Electronic Supplementary Information

Alkylguanidinium Based Ionic Liquids in a Screening Study for the Removal of Anionic Pollutants from Aqueous Solution

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Content

1. Characterization methods

NMR analyses were performed using a Bruker 200 and 300 MHz NMR spectrometer. Deuterated methanol was used as solvent. Chemical shifts are expressed in parts per million (ppm) relative to TMS. The multiplicity of the signals is indicated by the following abbreviations: s (singlet), d (doublet), t (triplet) and m (multiplet). Time of flight (TOF) mass spectrometry analysis was carried out on a mass spectrometer Synapt G2 -S (Waters) equipped with an ESI source. Mass spectra were recorded in the positive ion mode between 100 and 1500 Da. The capillary voltage was 1000 V and the cone voltage 30 V. The temperature of the ion source and desolvation were 120 °C and 250 °C, respectively. Fourier transform infrared (FTIR) spectra were recorded in the 4000-400 cm^{-1} range using 32 scans at a nominal resolution of 4 cm^{-1} by means of an AVATAR 320 FTIR spectrometer equipped with an ATR unit. Differential Scanning Calorimetry measurements were carried out on a NETSCH DSC 204-F1 apparatus. DSC thermograms were recorded on raising the temperature from -120 to 150 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analyses analysis (TGA) TGA was carried out using a NETSCH 409 PC under air atmosphere. Compounds were heated to from room temperature to 1000 °C at 10 °C/min. UV-Vis absorption spectra were recorded on a UV-SPECORD 210 spectrophotometer (Analytik Jena). Karl Fischer measurements were carried out on Titroline KF trace instrument using hydranal® coulomat E from Sigma Aldrich as Karl Fischer solution. Viscosity measurements were performed with a classical rheological test in plate geometry with 6 cm of diameter and at 200µm in height, the shear rate was fixed at 5 s^{-1} using a AR2000 rheometer (TA Instruments).

2. Synthesis and characterization of the guanidinium based ionic liquids

The guanidinium *bis*-trifluoromethane sulfonimides were obtained by reacting the primary amines with 1*H*-pyrazole-1-carboxamidine hydrochloride and subsequent anion exchange. As an example, the hexylguanidinium *bis*-trifluoromethane sulfonimide (C_6Gua NTf_2) was obtained as follows. Hexylamine (18.9 mmol, 1.91 g) and *1H*-pyrazole-1-carboxamidine hydrochloride (17.3 mmol, 2.54 g) were dissolved in methanol (30 mL). The resulting homogeneous solution was stirred during 15h at room temperature. After this time, the solvent was evaporated, and the formed pyrazole was eliminated by sublimation. The resulting guanidinium chloride was dissolved in water and mixed with an aqueous solution of lithium *bis*-trifluoromethane sulfonimide. The title compound demixed from the aqueous solution and was obtained by extraction with dichloromethane. After solvent evaporation, C_6Gua NTf_2 was obtained as a moderately viscous and colorless liquid. Yield: 6.66g/91%.

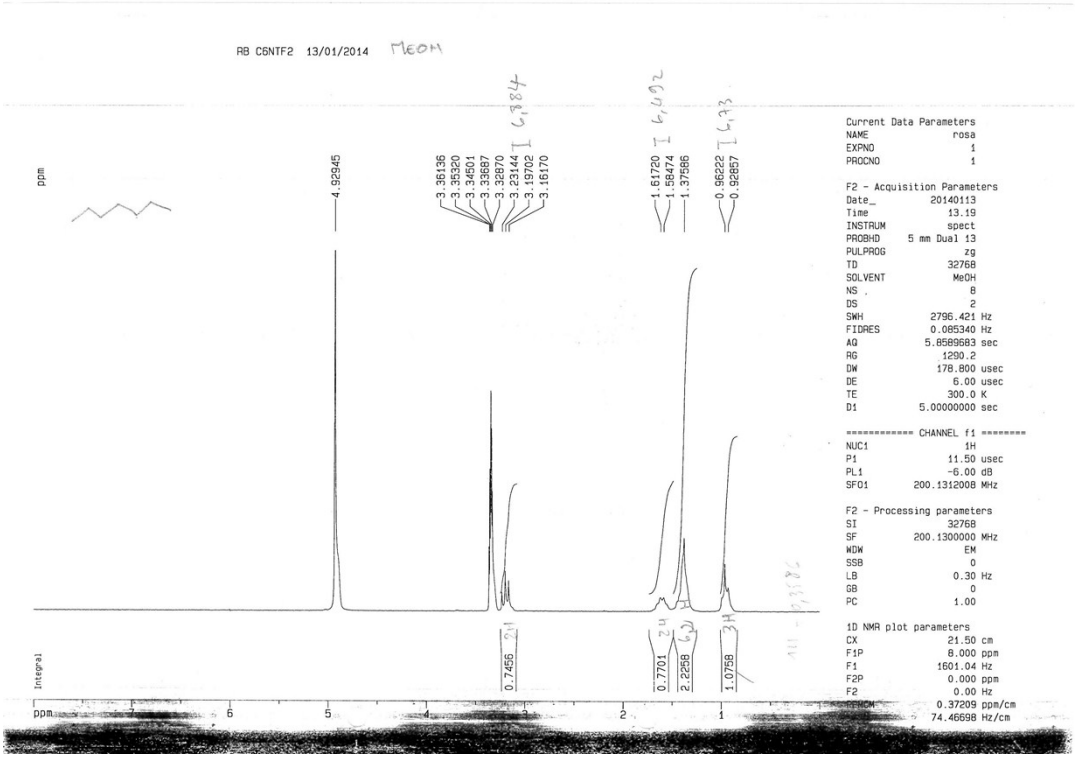
C_6Gua NTf_2: ^{1}H NMR (MeOH-d_4): δ = 0.96 (3H, m); 1.38 (6H, m); 1.62 (2H, m); 3.19 (2H, 't'). ^{13}C NMR (MeOH-d_4): δ = 13.35; 22.53; 26.27; 28.71; 31.46; 41.58; 120.13 (q, J = 320Hz); 157.47. FT-IR (neat) ν_{max}/cm$^-$ 3461, 3372, 3304, 3233, 2960, 2935, 2863, 1658, 1625, 1607, 1343, 1186, 1129, 1050. HRMS [ESI+] calcd. for $C_7H_{18}N_3$ $(M)^+$ 144.1501; found 144.1503.

C_8Gua NTf_2: ^{1}H NMR (MeOH-d_4): δ = 0.93 (3H, m); 1.37 (10H, m); 1.58 (2H, m); 3.19 (2H, 't'). ^{13}C NMR (MeOH-d_4): δ = 13.50; 22.68; 26.61; 28.76; 29.23; 29.26; 31.90; 41.59; 120.12 (q, J = 320Hz); 157.44. FT-IR (neat): ν_{max}/cm^{-1} 3461, 3373, 3308, 3240, 2929, 2859, 1658, 1626, 1343, 1187, 1130, 1051. HRMS [ESI+] calcd. for $C_9H_{22}N_3$ $(M)^+$ 172.1814; found 172.1815.

