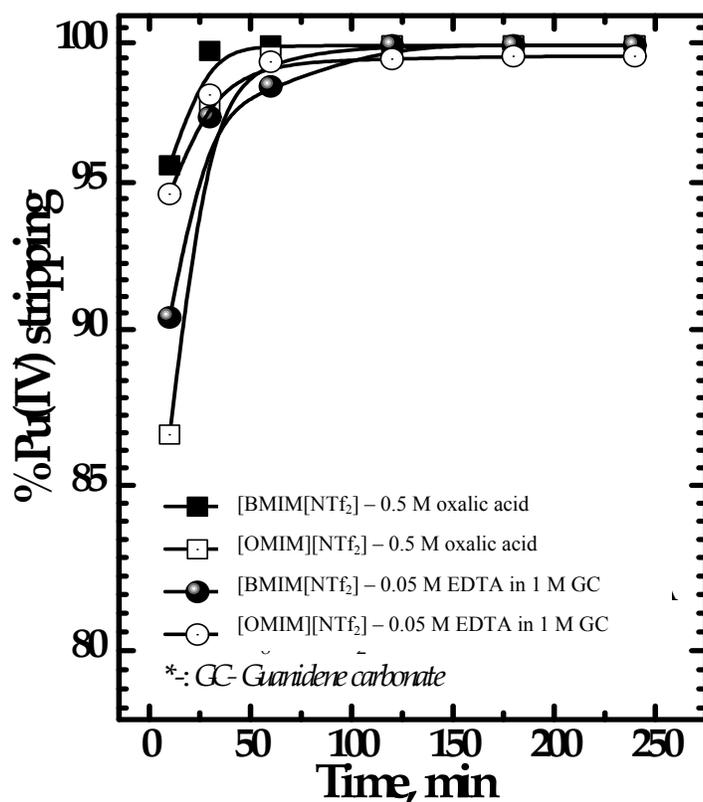


Fig. S8. Role of equilibration time on Pu(IV) stripping from both [BMIM]NTf₂ as well as [OMIM]NTf₂ using different strippants.

Table S1. Acid uptake by the ionic liquids when contacted with aqueous feeds containing different amounts of HNO₃. Data obtained by aqueous phase titration.

[HNO ₃], M	Amount of acid extracted (M)	
	[BMIM]NTf ₂	[OMIM]NTf ₂
1	0.065	0.045
2	0.120	0.080
3	0.186	0.126
4	0.252	0.172
6	0.408	0.288

Radiolytic degradation studies

Table S2. Distribution data of the actinide ions as a function of the absorbed dose with [BMIM]NTf₂. Values inside parentheses refer to those obtained with [OMIM]NTf₂.

Absorbed dose (kGy)	TSIL		TOPO	
	D _U	D _{Pu}	D _U	D _{Pu}
0	9.11 (9.9)	9.82 (13.5)	3.63 (23)	3.05 (136)
26	4.01 (7.56)	0.38 (0.78)	1.85 (22.4)	1.98 (2.06)
53	3.16 (4.89)	0.31 (0.30)	1.11 (16.2)	1.87 (1.82)
% Decrease	60.3 (50.6)	96.8 (97.8)	69.4 (29.6)	38.7 (98.7)

Fluorescence studies

Instrumentation

Emission and excitation spectra were recorded on an Edinburgh F-900 Fluorescence Spectrometer in the 200–750 nm regions with a Xe lamp as an excitation source, M-300 monochromators and a Peltier cooled photomultiplier tube as detector. The acquisition and analysis of the data were carried out by F-900 software procured from Edinburgh Analytical Instruments, UK.

Results

Photoluminescence investigation was carried out to probe local environment around uranyl ion in aqueous HNO₃ (1 M HNO₃) medium and the extracts generated after complexation of UO₂²⁺ ion with TOPO functionalized task specific ionic liquid in [BMIM]NTf₂ and [OMIM]NTf₂; and TOPO in [BMIM]NTf₂. The preliminary look on the emission spectra of these systems (**Fig. 5 of main text**) revealed that the nature of the species were entirely different in all the cases. Surprisingly, the emission profiles for UO₂²⁺- TOPO-TSIL complexes in [BMIM]NTf₂ and [OMIM]NTf₂ were also found to differ significantly. The emission maxima for UO₂²⁺ in aqueous nitric acid medium was found to be at 507.540 nm, which was found to be shifted to the higher wavelength region on complexation (λ_{\max} (TOPO) = 511.852 nm, λ_{\max} (TOPO-TSIL in [OMIM]NTf₂) = 516.907 nm, λ_{\max} (TOPO-TSIL in [BMIM]NTf₂)). The relative intensities of the vibronic structures of the emission spectra were also found to differ with each other. The symmetric stretching frequency of uranyl oxygen obtained from the emission spectra

revealed that in UO_2^{2+} TSIL complex, the U-O bonds were found to be shorter compared to U-TOPO complex. The decay profiles (**fig. S9 below**) revealed the presence of single species in case of U-TOPO extracts in $[\text{BMIM}]\text{NTf}_2$ ($93 \mu\text{s}$) and U-TSIL extract in $[\text{OMIM}]\text{NTf}_2$ ($106 \mu\text{s}$) whereas for U-TSIL extract in $[\text{BMIM}]\text{NTf}_2$ showed the bi-exponential nature of the decay profile revealing the presence of two species ($\tau_1 = 59 \mu\text{s}$ and $\tau_2 = 302 \mu\text{s}$). This fact can also be supported by the slope values of the $\log D$ vs $\log[\text{Ligand}]$ plots.

