Electronic Supplementary Material (ESI) for Dalton Transactions

A novel CMPO-functionalized task specific ionic liquid: Synthesis, extraction and spectroscopic investigations of actinide and lanthanide complexes

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Electronic Supplimentary Information

Experimental

Materials

Radiotracers

^{241}Am, Pu (mainly ^{239}Pu), and ^{233}U tracers from laboratory stock solutions were purified prior to their use by ion-exchange methods reported previously. ^{85,89}Sr and ^{137}Cs and ^{152,154}Eu tracers were purchased from BRIT, Mumbai. Assaying of ^{241}Am, ^{137}Cs, ^{85,89}Sr and ^{152,154}Eu was done by gamma counting using a NaI(Tl) scintillation counter (Para Electronics, India) interphased to a multi-channel analyzer (ECIL, India), while nuclides such as ^{239}Pu and ^{233}U were assayed by liquid scintillation counting (Hidex, Finland) using a toluene-based scintillator cocktail (Sisco Research Laboratory, Mumbai) to minimize quenching effects.

Reagents

CMPO (*n*-octylpheyl-*N*,*N*-di-iso-butylcarbamoylmethylphosphine oxide) was procured from Orion Chemicals, Mumbai and was passed through a basic alumina column prior to use. AR grade *n*-dodecane was obtained from Lancaster, UK, and was used as such. Suprapur nitric acid (Merck, Germany) was used for preparing nitric acid solutions using milliQ water (Millipore, India). For spectrophotometric studies, the uranyl nitrate (UED, BARC) and neodymium nitrate (Aldrich, USA) salts were used, which were standardized using a normal procedure.[24] All the other reagents were of AR grade.

Synthesis of TSILs

All reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. Solvents were dried according to standard procedures and stored over molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) chemical shift values are reported as δ using the residual solvent signal as an internal standard. All NMR measurements are recorded in $CDCl_3$ as a solvent. Electrospray Ionization (positive mode) high resolution mass spectra were recorded on a WATERS LCT mass spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminum).

*1-(3-(2-(Diphenylphosphoryl)acetamido)propyl)-3-dodecyl-1*H*-imidazol-3-ium bromide (2).*

To a solution of CMPO-imidazole-propanamide (Ref: I. L. Odinets, E. V. Sharova, O. I. Artyshin, K. A. Lyssenko, Y. V. Nelyubina, G. V. Myasoedova, N. P. Molochnikova, E. A. Zakharchenro, Dalton Trans., 2010, 39, 4170-4178) **1** (26.00 g, 70.8 mmol) in CH_3CN (150 mL), *n*-dodecyl bromide (21.2 g, 85.0 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for 12 h, followed by reflux at 80–85 °C for 2.5 d. Then the solvent was evaporated under reduced pressure and the resulting residue was washed with *n*-hexane (3 × 100 mL). Residual solvent was removed under reduced pressure and the residue was dried under vacuum for 5 h to afford **2** (37.9 g, 87%) as a dense oil. ^1H NMR: δ 0.85 (3H, t, *J* = 7.5 Hz, CH_3), 1.16-1.36 (18H, m, $(CH_2)_9$), 1.75-1.90 (2H, m, $ImCH_2CH_2$ (dodec.)), 1.97-2.10 (2H, m, $ImCH_2CH_2$), 3.02-3.14 (2H, m, NCH_2), 3.68 (2H, d, *J* = 12.0 Hz, PCH_2CO), 4.17 (2H, t, *J* = 7.5 Hz, $ImCH_2$(dodec.)), 4.26 (2H, t, *J* = 7.5 Hz, $ImCH_2$), 7.22 (1H, s, ImH), 7.38-7.55 (6H, m, ArH), 7.71 (1H, s, ImH), 7.77-7.91 (4H, m, ArH), 8.72 (1H, br s, NH), 10.00 (1H, s, ImH). ^{13}C NMR: δ 14.0, 22.6, 26.2, 28.9, 29.2, 29.3, 29.4, 29.5, 30.1, 31.8, 34.9, 38.6, 39.2, 46.3, 49.9, 122.0, 122.9, 128.6, 128.7, 131.0, 131.1, 131.6, 132.0, 132.6, 137.0, 165.7. HRMS calculated for $C_{32}H_{48}N_3O_2P$ 536.3400 $[M]^+$, found 536.3317.

General procedure for ion exchange

To a solution of an ionic liquid, containing bromide as anion, (1 equiv) in anhydrous CH_3CN, a solution of $NaPF_6$ or bis(trifluoromethane)sulfonimide lithium salt (2.5 equiv) in anhydrous CH_3CN was added. The mixture was stirred at room temperature for 48 h. The solvent was evaporated under reduced pressure and water (50 mL) was added to the solid residue. The product was extracted into CH_2Cl_2 (3 × 50 mL) and the organic phase was washed with water (3 × 50 mL). The collected organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. The obtained ionic liquid was dried under vacuum for 4 h.