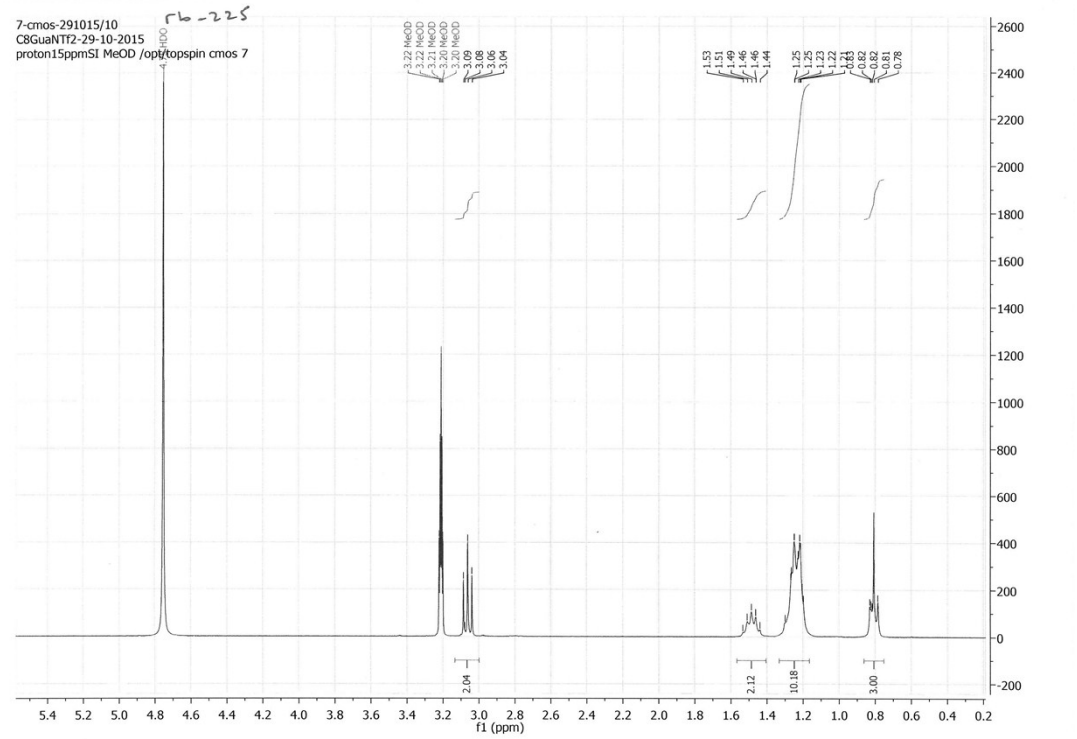
C_{10}Gua NTf_2: ^{1}H NMR (MeOH-d_4): δ = 0.91 (3H, m); 1.32 (14H, m); 1.60 (2H, m); 3.17 (2H, 't'). ^{13}C NMR (MeOH-d_4): δ = 13.03; 22.31; 26.26; 28.45; 28.90; 29.01, 29.23 (2H); 31.63; 41.10; 119.80 (q, J = 320Hz); 157.16. FT-IR (neat): ν_{max}/cm^{-1} 3461, 3372, 3306, 3233, 2927, 2857, 1658, 1625, 1344, 1189, 1130, 1052. HRMS [ESI+] calcd. for $C_{11}H_{26}N_3$ $(M)^+$ 200.2127; found 200.2128.

3. ^{1}H liquid NMR spectra of Guanidinium type ionic liquids (solvent:MeOD)

