Supplementary Material (ESI) for New Journal of Chemistry
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Non-ionic Metal-Chelating Surfactants Mediated Solvent-Free Thermo-induced Separation of Uranyl

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Supplementary Information

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Synthesis of Surfactant 1

Synthesis of intermediate acid (*A*) : A solution of dodecyloxypentaethylene glycol $\mathrm{C_{12}E_5}$ (4.00 g, 9.9 mmol, high purity monodisperse obtained from Nikko) in 10 mL anhydrous THF was added under $\mathrm{N_2}$ upon stirring to a suspension of NaH (60% in mineral oil, 1.38 g, 34.5 mmol) in 10 mL anhydrous THF. After 30 min, a solution of bromoacetic acid (2.07 g, 14.8 mmol) in 7 mL anhydrous THF was added dropwise over 0.5 h. After stirring for 12 hours at 60°C, the reaction mixture was quenched with 1N HCl and THF was removed under vacuum. The aqueous phase was extracted with $\mathrm{Et_2O}$ and the organic phase was washed with 1N HCl, brine and then dried over $\mathrm{MgSO_4}$. **A** was isolated after removal of the solvent (4.10 g, 90%) as a yellow oil and used without further purification for the following step. Rf (AcOEt/MeOH 4:1) = 0.2. ^{1}H NMR ($\mathrm{CDCl_3}$) : δ (ppm) = 4.13 (s, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CO}$); 3.66-3.52 (m, 20H, $\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O}$); 3.42 (t, J=6.7Hz, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{O}$); 1.50 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$); 1.19 (s, 18H, $\mathrm{C}\mathit{H}_2$); 0.85 (t, J=6.7Hz, 3H, $\mathrm{C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CDCl_3}$): δ (ppm) = 172.10 (C=O); 71.32 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2O}$); 70.36, 70.32, 70.29, 70.27, 70.20, 69.82, 69.79 ($\mathrm{O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O}$, $\mathrm{O}\mathit{C}\mathrm{H_2CO}$); 31.70, 29.45, 29.42, 29.39, 29.27, 29.12, 25.86, 22.46 ($\mathit{C}\mathrm{H_2}$); 14.02 ($\mathit{C}\mathrm{H_3}$). IR ν(cm^{-1}) : 3473 (OH), 2919, 2848 (C-H), 1752 (C=O), 1117 (C-O).

Synthesis of MCTS 1 : 1-hydroxybenzotriazole HOBt (1.25 g, 9.2 mmol) and Ac-Lys-OMe (0.60 g, 3.2 mmol) were added under $\mathrm{N_2}$ to a solution of acid **A** (1.22 g, 2.6 mmol) in 100 mL dry DMF. After stirring for 15 min, EDC (1.26 g, 6.6 mmol) was added and the reaction mixture was allowed to stir for 12 hours at room temperature. After evaporation of DMF, the residue was solubilized in $\mathrm{CH_2Cl_2}$ and the organic phase was washed with 1N HCl, brine and dried over $\mathrm{MgSO_4}$. The crude product isolated after removal of the solvent (1.56 g) was purified by column chromatography on silica gel with AcOEt/MeOH (6:1) as eluent to provide **1** (1.20 g, 70%) as a yellow oil. Rf (AcOEt/MeOH 1:1) = 0.7. $[\alpha]_D$ +7°, $[\alpha]_{546}$ +8°, $[\alpha]_{436}$ +12°, $[\alpha]_{365}$ +20° (c = 1.0, $\mathrm{CHCl_3}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ (ppm) = 7.14 (t, J=6.6Hz, 1H, $\mathrm{N}\mathit{H}_\varepsilon$); 6.38 (d, J=7.9Hz, 1H, $\mathrm{N}\mathit{H}_\alpha$); 4.54 (dt, J=7.9Hz, J=4.9Hz, 1H, $\mathrm{C}\mathit{H}$ Lys); 3.97 (s, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CO}$); 3.73 (s, 3H, $\mathrm{CO_2C}\mathit{H}_3$); 3.66-3.55 (m, 20H, $\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O}$); 3.44 (t, J=6.9Hz, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{O}$); 3.28 (m, 2H, $\mathrm{NC}\mathit{H}_2$); 2.02 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CO}$); 1.84-1.23 (m, 26H, $\mathrm{C}\mathit{H}_2$); 0.87 (t, J=6.5Hz, 3H, $\mathrm{CH_2C}\mathit{H}_3$).