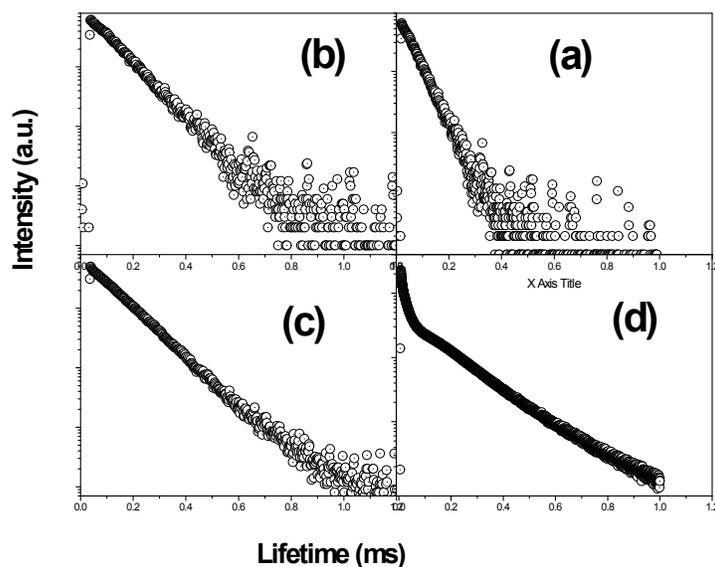


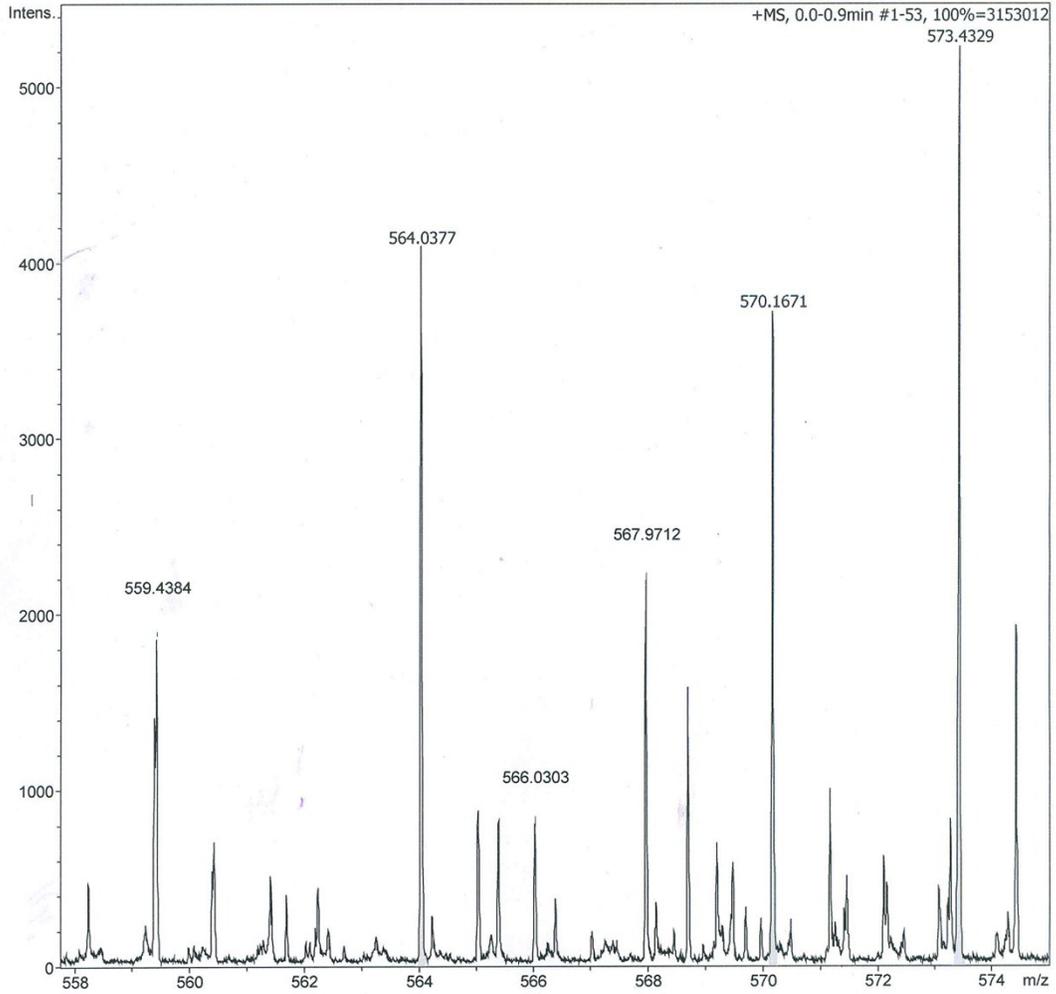
Fig. S9: Decay profiles for Luminescence spectra of (a) aq. uranyl, (b) U-TOPO extracts in $[\text{BMIM}]\text{NTf}_2$ (c) U-TSIL extracts in $[\text{OMIM}]\text{NTf}_2$ and (d) U-TSIL extracts in $[\text{BMIM}]\text{NTf}_2$