*1-(3-(2-(Diphenylphosphoryl)acetamido)propyl)-3-dodecyl-1*H*-imidazol-3-ium hexafluorophosphate (L-I).*

It was prepared by the general procedure described above from CMPO-imidazole-propanamide-dodecyl bromide (**2**) (20.0 g, 32.4 mmol) in anhydrous CH_3CN (150 mL) and $NaPF_6$ (14.0 g, 83.1 mmol) in anhydrous CH_3CN (35 mL) as a gel (21.2 g) in 96% yield. ^1H NMR: δ 0.87 (3H, t, *J* = 7.5 Hz, CH_3), 1.13-1.36 (18H, m, $(CH_2)_9$), 1.71-1.87 (2H, m, $ImCH_2CH_2$ (dodec.)), 1.87-2.04 (2H, m, $ImCH_2CH_2$), 3.04-3.16 (2H, m, NCH_2), 3.44 (2H, d, *J* = 12.0 Hz, PCH_2CO), 3.97-4.09 (4H, m, $ImCH_2$), 7.17 (1H, s, ImH), 7.34 (1H, br s, NH), 7.37 (1H, s, ImH), 7.41-7.58 (6H, m, ArH), 7.67-7.81 (4H, m, ArH), 8.83 (1H, s, ImH). ^{13}C NMR: δ 14.1, 22.7, 26.2, 28.9, 29.3, 29.4, 29.5, 29.6, 29.9, 31.9, 35.3, 38.4, 39.1, 46.4, 50.0, 122.0, 122.5, 128.9, 129.0, 130.8, 130.9, 131.2, 132.2, 132.4, 136.1, 165.7. HRMS calculated for $C_{32}H_{48}F_6N_3O_2P_2$ 682.3126 $[M+PF_6+H]^+$, found 682.3185.

1-(3-(2-(Diphenylphosphoryl)acetamido)propyl)-3-dodecyl-1*H*-imidazol-3-ium bis(trifluoromethane)sulfonimide (L-II).

It was prepared according to the general procedure starting from **2** (20.0 g, 32.4 mmol) and bis(trifluoromethane)sulfonimide lithium salt (22.1 g, 81.0 mmol) as a gel (25.2 g) in 97% yield. ^1H NMR: δ 0.87 (3H, t, *J* = 7.5 Hz, CH_3), 1.16-1.37 (18H, m, $(CH_2)_9$), 1.73-1.89 (2H, m, $ImCH_2CH_2$ (dodec.)), 1.90-2.03 (2H, m, $ImCH_2CH_2$), 3.10-3.20 (2H, m, NCH_2), 3.47 (2H, d, *J* = 12.0 Hz, PCH_2CO), 3.99 (2H, t, *J* = 7.5 Hz, $ImCH_2$ (dodec.)), 4.07 (2H, t, *J* = 7.5 Hz, $ImCH_2$), 7.17 (1H, s, ImH), 7.37 (1H, br s, NH), 7.40 (1H, s, ImH), 7.43-7.60 (6H, m, ArH), 7.72-7.84 (4H, m, ArH), 8.97 (1H, s, ImH). ^{13}C NMR: δ 14.1, 22.6, 26.1, 28.8, 29.3, 29.5, 29.6, 29.9, 31.9, 35.3, 38.3, 38.9, 46.5, 50.0, 114.5, 118.2, 121.4, 122.2, 122.6, 124.6, 128.9, 129.0, 130.8, 130.9, 131.8, 132.6, 135.9, 166.0. HRMS calculated for $C_{34}H_{48}F_6N_3O_6PS_2$ 803.2621, $[M+NTf_2+H]^+$ found 803.2691.

Methods

Distribution studies

The solvent extraction studies were carried out by vortexing 1 mL of the ligand solution (CMPO or CMPO-functionalized TSIL) in a suitable room temperature ionic liquid, taken in Pyrex tubes, with an equal volume of the aqueous phase containing the required radiotracers at a given HNO_3 concentration in a thermostated water bath at

25±0.1 °C for about 2 h, which was optimized after the studies with varying equilibration time. Aliquots (usually 100 μL) were removed from both phases after centrifugation and assaying was done by radiometry as indicated above (Section 4.1.1). Studies with Am, Pu, and U at tracer scale typically involved metal ion concentrations in the range of 10^{-7} M, 10^{-6} M, and 10^{-5} M, respectively. The distribution ratio, D_M, was defined as the ratio of the activity per unit volume in the ionic liquid phase to that in the aqueous phase. The experiments were carried out in duplicate and the precision was within ± 5%.

Pu valency state adjustment

The valency of Pu was adjusted to the +4 state by the addition of 20 μL of a $NaNO_2$ solution (5.0×10^{-2} M) into a beaker containing the Pu radiotracer in 1 M HNO_3. The aqueous solution was subsequently contacted with a 0.5 M TTA (2-thenoyltrifluoroacetone) solution in xylene, whereby the Pu^{4+} ion is quantitatively extracted. The extract was stripped using 7 M HNO_3, which was further equilibrated (three successive times) with xylene to remove the dissolved TTA from the aqueous phase. The stripped Pu in the +4 state was subsequently used for the extraction studies after appropriate dilutions.