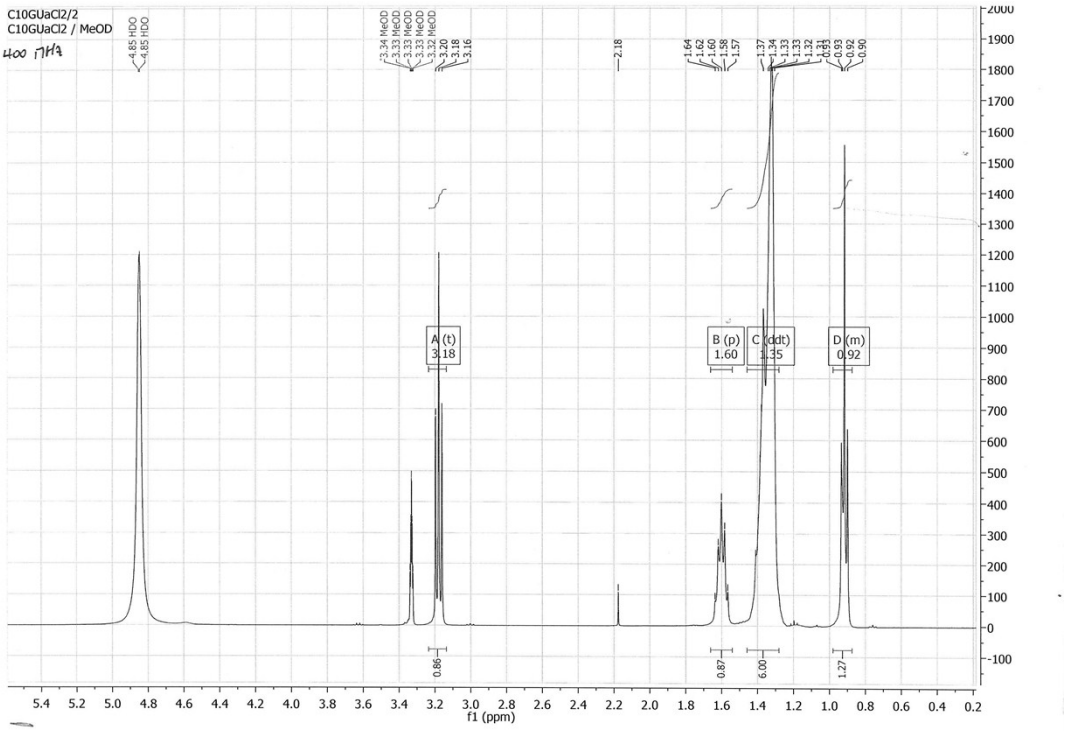
C_6Gua NTf_2



C_8Gua NTf_2

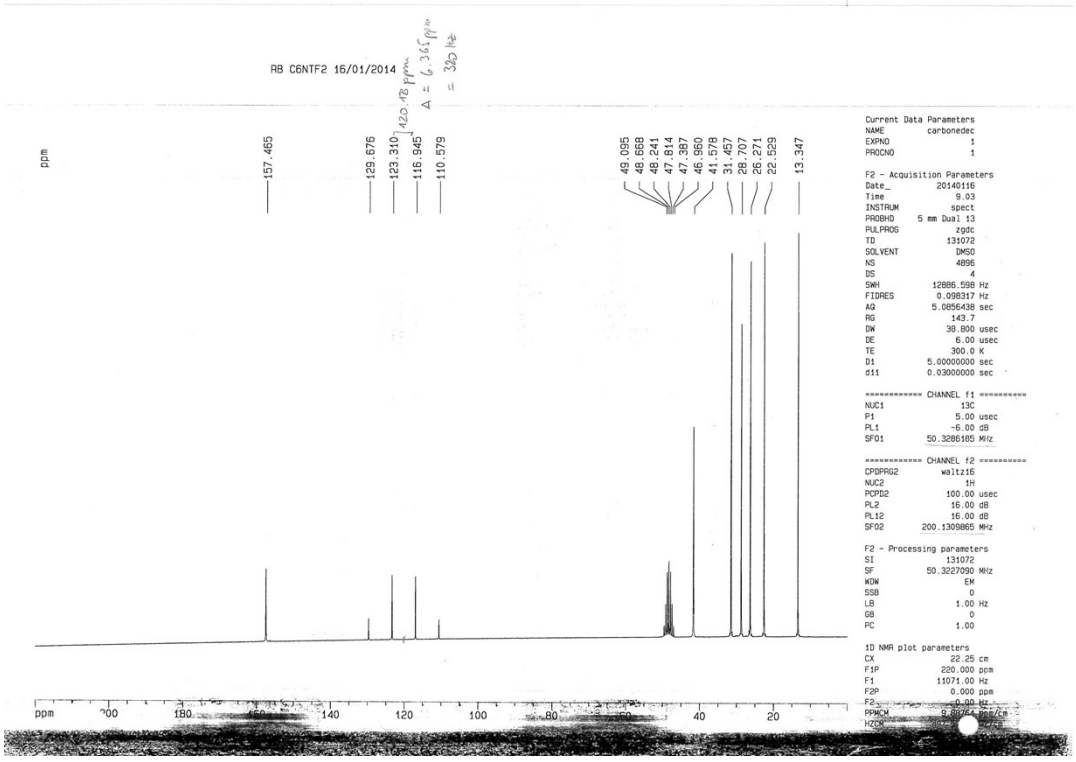


C_{10}Gua NTf_2

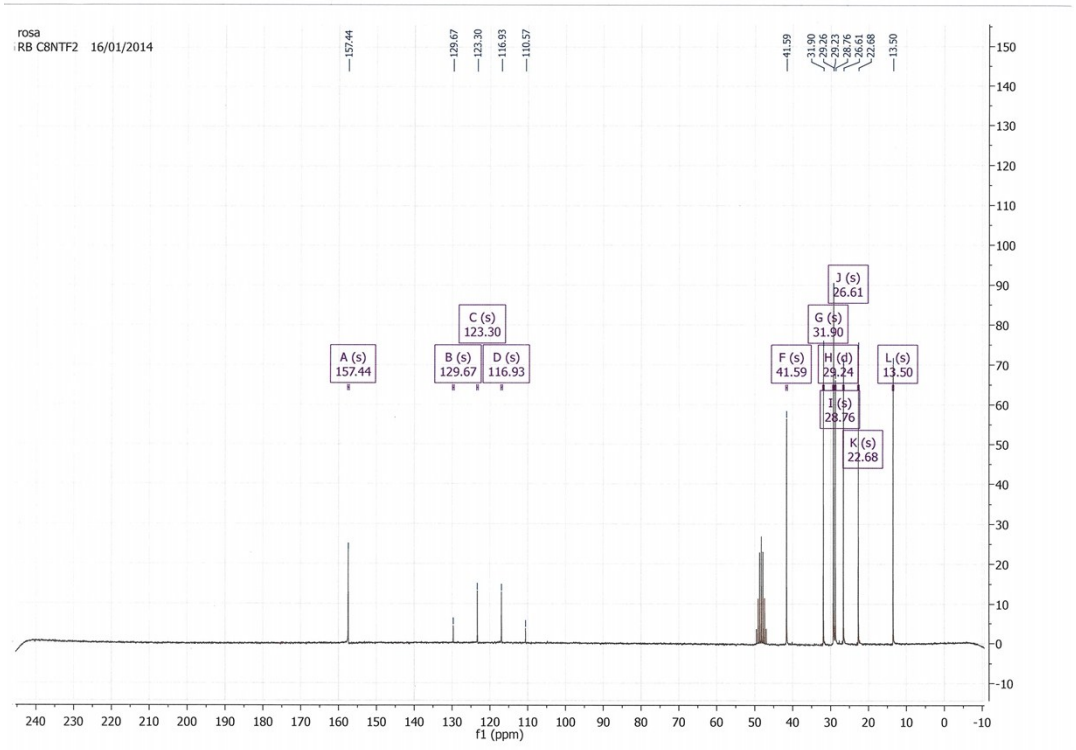

C10GUaCl2/2
C10GUaCl2 / MeOD
400 MHz
4.85 HDO
4.85 HDO
3.34 MeOD
3.33 MeOD
3.33 MeOD
3.32 MeOD
3.20
3.18
3.16
2.18
1.64
1.62
1.60
1.58
1.57
1.37
1.34
1.33
1.33
1.32
0.93
0.92
0.90
A (t)
3.18
B (p)
1.60
C (ddt)
1.35
D (m)
0.92
0.86
0.87
6.00
1.27
f1 (ppm)

4. ^{13}C liquid NMR spectra of Guanidinium type ionic liquids (solvent:MeOD)

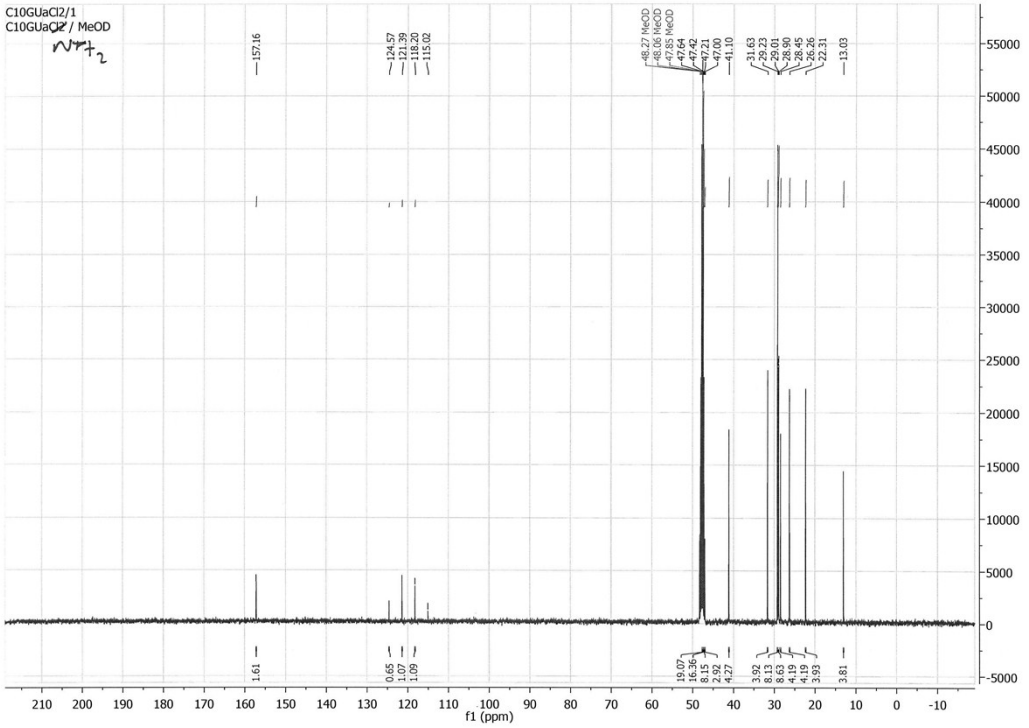
$C_6Gua\ NTf_2$



$C_8Gua\ NTf_2$

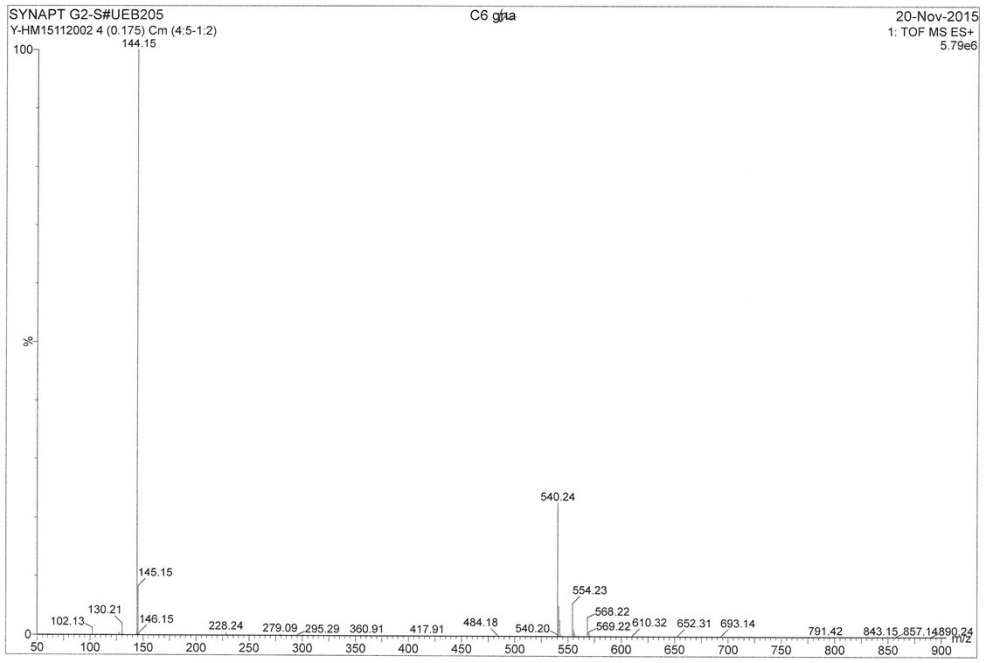


C_{10}Gua NTf_2

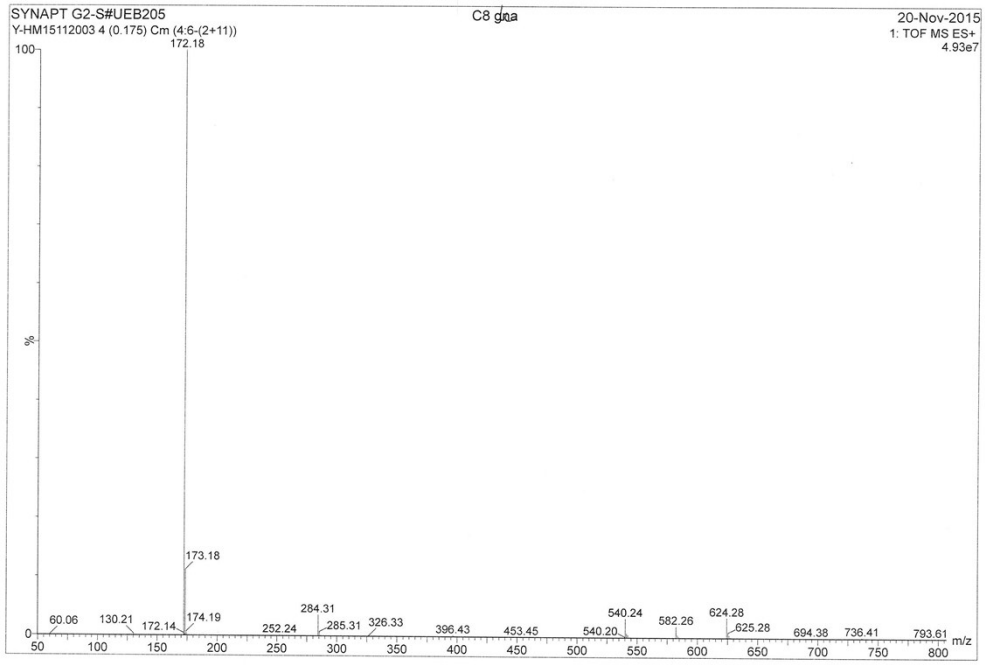

C10GUaCl2/1
C10GUaCl2 / MeOD
NTf2
157.16
124.57
121.39
118.20
115.02
48.27 MeOD
48.06 MeOD
47.85 MeOD
47.64
47.42
47.21
47.00
41.10
31.63
29.23
29.01
28.90
28.45
26.26
22.31
13.03
1.61
0.65
1.07
1.09
19.07
16.36
8.15
2.92
4.27
3.92
8.13
8.63
4.19
4.19
3.93
3.81
f1 (ppm)