ESI-MS studies:

Extracted species: $\text{UO}_2(\text{TSIL})_2(\text{NO}_3)_2^{2+}$; Calculated mass: ca. 566

Acquisition Parameter

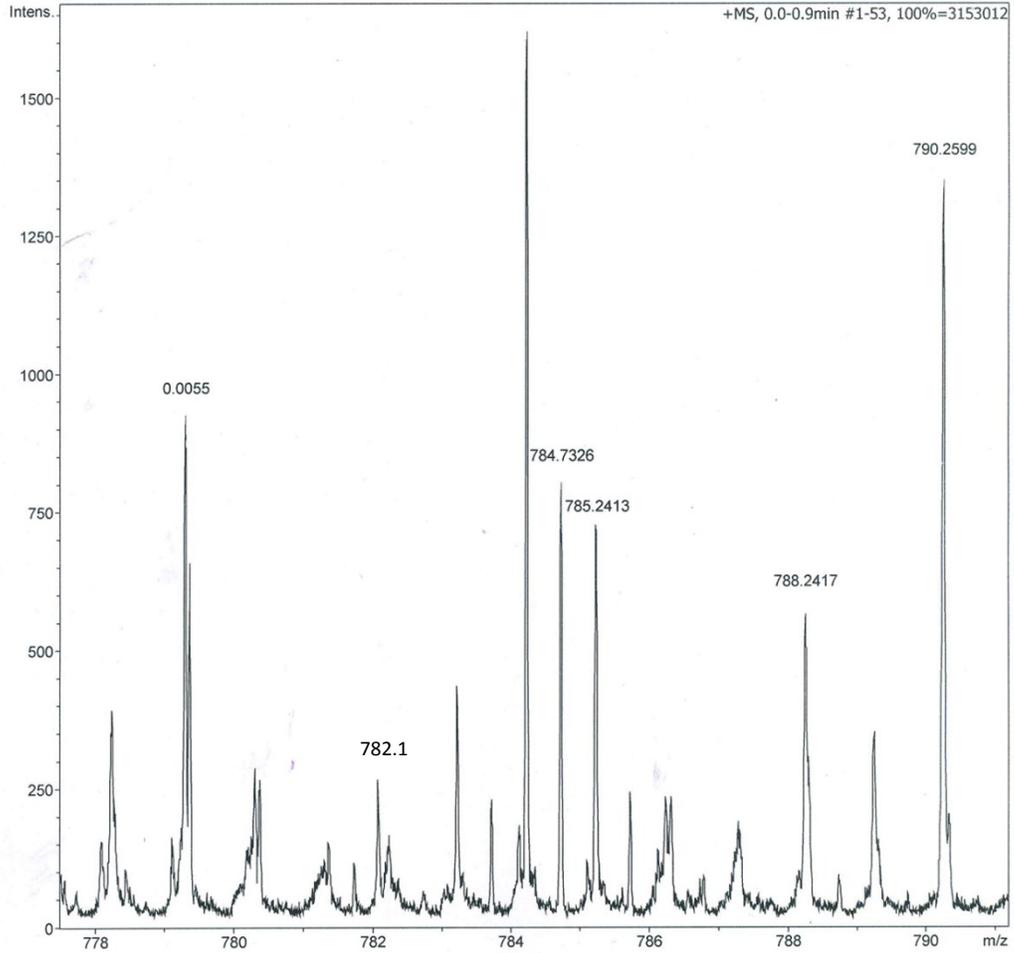
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Focus	Active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Extracted species: $\text{UO}_2(\text{PO-TSIL})_3(\text{NO}_3)_3^{2+}$; Calculated mass: ca. 782

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



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Measurements of viscosity and water content in TSIL

Table S3: Viscosity and water content data (by Karl Fischer titration) obtained using 0.05 M TSIL (in either [C₄mim][Tf₂N] or [C₈mim][Tf₂N] as indicated below). Aq. phase for equilibration: 0.005 M uranyl nitrate solution in 1 M HNO₃; Equilibration time: 1 h; Temperature: 25°C

Diluent	Viscosity, mPa·s		Water content, mg/mL	
	Before equilibration	After equilibration	Before equilibration	After equilibration
[C ₄ mim][Tf ₂ N]	46.13 ± 0.09	33.37 ± 0.04	6.62 ± 0.11	19.74 ± 0.18
[C ₈ mim][Tf ₂ N]	81.41 ± 0.43	65.82 ± 0.04	5.50 ± 0.05	12.34 ± 0.08

The dynamic viscosity and density values of different solvents used in present studies were measured using an Anton Paar, Austria viscometer (model number SVN 3000).