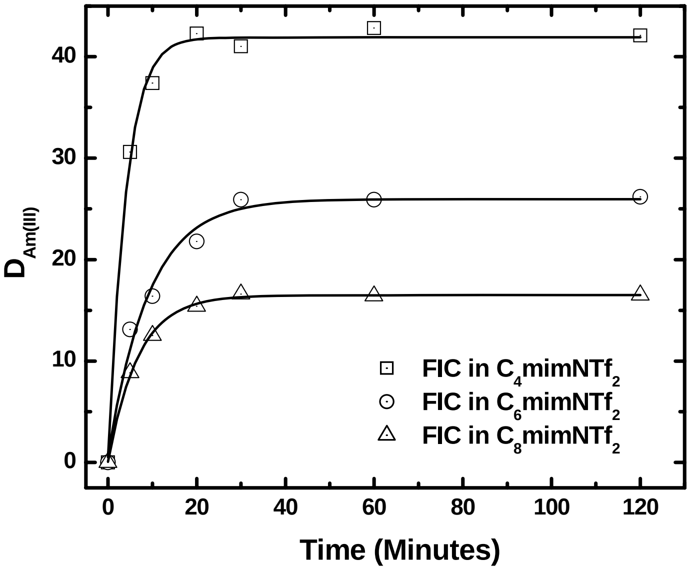
Spectroscopic investigations

U(VI) and Nd(III) extracts in ionic liquid solutions of CMPO or CMPO-functionalized TSIL were used for spectroscopic investigations. The UV-visible spectra of the extracts were compared with those obtained using aqueous nitrate solutions of the metal ions. UV-visible spectra of the solutions were recorded using a JASCO V530 (Tokyo, Japan) spectrophotometer using D_2 and Xe lamps with a working wavelength range of 200–1100 nm. Typically, digital data were recorded at 1 nm intervals. IR spectra were recorded using a JASCO FT-IR 6100 equipment using NaI cells.

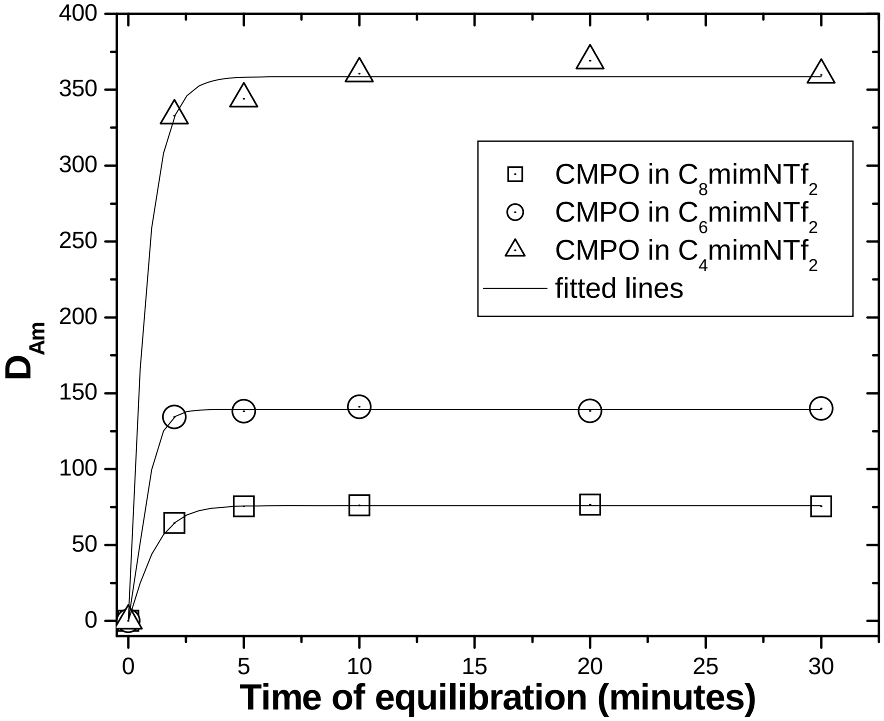
Results and Discussion

Time taken to attain equilibrium

Fig. S-1: D_{Am} values at different equilibration times using (a) CMPO-TSIL **L-II** and (b) CMPO in different ionic liquids. [Ligand]: 0.09 M CMPO-TSIL **L-II** in different ionic liquids; Aqueous phase: 3 M HNO_3 spiked with ^{241}Am