5. HRMS [ESI+] of Guanidinium type ionic liquids

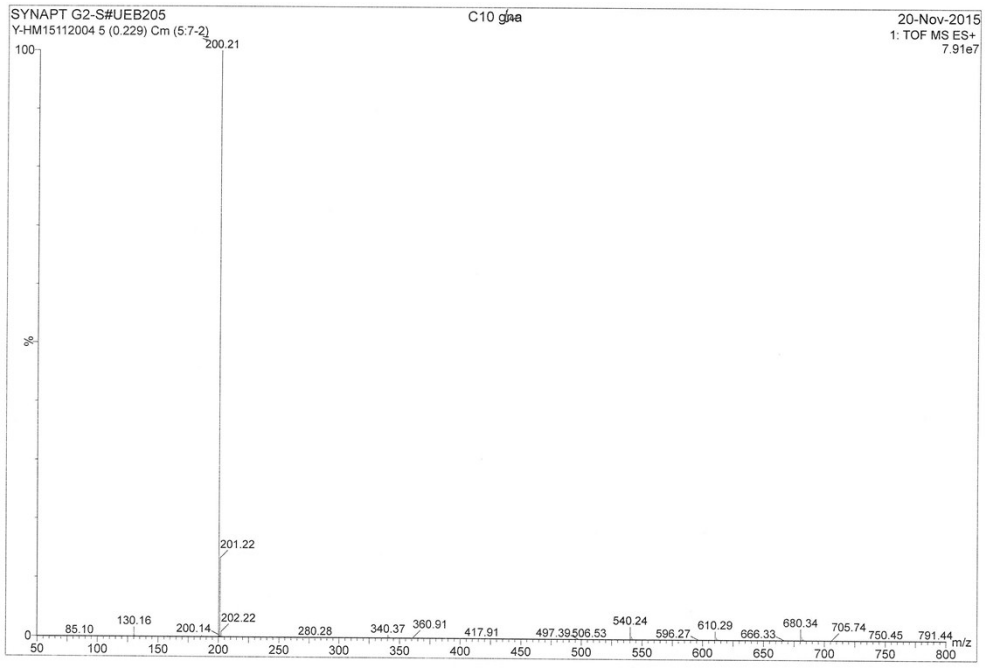
C_6Gua NTf_2



C_8Gua NTf_2



C_{10}Gua NTf_2

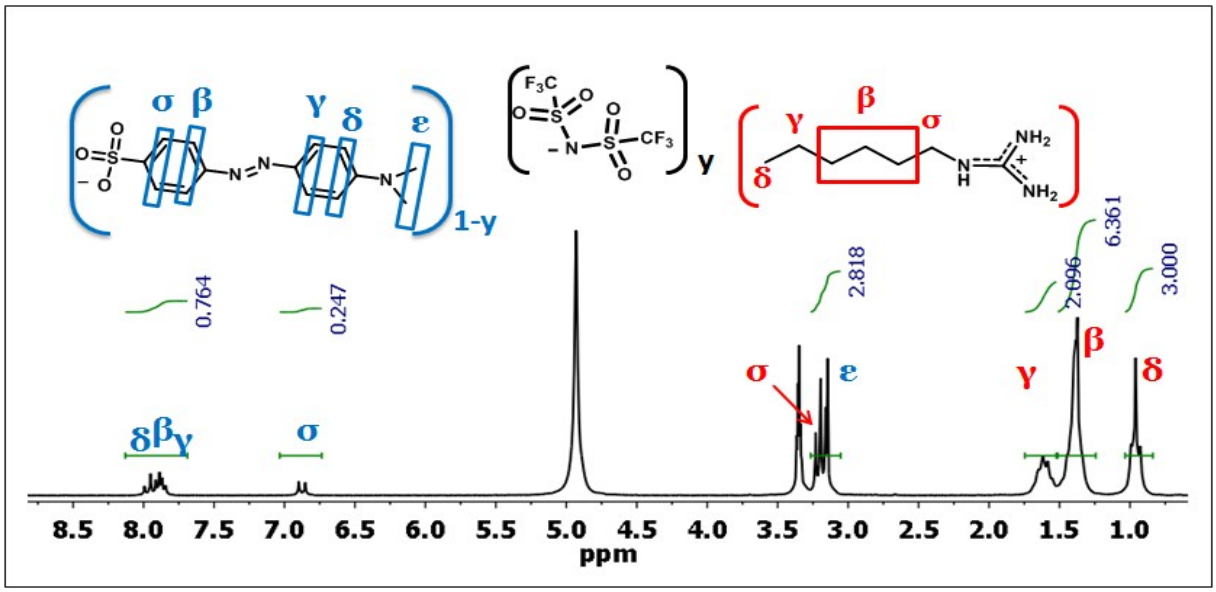

SYNAPT G2-S#UEB205
Y-HM15112004 5 (0.229) Cm (5:7-2)
C10 gua
20-Nov-2015
1: TOF MS ES+
7.91e7
100
%
0
200.21
201.22
202.22
85.10
130.16
200.14
280.28
340.37
360.91
417.91
497.39
506.53
540.24
596.27
610.29
666.33
680.34
705.74
750.45
791.44
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z

6. Viscosities of the Guanidinium based ionic liquids

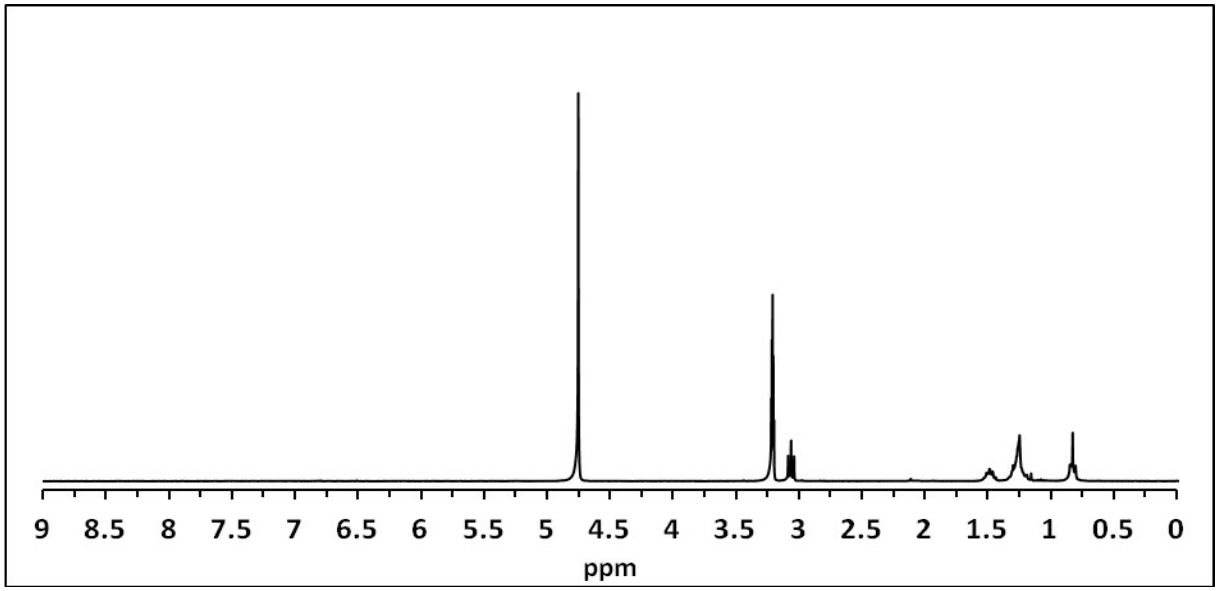
Sample	Viscosity (cP)
C_4Gua NTf_2*	264
C_6Gua NTf_2	421
C_8Gua NTf_2	*n.d.*
C_{10}Gua NTf_2	479
for comparison:	
C_4MIM NTf_2	69