^{13}C NMR ($\mathrm{CDCl_3}$): δ (ppm) = 172.95, 170.13, 170.00 (C=O); 71.55 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2O}$); 70.99, 70.61, 70.56, 70.54, 70.52, 70.40, 70.18, 70.02 ($\mathrm{O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O}$, $\mathrm{O}\mathit{C}\mathrm{H_2CO}$); 52.28, 52.08 ($\mathit{C}$H Lys, $\mathrm{CO_2}\mathit{C}\mathrm{H_3}$); 38.00 ($\mathrm{N}\mathit{C}\mathrm{H_2}$); 31.89, 31.52, 29.64, 29.61, 29.59, 29.48, 29.32, 29.19, 26.08, 22.66, 22.30 ($\mathit{C}\mathrm{H_2}$); 22.91 ($\mathit{C}\mathrm{H_3CO}$); 14.06 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$). IR ν(cm^{-1}) : 3303 (NH), 2919, 2853 (C-H), 1737 (C=O ester), 1650 (C=O amide), 1112 (C-O-C). SM (ESI, $\mathrm{H_2O}$/MeCN), m/z: 649.5 (MH$^+$, 100%); 671 (MNa$^+$, 43%); 687.5 (MK$^+$, 66%). Anal. Calcd. for $\mathrm{C_{33}H_{64}O_{10}N_2}$,1.25 $\mathrm{H_2O}$: C, 59.04; H, 9.98; N, 4.17; Found: C, 58.94; H, 9.82; N, 4.72.

II- NMR Spectra

Figure S.1

^{1}H NMR spectra (500MHz) of **2** (67mM) in $CDCl_3$ in the absence (bottom, dark) and in the presence of $UO_2(NO_3)_2$ [U/**2**= 1.5] (top, red)