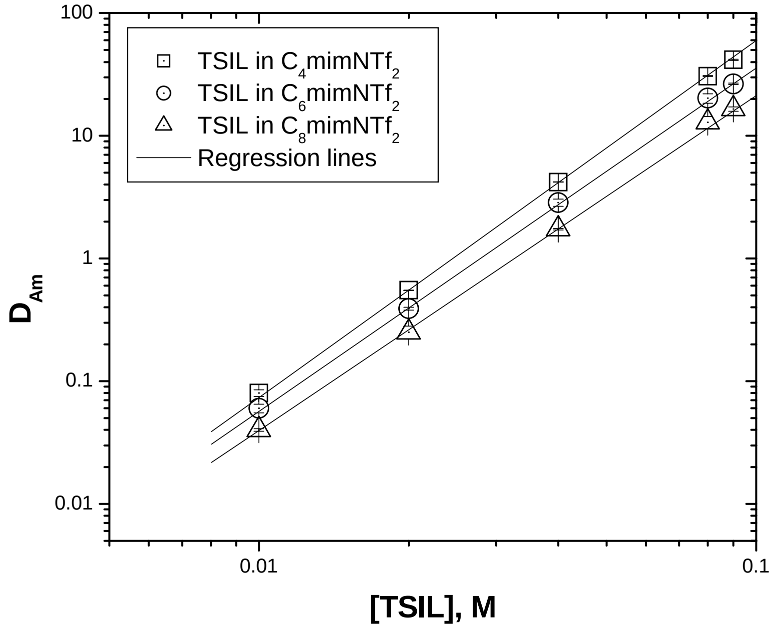


(a)

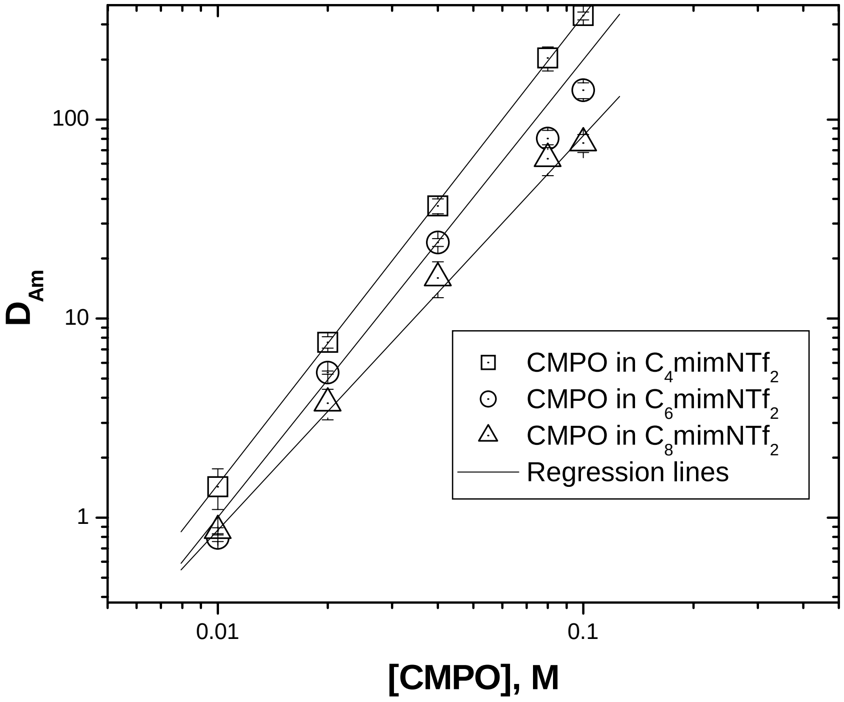


Ligand concentration variation

Fig. S-2 Variation of D_{Am} with ligand concentration; (a) CMPO-TSIL **L-II** as ligand and (b) CMPO as ligand. [Ligand]: 0.1 M in ionic liquid; Aqueous phase: 3 M HNO_3