*This compound is not further discussed in this manuscript

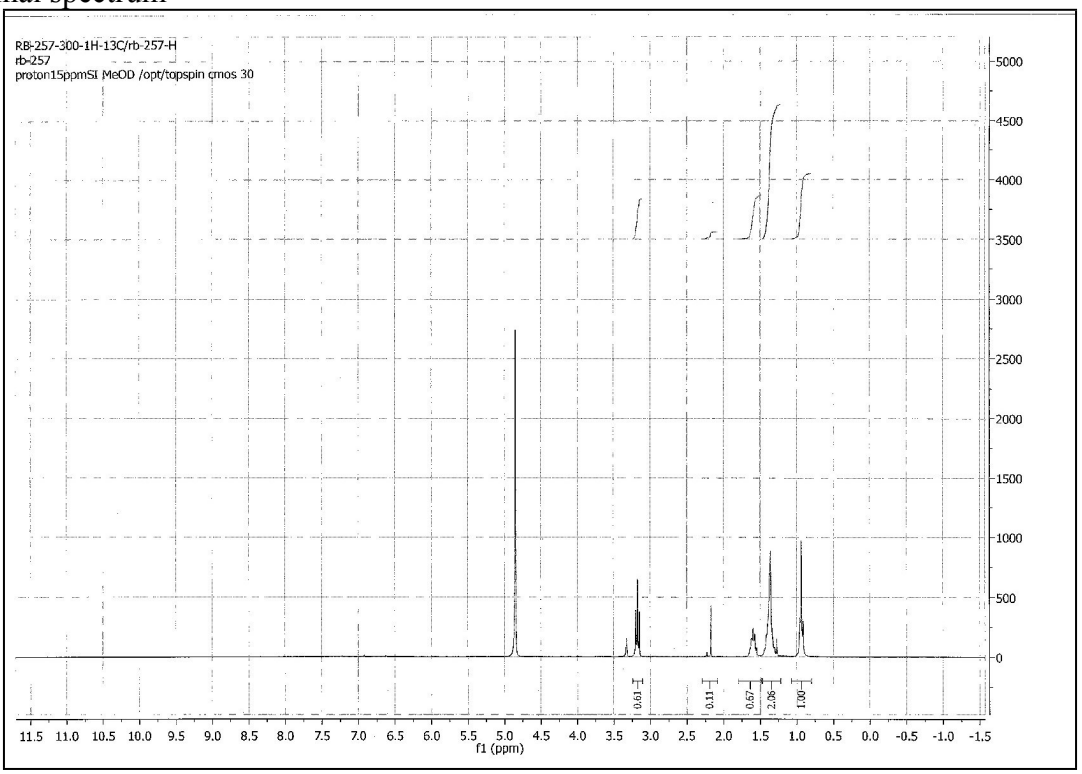
7. ^{1}H liquid NMR spectra of the $C_6Gua\ (NTf_2)_{0.9}(MO)_{0.1}$ phase (solvent:MeOD)

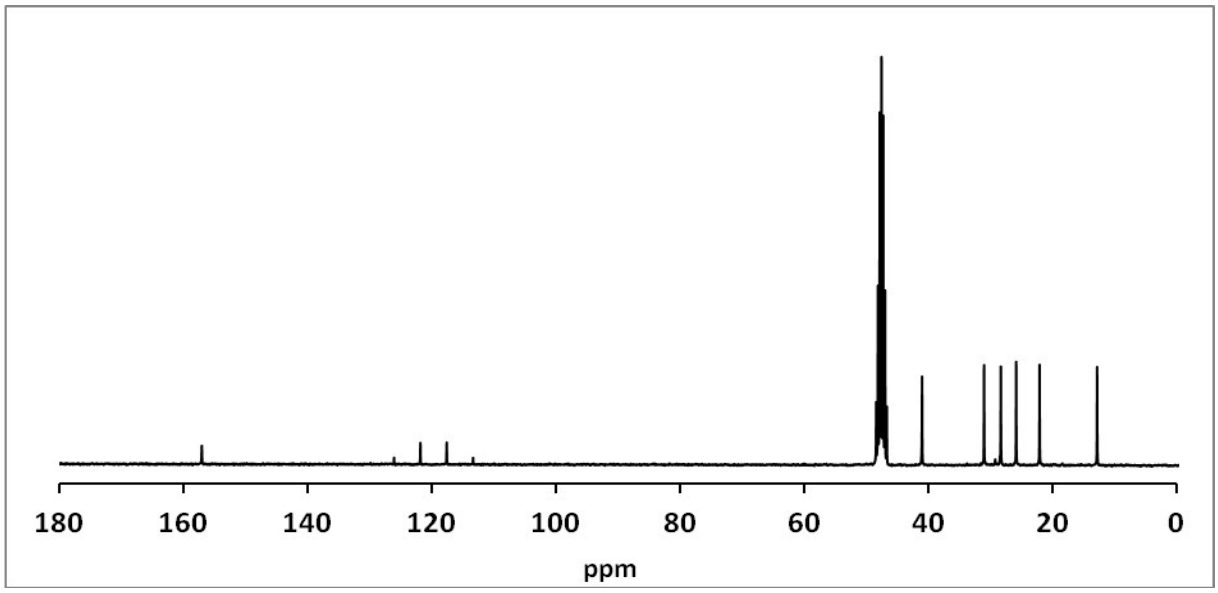


8. ^{1}H and ^{13}C liquid NMR spectra of the recovered $C_6Gua\ (NTf_2)$ phase

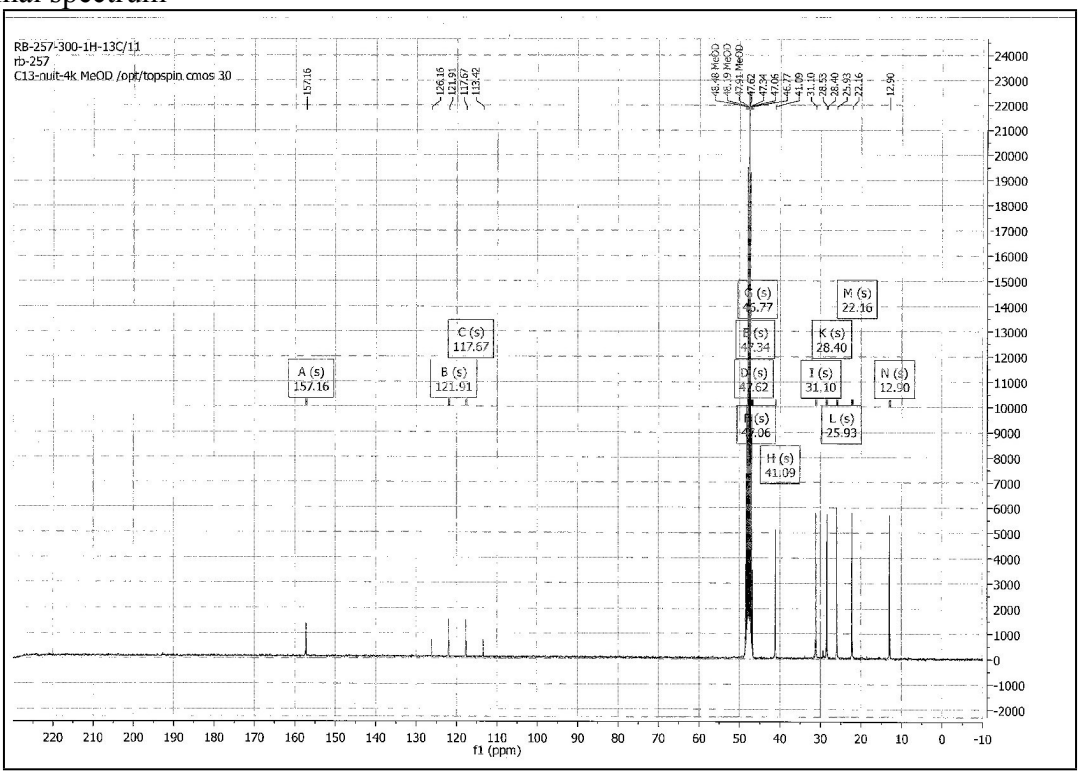


Original spectrum





Original spectrum



9. Water content of dried and water saturated ionic liquids

Sample	Water content (dried)	Water content (saturated)
C_6Gua NTf_2	300 ppm	22500 ppm
C_8Gua NTf_2	300 ppm	21400 ppm
C_{10}Gua NTf_2	500 ppm	22200 ppm