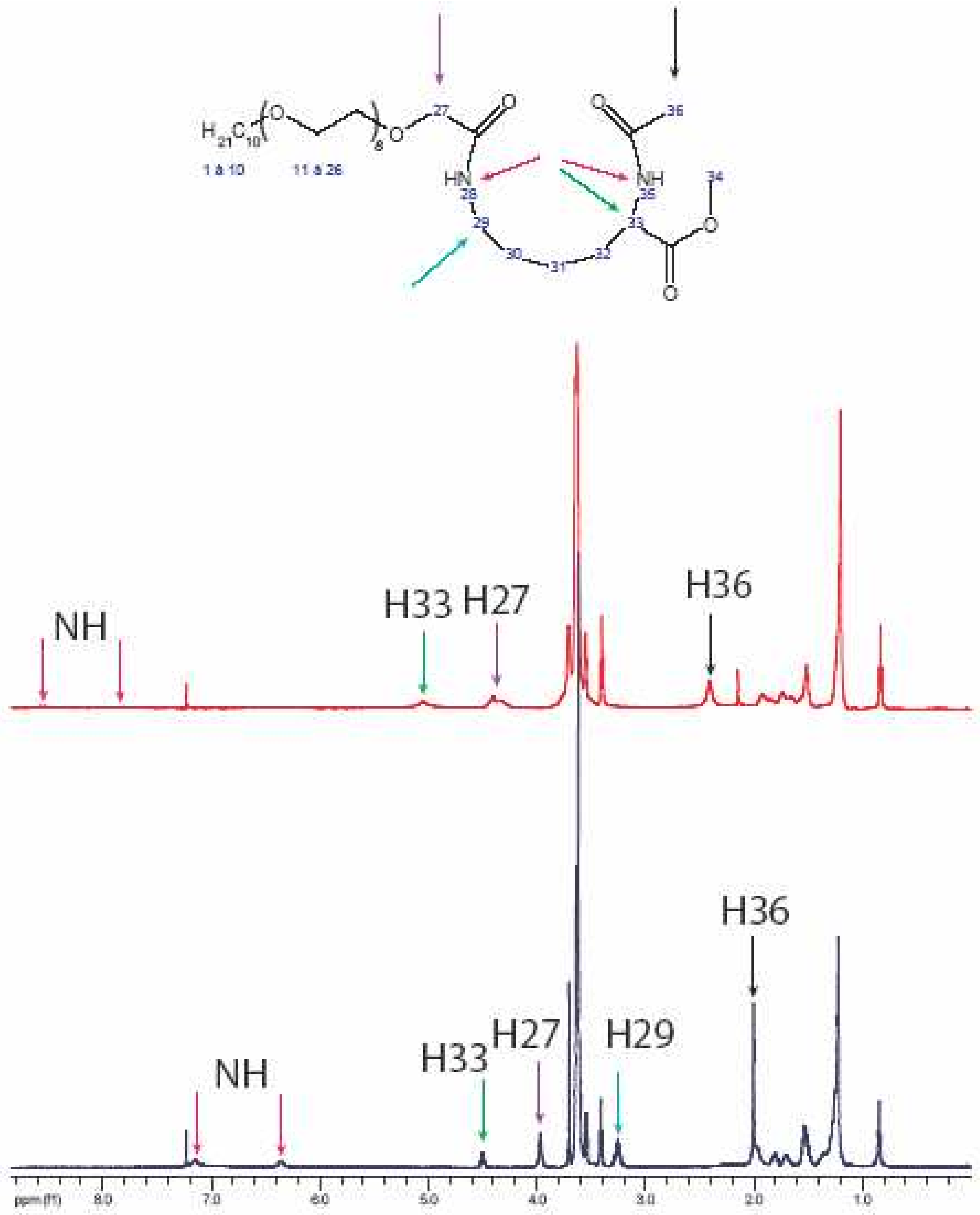
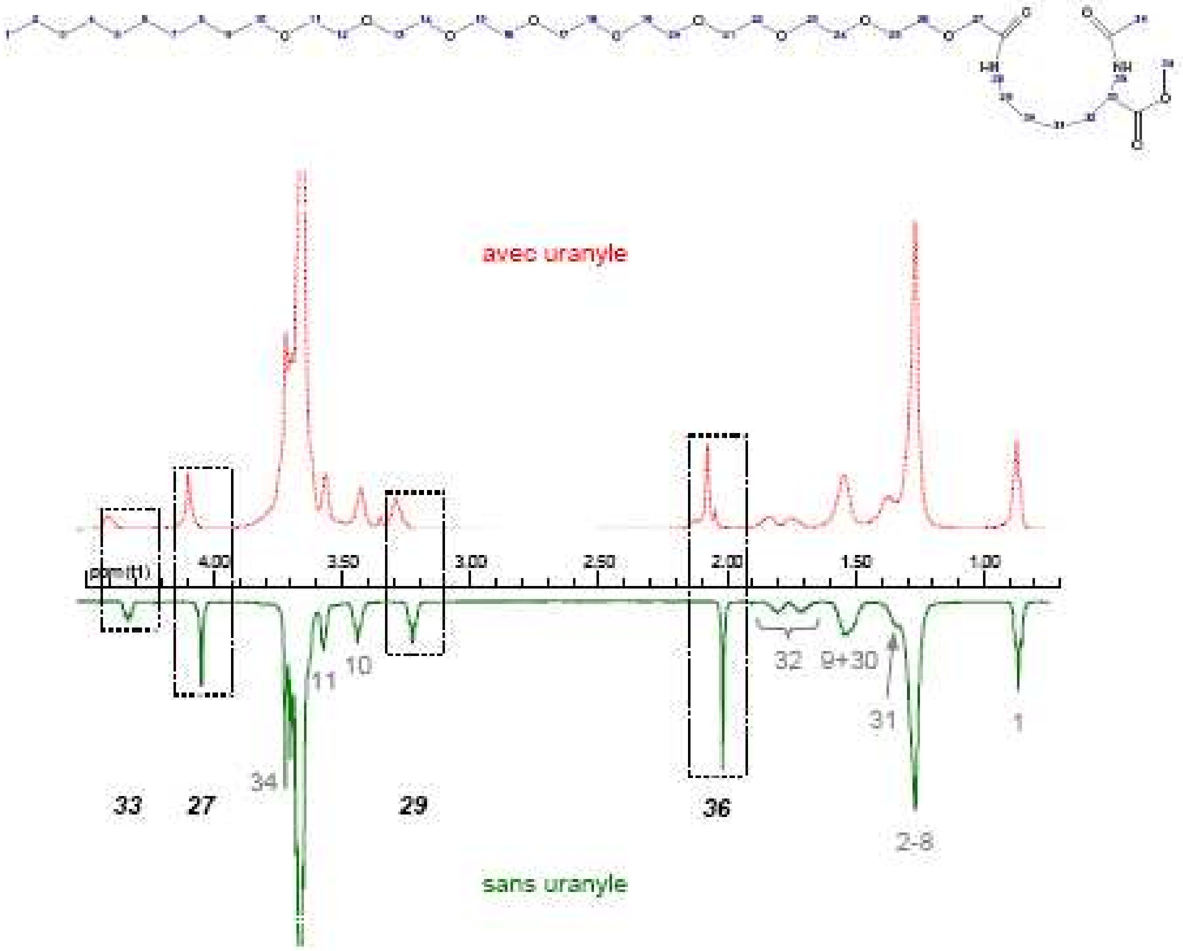