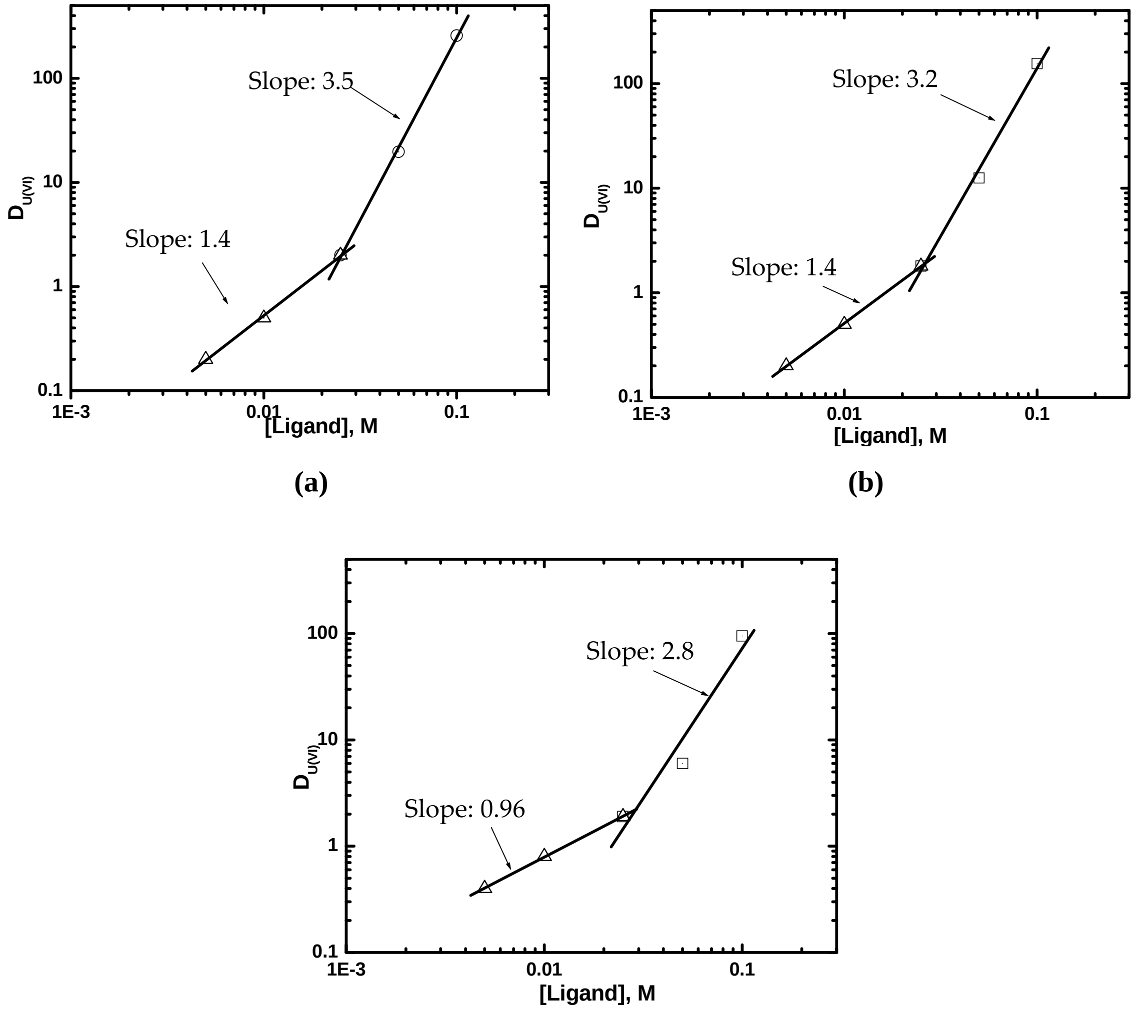


(a)



(b)

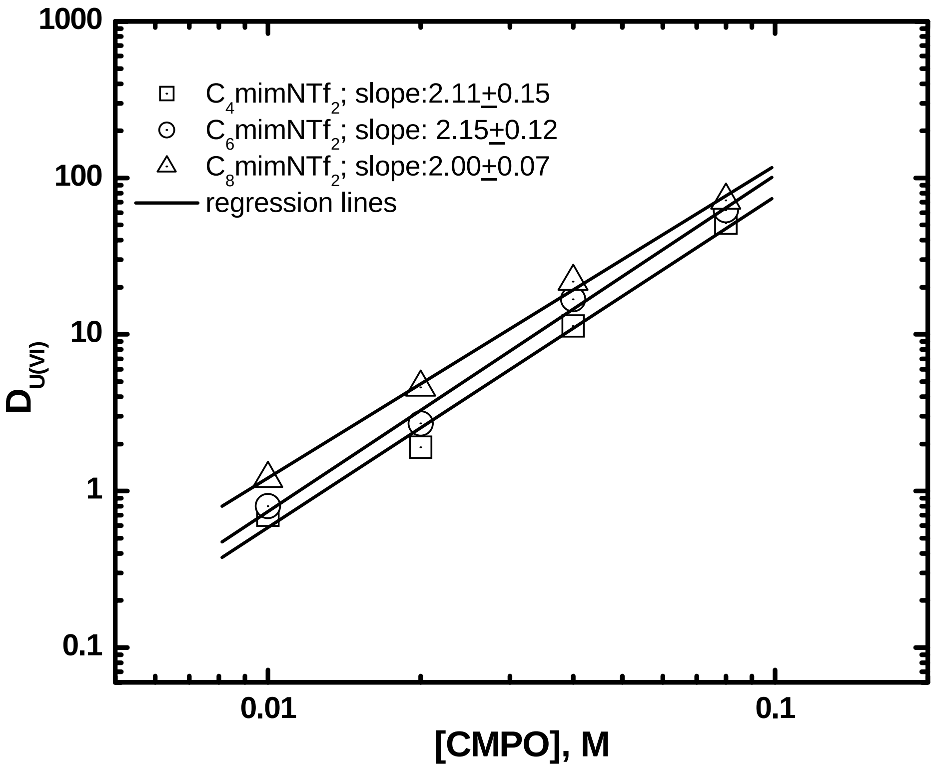
Fig. S-3: Log-log plot of $D_{U(VI)}$ *vs*. CMPO-TSIL **L-II** concentration at 3 M HNO_3 in – (a) $C_4mimNTf_2$; (b) $C_6mimNTf_2$; and (c) $C_8mimNTf_2$



(a) **(b)**

(c)

Fig.S-4: Log-log plot of $D_{U(VI)}$ *vs.* CMPO concentration at 3 M HNO_3 in $C_n$mimNTf$_2$