10. Table 1*bis*

Entry	Quantity of IL /mg (mmol)	Quantity of MO /mg (µmol)[a]	MO/IL ratio	Percentage of extracted anion / %	Quantity of extracted anion / µmol	Quantity of extracted anion / µg
			with C_6Gua NTf_2			
1	100.6 (0.237)	0.76 (2.33)	0.01	99.4%	2.32	0.76
2	100 (0.236)	1.60 (4.90)	0.02	99.6%	4.88	1.60
3	101.1 (0.238)	3.23 (9.88)	0.04	99.8%	9.86	3.23
6	100.7 (0.237)	7.80 (23.84)	0.10	99.9%	23.82	7.80
			with C_8Gua NTf_2			
5	100.5 (0.222)	0.73 (2.24)	0.01	99.5%	2.23	0.73
6	100.6 (0.222)	1.47 (4.5)	0.02	99.7%	4.49	1.47
7	100.1 (0.221)	2.93 (8.96)	0.04	99.8%	8.94	2.93
8	101 (0.221)	7.27 (22.2)	0.10	99.9%	22.18	7.26
			with C_{10}Gua NTf_2			
9	100.3 (0.209)	0.69 (2.1)	0.01	99.6%	2.09	0.68
10	100 (0.208)	1.36 (4.15)	0.02	99.7%	4.14	1.36
11	100.2 (0.209)	2.74 (8.38)	0.04	99.8%	8.37	2.74
12	100.1 (0.208)	6.81 (20.79)	0.10	100.0%	20.79	6.80
			with C_4mim NTf_2			
13	104.5 (0.249)	0.80 (2.43)	0.01	22.39%	0.03	0.01
14	110.6 (0.264)	1.55 (4.74)	0.02	23.79%	0.08	0.02
15	102.3 (0.244)	3.15 (9.61)	0.04	19.04%	0.17	0.06
16	105.5 (0.252)	7.75 (23.7)	0.09	25.56%	0.42	0.14

11. Table 2*bis*

Entry	Quantity of IL /mg (µmol)	Quantity of MO /mg (µmol)[a]	MO/IL ratio	Percentage of extracted anion / %	Quantity of extracted anion / µmol	Quantity of extracted anion / mg
			with C_6Gua NTf_2			
1	10 (23.56)	1.58 (4.83)	0.20	99.1%	4.79	1.57
2	9.9 (23.33)	3.24 (9.91)	0.42	99.3%	9.84	3.22
3	10.3 (24.27)	4.88 (14.91)	0.61	99.2%	14.79	4.84
4	10.1 (23.8)	6.49 (19.83)	0.83	98.8%	19.59	6.41
5	10.4 (24.51)	7.82 (23.89)	0.97	87.9%	20.99	6.87
			with C_8Gua NTf_2			
6	10 (22.1)	1.46 (4.47)	0.20	100.0%	4.47	1.46
7	10.5 (23.21)	2.92 (8.93)	0.38	100.0%	8.92	2.92
8	10 (22.1)	4.35 (13.3)	0.60	100.0%	13.27	4.35
9	10.2 (22.55)	5.81 (17.8)	0.79	99.9%	17.74	5.81
10	10.4 (22.99)	7.29 (22.3)	0.97	94.5%	21.03	6.88
			with C_{10}Gua NTf_2			
11	10.2 (21.23)	1.36 (4.16)	0.20	100.0%	4.16	1.36
12	10.4 (21.65)	2.73 (8.34)	0.39	100.0%	8.34	2.73
13	10 (20.81)	4.09 (12.5)	0.60	99.9%	12.49	4.09
14	10.2 (20.23)	5.45 (16.6)	0.78	100.0%	16.64	5.45
15	10 (20.81)	6.86 (21)	1.01	94.8%	19.86	6.50

12. Table 3*bis*

Entry	Quantity of IL /mg (mmol)	Quantity of anionic species /mg (µmol)[a]	Anion/IL ratio	Percentage of extracted anion / %	Quantity of extracted anion / µmol	Quantity of extracted anion / mg
			DCF			
1	99.8 (0.235)	0.9 (2.74)	0.01	96.4%	2.64	0.84
2	101.7 (0.24)	1.79 (5.45)	0.02	98.8%	5.39	1.71
3	99.9 v(0.235)	3.61 (11.01)	0.05	99.6%	10.97	3.49
4	102.3 (0.241)	5.4 (16.5)	0.07	99.4%	16.41	5.22
5	101.8 (0.24)	6.95 (21.85)	0.09	99.6%	21.69	6.90
6	101.3 (0.239)	8.62 (27.1)	0.11	99.5%	26.94	8.57
			Chromate			
7	107.9 (0.254)	0.466 (2.4)	0.01	68.8%	1.65	0.32
8	103.2 (0.243)	0.858 (4.42)	0.02	66.2%	2.93	0.57
9	102.1 (0.241)	1.7 (8.76)	0.04	62.4%	5.47	1.06
10	102.4 (0.241)	2.52 (12.98)	0.05	58.3%	7.57	1.47
11	101.3 (0.239)	3.36 (17.3)	0.07	53.5%	9.25	1.80
12	101.9(0.24)	4.28 (22.04)	0.09	59.5%	9.53	1.85

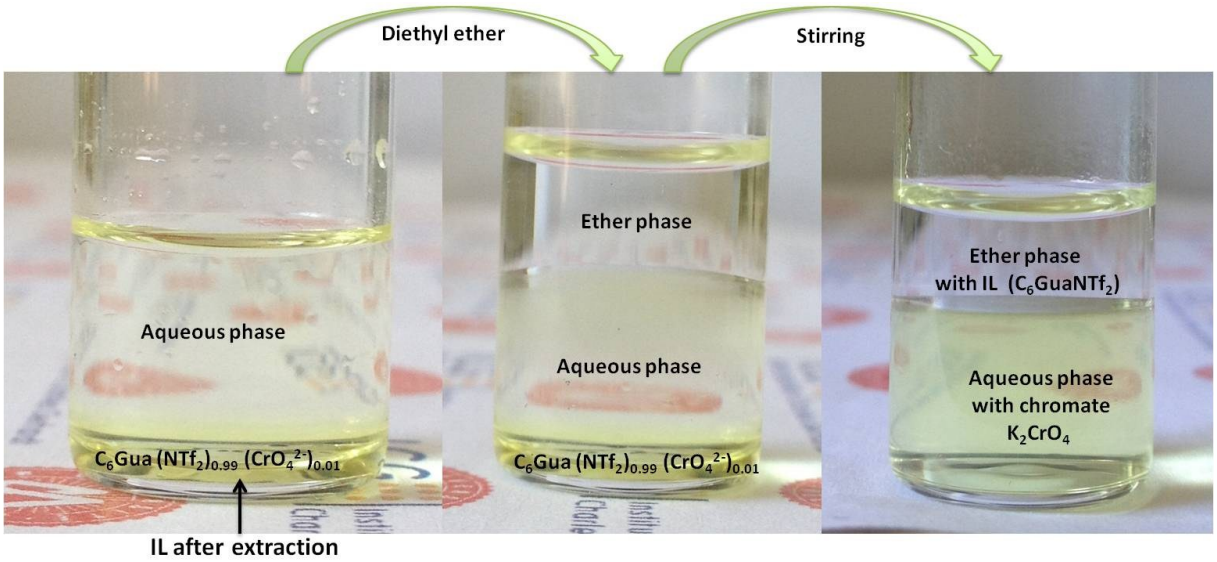
13. Extraction of diclofenac (DCF) and Chromate using C_6Gua NTf_2 in high anion/IL ratios