Figure S.2

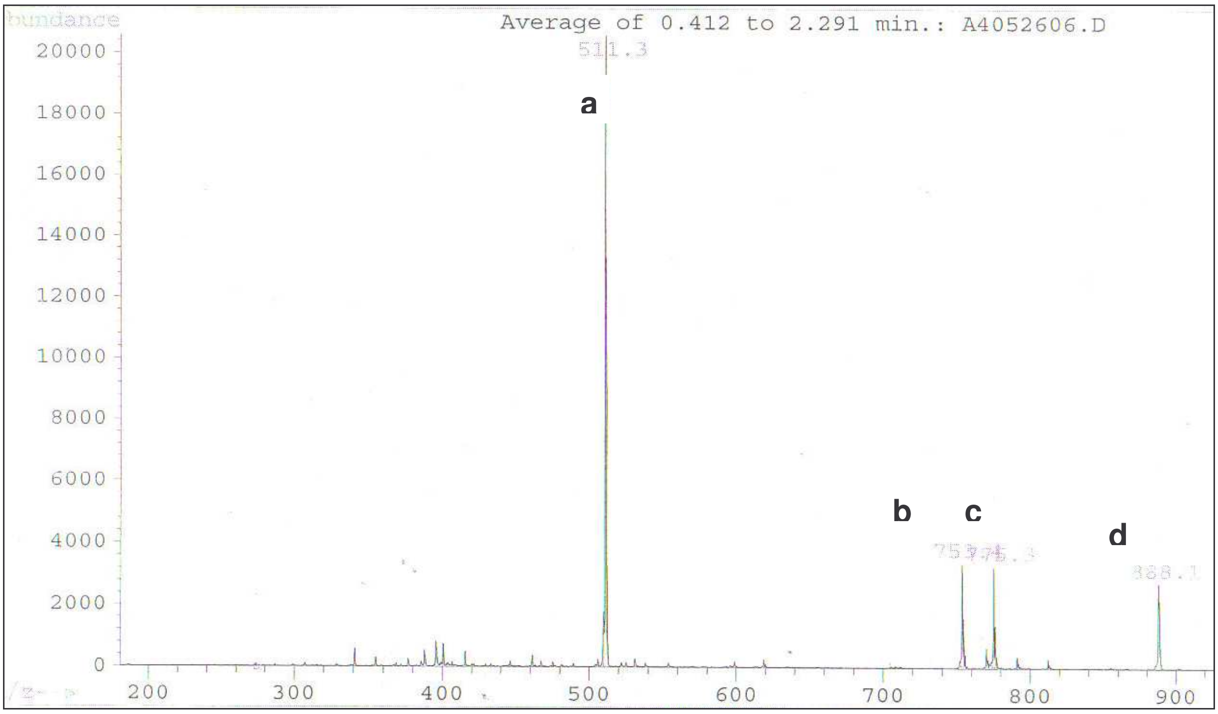
^{1}H NMR spectra (500MHz) of **2** (80mM) in D_2O + $LiNO_3$ (4M) in the absence (bottom, green) and in the presence of $UO_2(NO_3)_2$ (40mM) [U/**2**=0.5] (top, red)