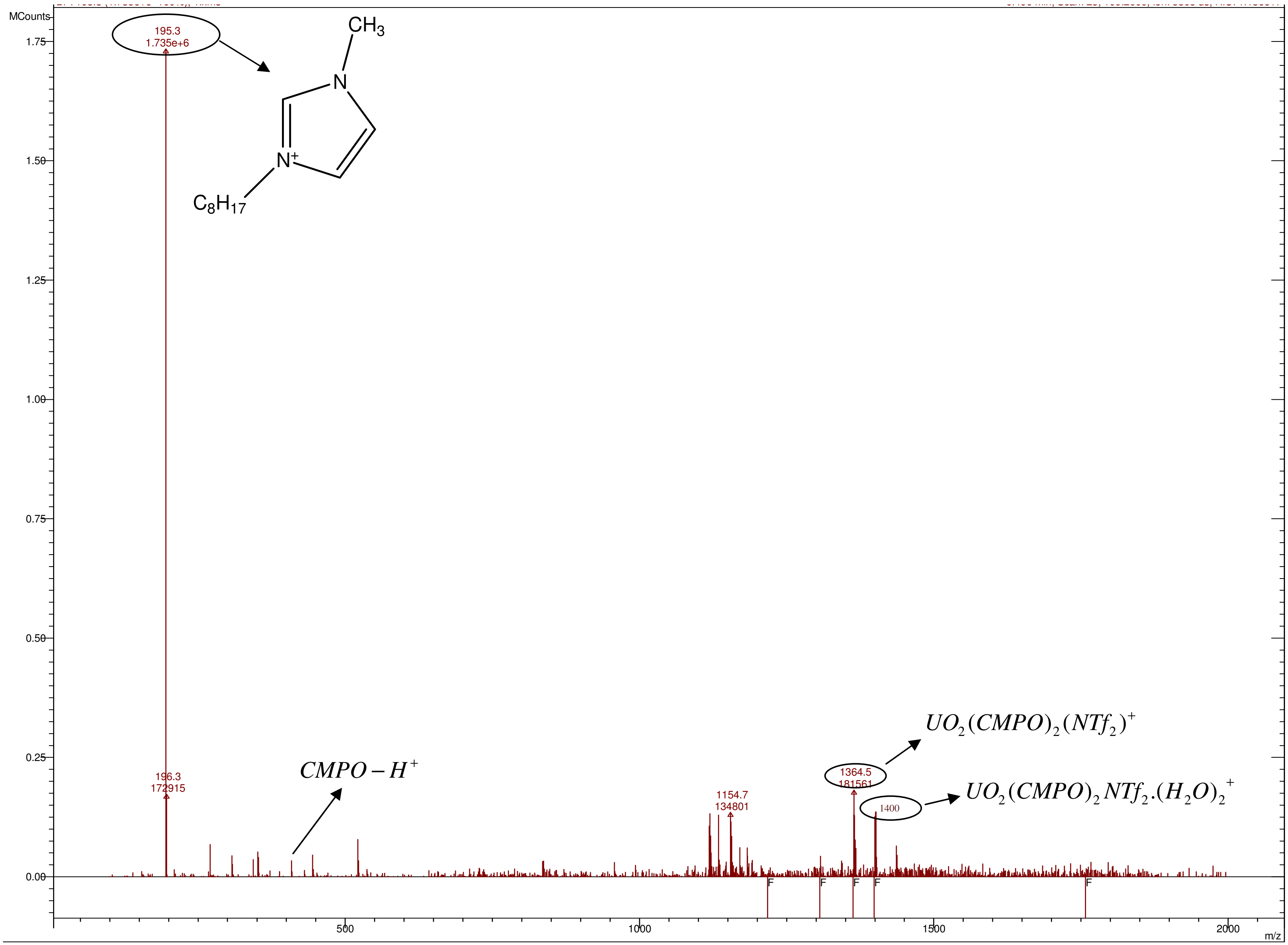
IR Spectral study

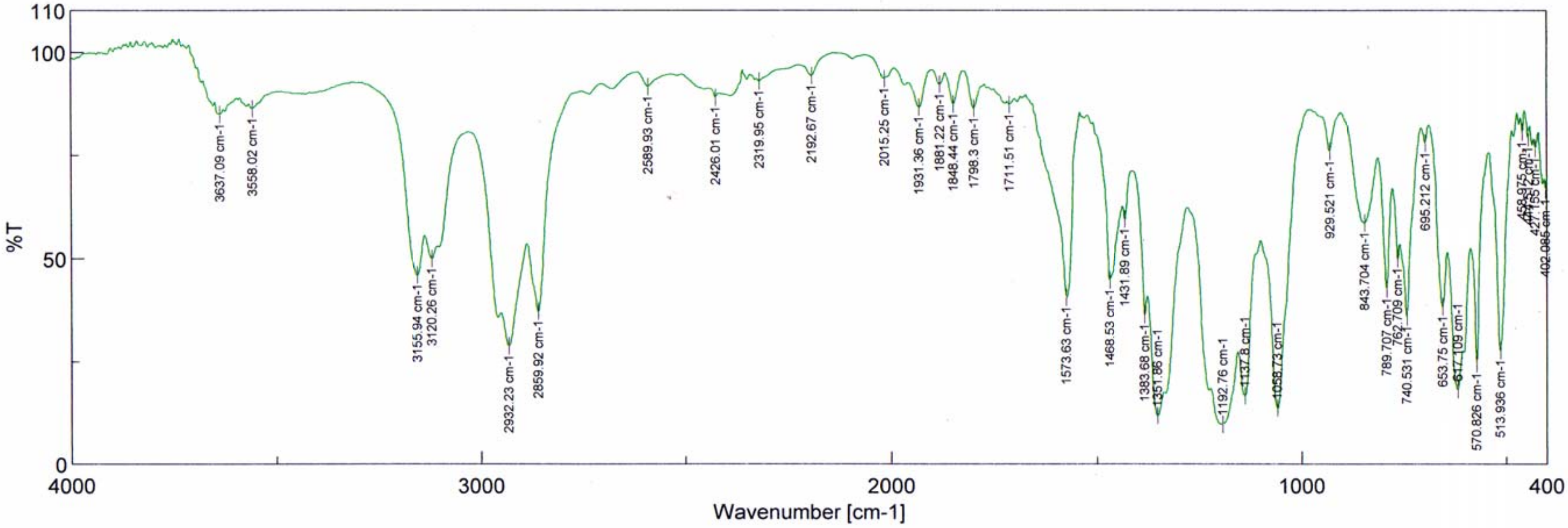
The IR spectra of the following samples are enclosed at the end of the ESI.

S.No.	Sample name	Details
1.	PK3	Uranyl nitrate extract using 0.1 M CMPO in C_8mimNTf$_2$
2.	PK4	0.1 M CMPO in C_8mimNTf$_2$
3.	PK6	0.1 M TSIL in C_8mimNTf$_2$

Table S-1: Metal ion stripping data using 1M Na_2CO_3 or pH 2 (0.01 M HNO_3) solution as the strippant

Metal ion	Extractant (0.1 M)	Strippant	D_M	% Stripping	% Stripping in 3 contacts
U	CMPO in C_8mimNTf$_2$	1 M Na_2CO_3	0.325	75.5	98.5
	CMPO in C_8mimNTf$_2$	pH 2	630	0.16	Too less
U	TSIL in C_8mimNTf$_2$	1 M Na_2CO_3	0.258	79.5	98.8
	TSIL in C_8mimNTf$_2$	pH 2	43	2.28	Too less
Am	CMPO in C_8mimNTf$_2$	1 M Na_2CO_3	0.1	92.2	>99%
	CMPO in C_8mimNTf$_2$	pH 2	1820	0.05	Too less
Am	TSIL in C_8mimNTf$_2$	1 M Na_2CO_3	0.1	92.3	>99%
	TSIL in C_8mimNTf$_2$	pH 2	72	1.37	Too less


MCounts
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