Entry	Quantity of IL /mg (mmol)	Quantity of anionic species /mg (µmol)[a]	Anion/IL ratio	C_{init} / mmol/L	C_{eq} / mmol/L	Distribution coefficient D	Percentage of extracted anion / %	Quantity of extracted anion / µmol	Quantity of extracted anion / mg
				DCF					
1	101 (23.8)	7.63 (23.99)	0.10	7.918	0.0504	156.17	99.4%	23.8	7.58
2	100.2 (23.61)	15.2 (47.778)	0.20	15.754	0.1124	139.11	99.3%	47.4	15.09
3	100.6 (23.71)	30.48 (95.82)	0.40	31.776	0.3485	90.17	98.9%	94.8	30.15
4	102.3 (24.11)	46.72 (146.9)	0.61	48.384	1.1406	41.42	97.6%	143.4	45.62
5	100.8 (23.75)	60.52 (190.2)	0.80	63.186	4.2482	13.87	93.3%	177.4	56.45
6	101.2 (23.85)	75.92 (238.7)	1.00	76.947	13.0286	4.91	83.1%	198.2	63.07
				Chromate					
7	102.6 (0.242)	4.77 (24.56)	0.10	12.26	4.97	1.468	59.5%	0.68	0.13
8	101.5 (0.239)	8.99 (46.28)	0.19	23.12	13.53	0.709	41.5%	1.70	0.33
9	100 (0.236)	17.95 (92.43)	0.39	45.83	29.16	0.572	36.4%	6.03	1.17
10	100.1 (0.236)	26.5 (136.47)	0.58	67.54	48.75	0.386	27.8%	10.05	1.95
11	100.8 (0.238)	36.34 (187.15)	0.79	92.74	68.39	0.356	26.3%	17.72	3.44
12	100.2 (0.236)	43.88 (225.98)	0.96	111.17	77.27	0.439	30.5%	30.18	5.86

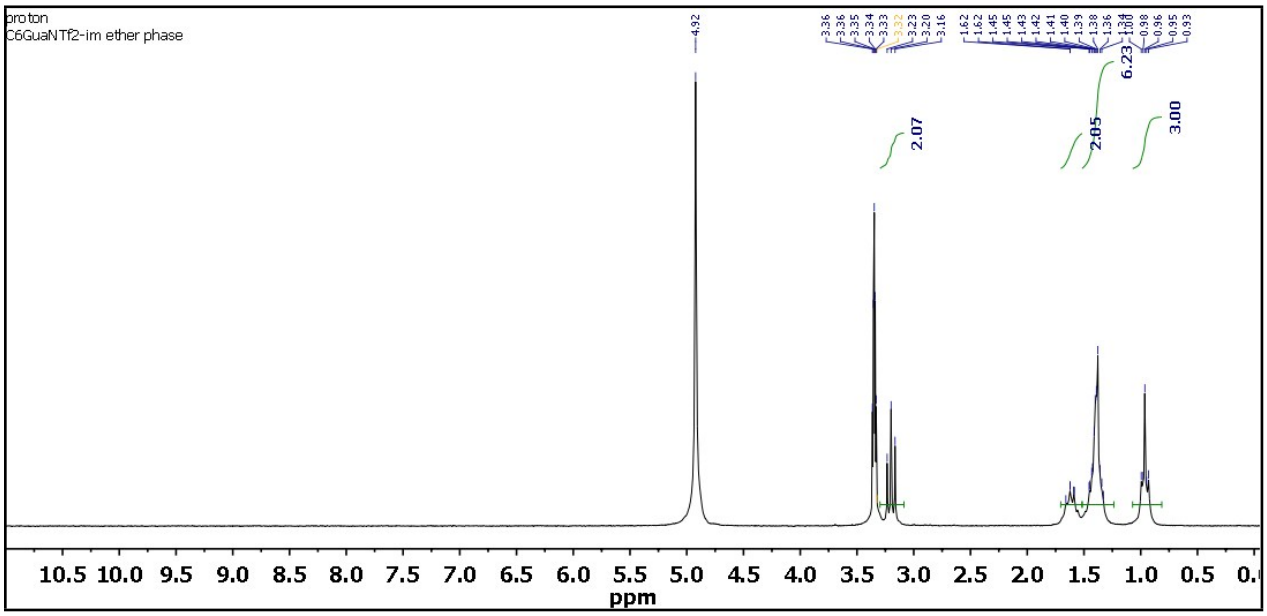
14. Extraction of diclofenac (DCF) and Chromate using the imidazolium IL C_4mim NTf_2 in low anion/IL ratios

Entry	Quantity of IL /mg (mmol)	Quantity of anionic species /mg (µmol)[a]	Anion/IL ratio	C_{init} / mmol/L	C_{eq} / mmol/L	Distribution coefficient D	Percentage of extracted anion / %	Quantity of extracted anion / µmol	Quantity of extracted anion / mg
					DCF				
1	100.5 (0.24)	0.87 (2.73)	0.01	0.907	0.913	0.000	0.0%	0	0
2	100.3 (0.239)	1.74 (5.46)	0.02	1.819	1.728	0.053	5.0%	0.27	0.09
3	100.1 (0.239)	3.49 (10.95)	0.05	3.649	3.532	0.033	3.2%	0.35	0.11
4	100.1 (0.239)	5.19 (16.32)	0.07	5.442	5.226	0.041	4.0%	0.65	0.21
5	100.2 (0.239)	6.95 (21.85)	0.09	7.242	7.116	0.018	1.7%	0.15	0.05
6	100.2 (0.239)	8.62 (27.1)	0.11	9.024	8.687	0.039	3.7%	1.17	0.37
					Chromate				
7	101.5 (0.242)	0.464 (2.39)	0.01	1.196	1.187	0.0075	0.7%	0.02	0.00
8	101.8 (0.243)	0.932 (4.8)	0.02	2.383	2.304	0.0344	3.3%	0.16	0.03
9	100.4 (0.239)	1.86 (9.56)	0.04	4.768	4.607	0.0351	3.4%	0.32	0.06
10	100 (0.238)	2.8 (14.41)	0.06	7.172	7.173	0	0%	0	0.00
11	101.6 (0.242)	3.71 (19.08)	0.08	9.513	9.523	0	0%	0	0.00
12	100.4 (0.239)	4.67 (24.02)	0.10	11.925	11.752	0.0147	1.4%	0.35	0.07

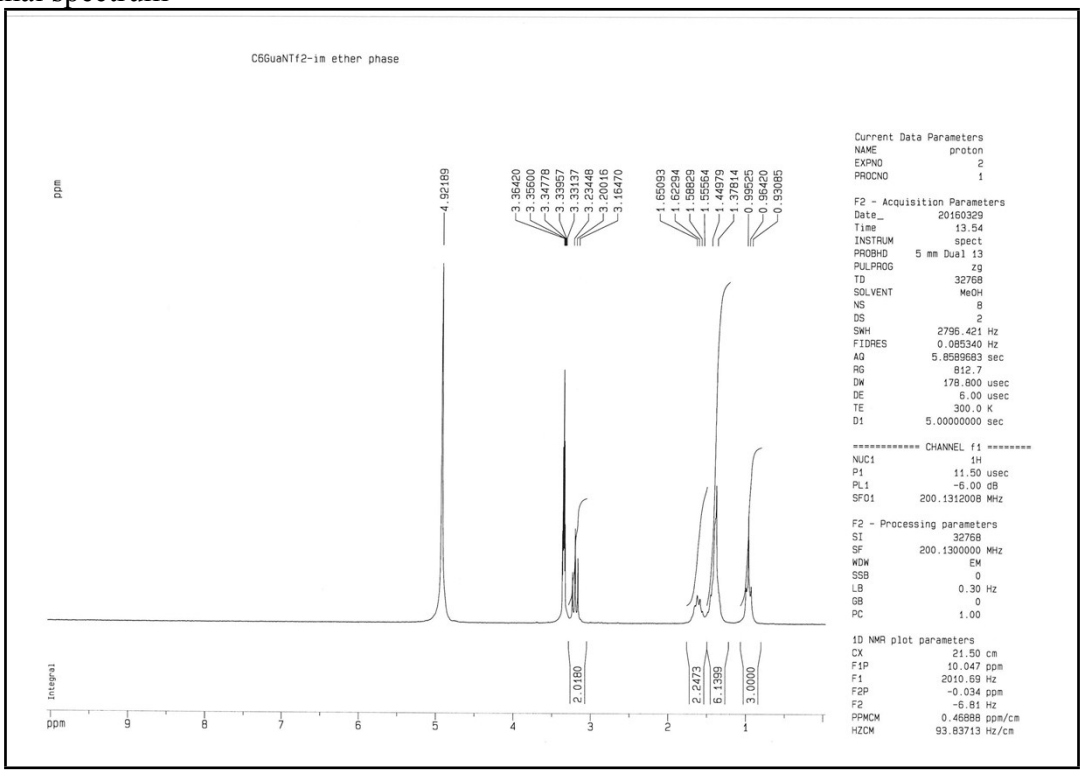
15. Regeneration of chromate with $C_6GuaNTf_2$ ionic liquid