III- ESI-MS spectra of mixtures of MCTSs and uranyle nitrate in water

Figure S.3

ESI-MS spectrum of **2** + $UO_2(NO_3)_2$ (U/**2** = 0.5) in water



2 (50mM) , $UO_2(NO_3)_2$ (25mM), HNO_3 (15mM) in water.

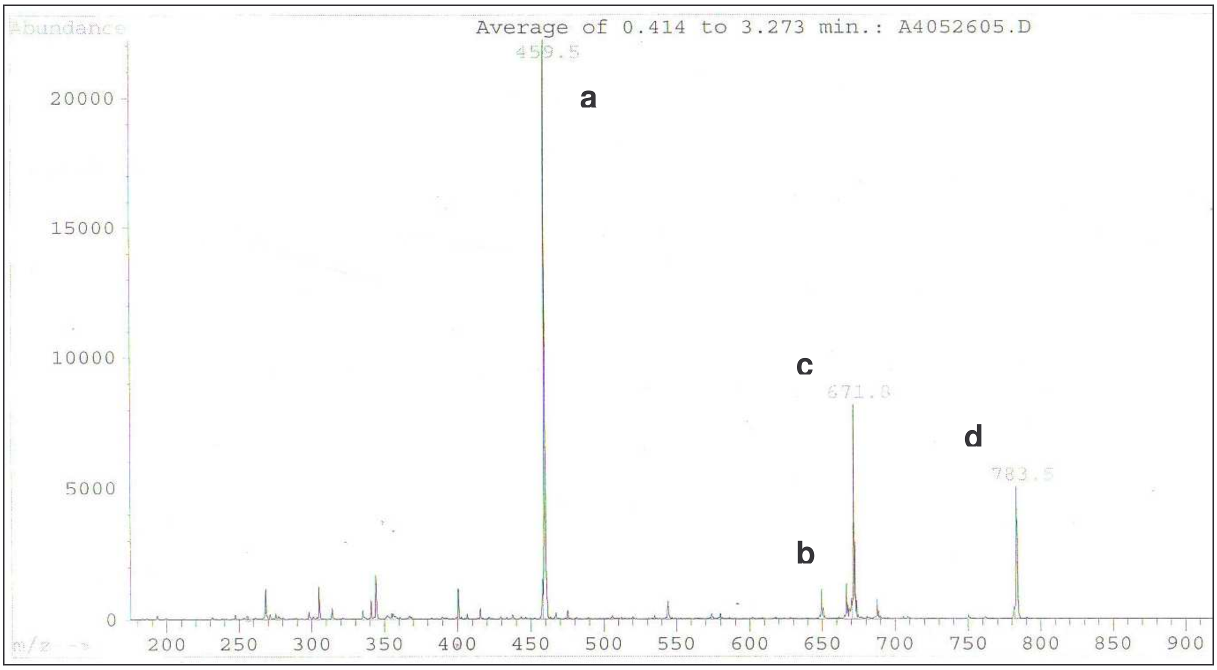
The solution was allowed to stand at RT for 4h and diluted in methanol just before injection

Peak	m/z	Assignement*	%
a	511.3	LUO_2^{2+}	100
b	753.5	LH^+	13
c	775.5	LNa^+	14
d	888	$L_2UO_2^{2+}$	10

* : L= **2**

Figure S.4

ESI-MS spectrum of **1** + $UO_2(NO_3)_2$ (U/**1** = 0.5) in water



1 (50mM) , $UO_2(NO_3)_2$ (25mM), HNO_3 (15mM) in water.