195.3
1.735e+6
CH_3
N
N^+
C_8H_{17}
196.3
172915
$CMPO-H^+$
1154.7
134801
1364.5
181561
1400
$UO_2(CMPO)_2(NTf_2)^+$
$UO_2(CMPO)_2NTf_2.(H_2O)_2^+$
F
F
F
F
F
500
1000
1500
2000
m/z



[Comments]

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Comment	Liladhar
User	Liladhar
Division	ChD-BARC
Company	BARC

[Detailed Information]

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Horizontal axis	Wavenumber [cm-1]
Vertical axis	%T
Start	349.053 cm-1
End	7800.65 cm-1
Data interval	0.964233 cm-1
Data points	7729

[Measurement Information]

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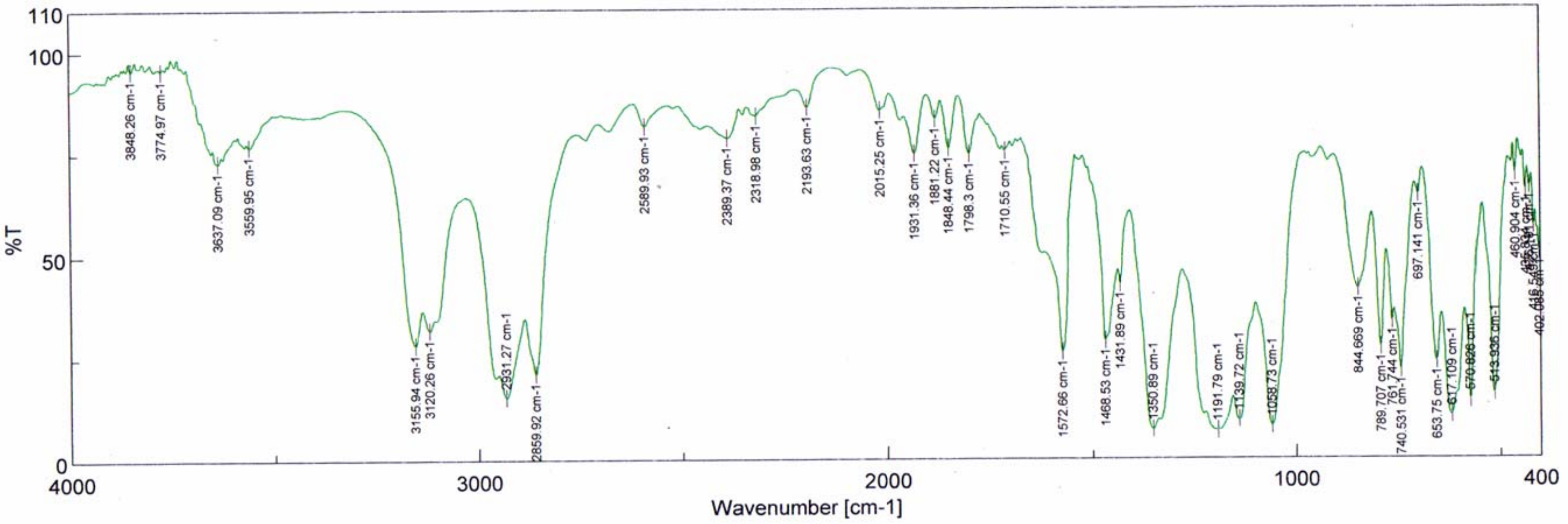
Serial Number	A044261020
Accessory	DR PRO410-M
Accessory S/N	A015261046
Measurement Date	7/5/2012 12:02 PM
Light Source	Standard
Detector	TGS
Accumulation	30
Resolution	4 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (16)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (10000 Hz)