16. ^{1}H liquid NMR spectra of the recovered C_6Gua NTf_2 from the ether phase

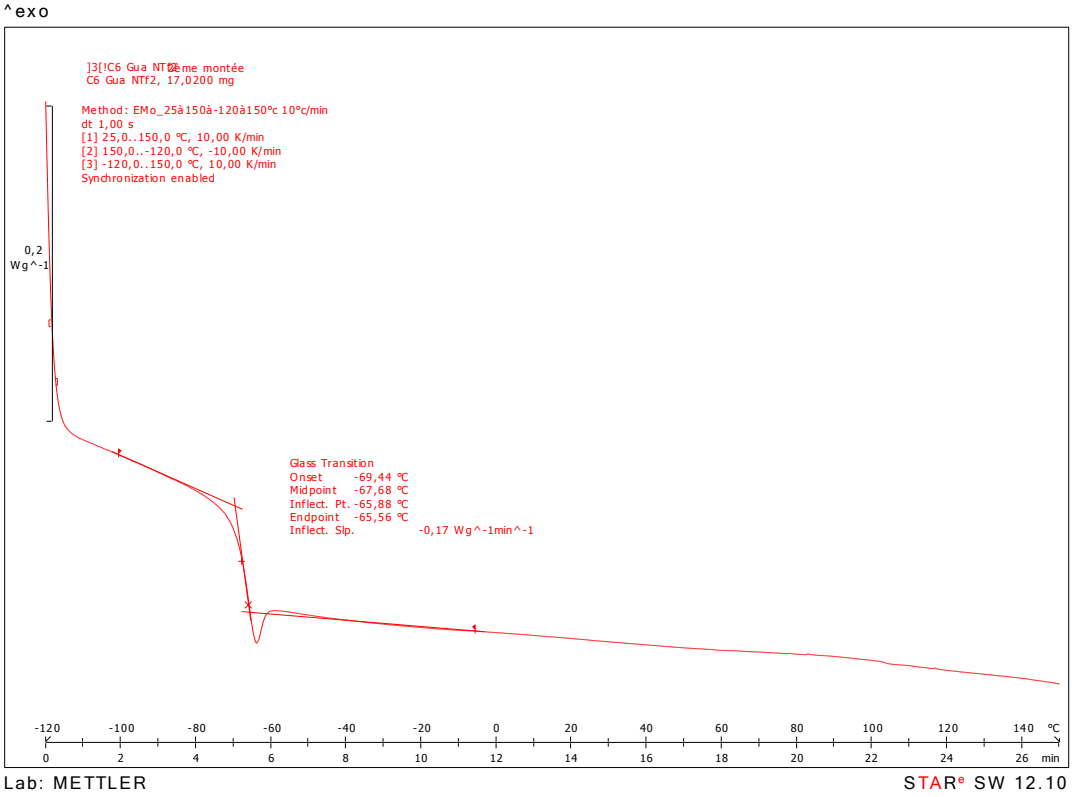


Original spectrum

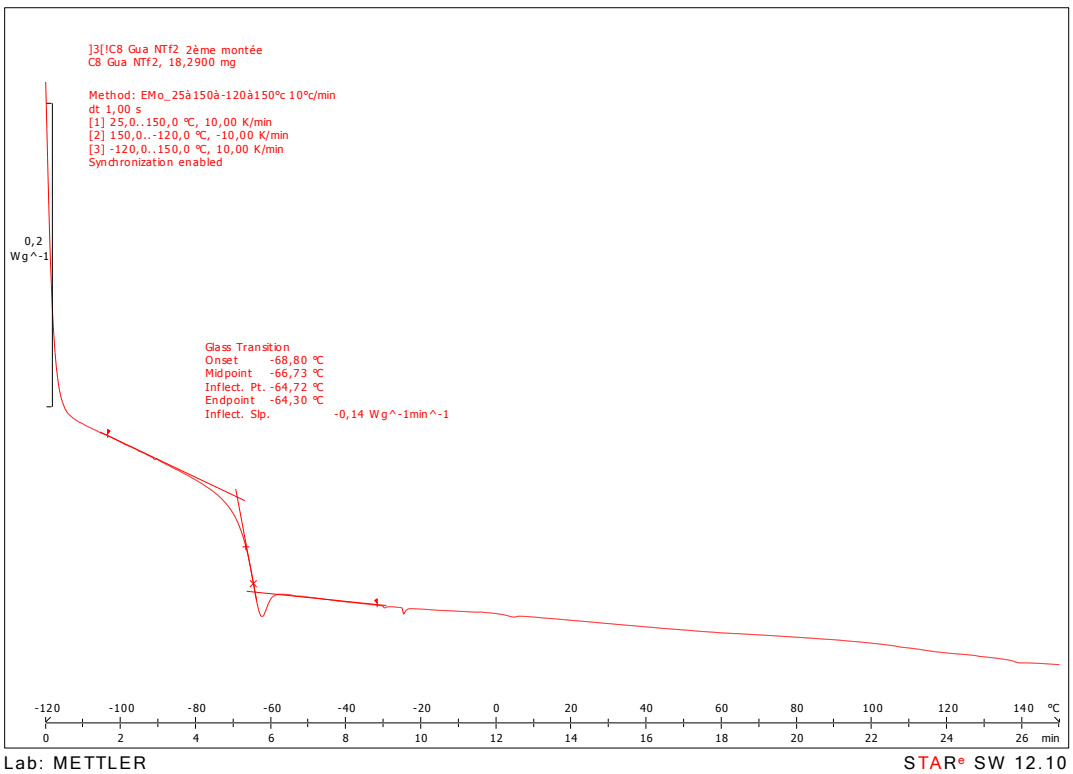


17. DSC thermograms of Guanidinium type ionic liquids

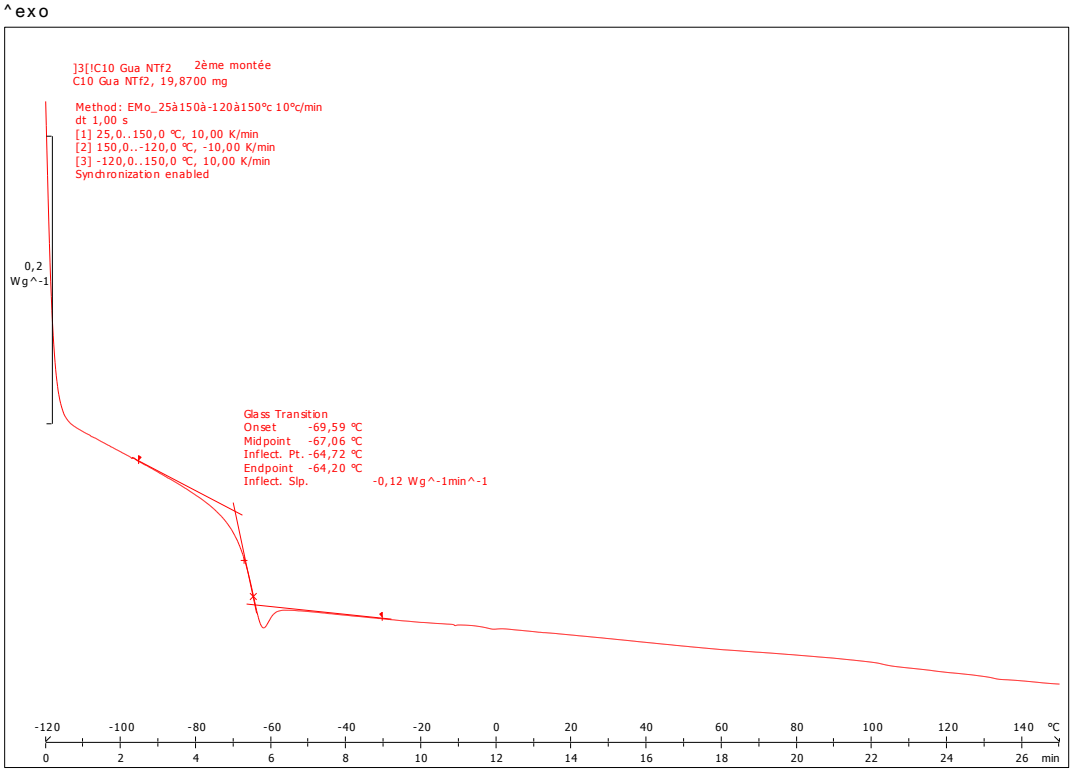
C_6Gua NTf_2



C_8Gua NTf_2



C_{10}Gua NTf_2



Lab: METTLER STARe SW 12.10