The solution was allowed to stand at RT for 4h and diluted in methanol just before injection

Peak	m/z	Assignement*	%
a	459.5	LUO_2^{2+}	100
b	649.4	LH^+	<5%
c	671.8	LNa^+	33
d	783.6	$L_2UO_2^{2+}$	23

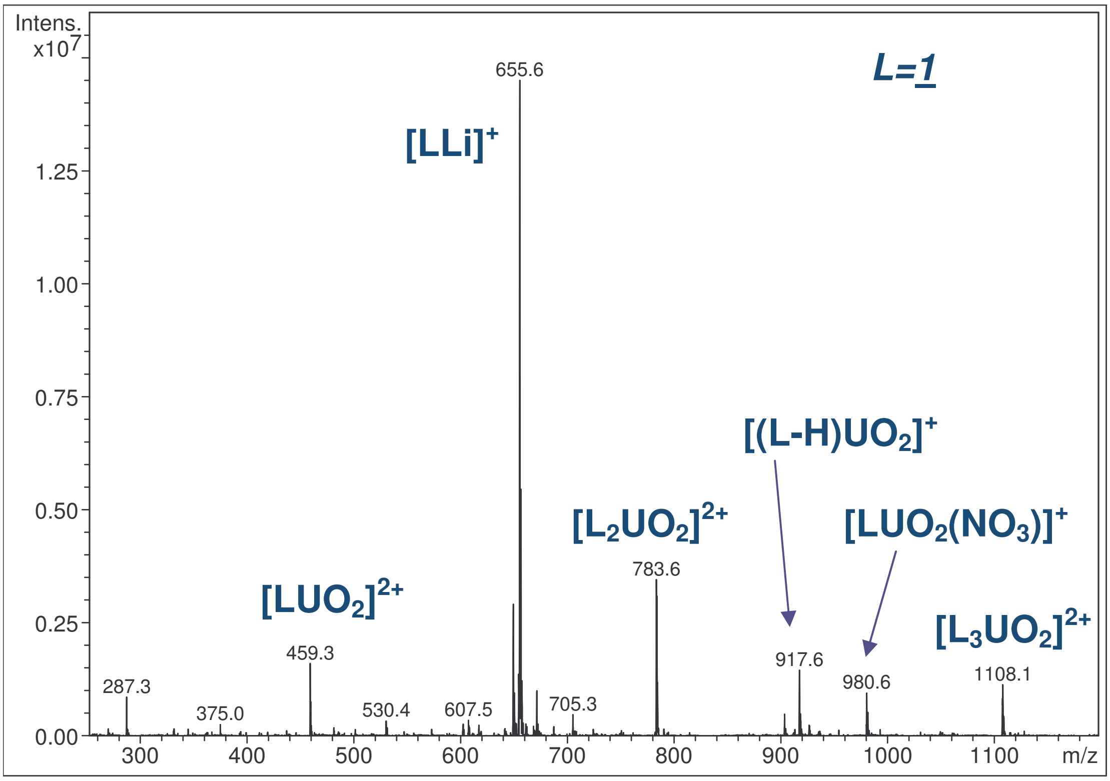
* : L= **1**

IV- ESI-MS spectrum of a coacervate resulting from CPE with 1

Figure S.5

ESI-MS spectrum of the coacervate resulting from CPE with **1** (entry 6, Table)

Mol. U-per-mol. surfactant in the coacervate (R_{Uc}) = 0.28



Experimental conditions: [1] = 0.04M, [$UO_2(NO_3)_2$] = 0.02M (R_{Ui} = 0.5), [$LiNO_3$]=4M, [HNO_3]=0.01M, separation performed at 33℃ (CP+10℃) .

The relative abundances of ions corresponding to 1/1, 1/2 and 1/3 complexes are about 100%, 90% and 27% respectively.

In the starting aqueous solution (R_{Ui} = 0.5) the relative abundances of ions corresponding to 1/1 and 1/2 complexes are 100% and 23%, respectively (figure S.4). 1/3 complexes were not detected.