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Sample name	PK4
Comment	Liladhar
User	Liladhar
Division	ChD-BARC
Company	BARC

[Detailed Information]	
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Data array type	Linear data array
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End	7800.65 cm-1
Data interval	0.964233 cm-1
Data points	7729

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Accessory	DR PRO410-M
Accessory S/N	A015261046
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Detector	TGS
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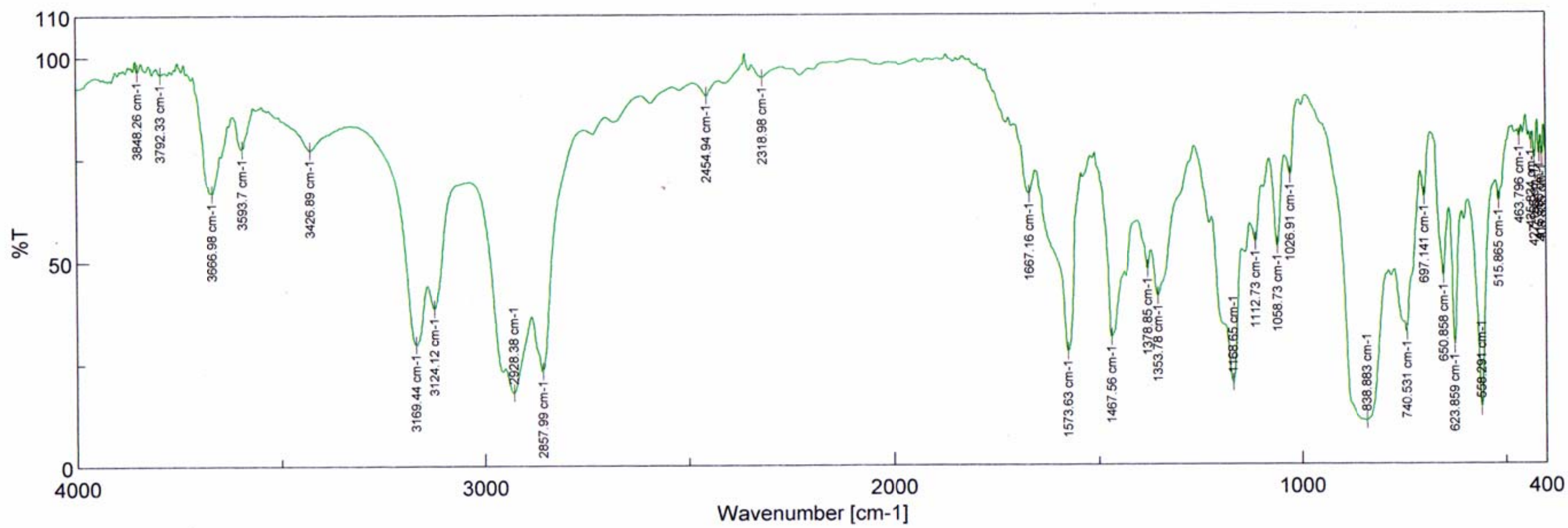
Filter	Auto (10000 Hz)

PK4



[Comments]	
Sample name	PK6
Comment	Liladhar
User	Liladhar
Division	ChD-BARC
Company	BARC

[Detailed Information]	
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Data array type	Linear data array
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Vertical axis	%T
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End	7800.65 cm-1
Data interval	0.964233 cm-1
Data points	7729

[Measurement Information]	
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Accessory	DR PRO410-M
Accessory S/N	A015261046
Measurement Date	7/5/2012 12:18 PM
Light Source	Standard
Detector	TGS
Accumulation	30
Resolution	4 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (16)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (10000 Hz)