Supporting Information for

"Sweet" Ionic Liquid Gels: Materials for Sweetening of Fuels

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General neutralization reaction procedure:

The hydroxide salt aqueous solution (0.020 mol of salt) and the gluconic acid aqueous solution (0.024 mol of gluconic acid) were put in a round flask and stirred for 24 hours. After this time the neutralization reaction was stopped and the water was removed under vacuum. The white solid obtained was dry under nitrogen vacuum overnight.

Trihexyltetradecylphosphonium gluconate $[P_{6\,6\,6\,14}]$[Glu]:

The first step of this synthesis was the anion exchange to replace the Cl^- anion with $[OH]^-$ anion using the Amberlite™ IRN-78 ion-exchange resin, OH-form according to a previously reported procedure.[1]

Yield: 89%; white solid; m.p.: 35.6 °C; ^{1}H NMR (600 MHz; DMSO-d6); δ (ppm): 3.73 (dd, 1H); 3.57 (m, 2H); 3.50, (m, 1H); 3.41 (dd, 2H); 3.31 (m, 3H); 2.17 (m, 7H); (m, 13H); 1.30 (m, 50H); 0.88 (m, 12H). ^{13}C NMR (600 MHz, DMSO-d_6); δ (ppm): 176.4; 72.8; 72.4; 72.1; 71.6; 64.2; 31.8; 30.7; 30.3; 30.1; 29.5; 29.2; 29.1; 28.5; 22.6; 22.3; 21.0; 18.2; 17.7; 14.4; 14.3. TOFMS calcd for $C_{38}H_{79}O_7P$ 678.5563, found 678.5575.

Tetrabutylphosphonium gluconate $[P_{4\,4\,4\,4}]$[Glu]:

Yield: 98%; white solid; m.p.: 81.5 °C; ^{1}H NMR (600 MHz; DMSO-d6); δ (ppm): 4.63 (s, 1H); 4.50 (d, 1H); 4.41 (s, 1H); 4.17 (s, 1H); 3.71 (m, 1H); 3.55 (d, 1H); 3.48 (t, 1H, J=6 Hz); 3.40 (s, 1H); 3.3 (m, 1H); 2.18 (m, 6H); 1.45 (m, 16H); 0.92 (t, 12H, J=12 Hz). ^{13}C NMR (600 MHz, D_2O); δ (ppm): 178.5; 74.0; 72.5; 71.1; 70.9; 62.6; 23.3; 23.2; 22.7; 17.8; 17.4; 12.5. TOFMS calcd for $C_{22}H_{47}O_7P$ 454.3059, found 454.3099.

Tetrabutylammonium gluconate $[N_{4\,4\,4\,4}]$[Glu]:

Yield: 95%; white solid; m.p.: 134.9 °C; ^{1}H NMR (400 MHz; D_2O); δ (ppm): 4.11 (d, 1H); 4.01 (t, 1H, J=4 Hz); 3.82 (m, 1H); 3.80 (d, 1H); 3.75 (m, 2H); 3.65 (m, 1H); 3.19 (m, 8H); 1.64 (m, 8H); 1.36 (st, 8H); 0.94 (t, 12H, J=8 Hz). ^{13}C NMR (400 MHz, $CDCl_3$); δ (ppm): 175.5; 72.8; 72.4; 72.0; 71.5; 70.8; 64.2; 57.9; 30.2; 23.5; 19.7; 14.0. TOFMS calcd for $C_{22}H_{47}NO_7$ 437.3353, found 454.3056.

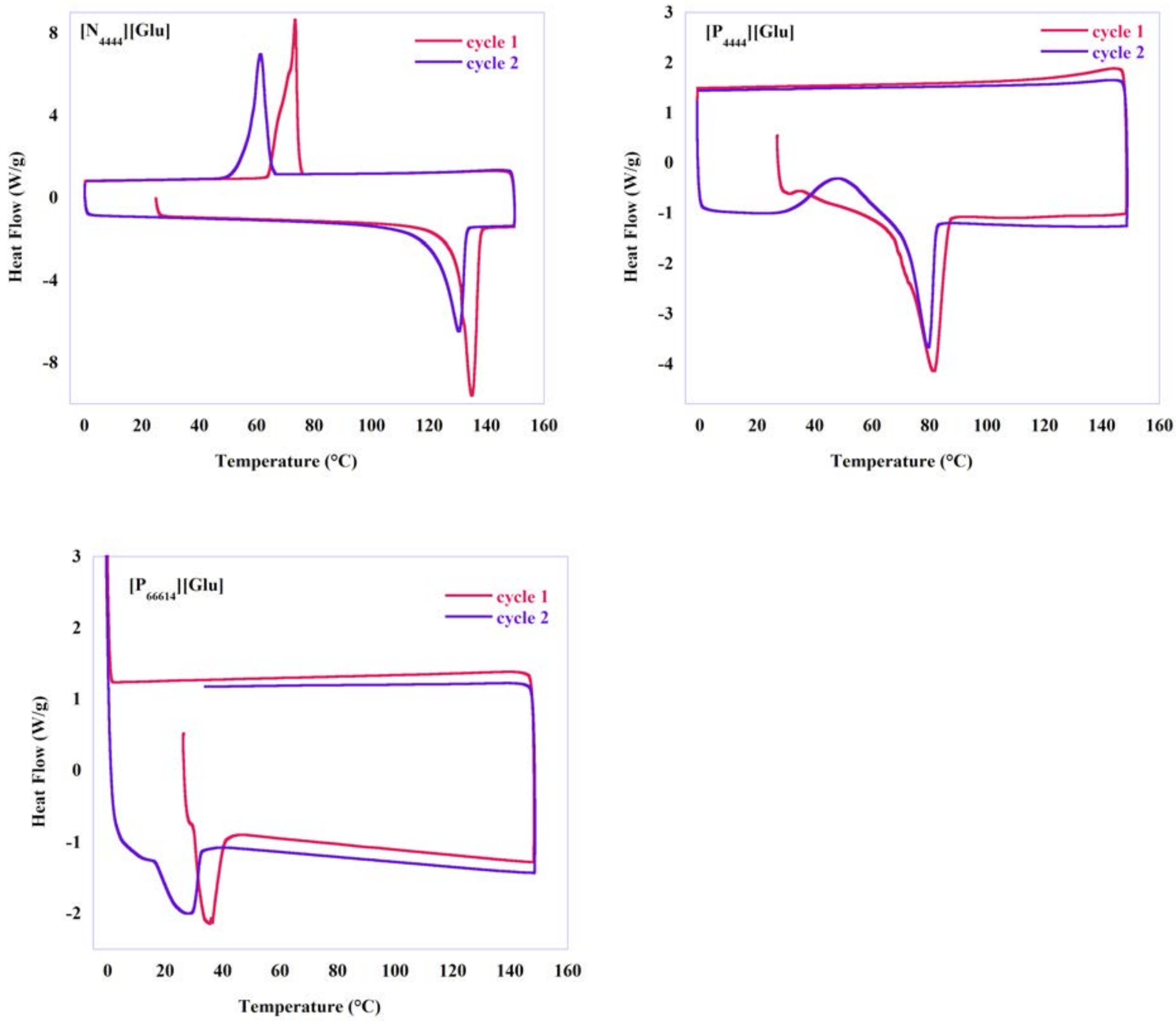


Figure S1. DSC thermograms for salts used (endothermic transition points downwards).

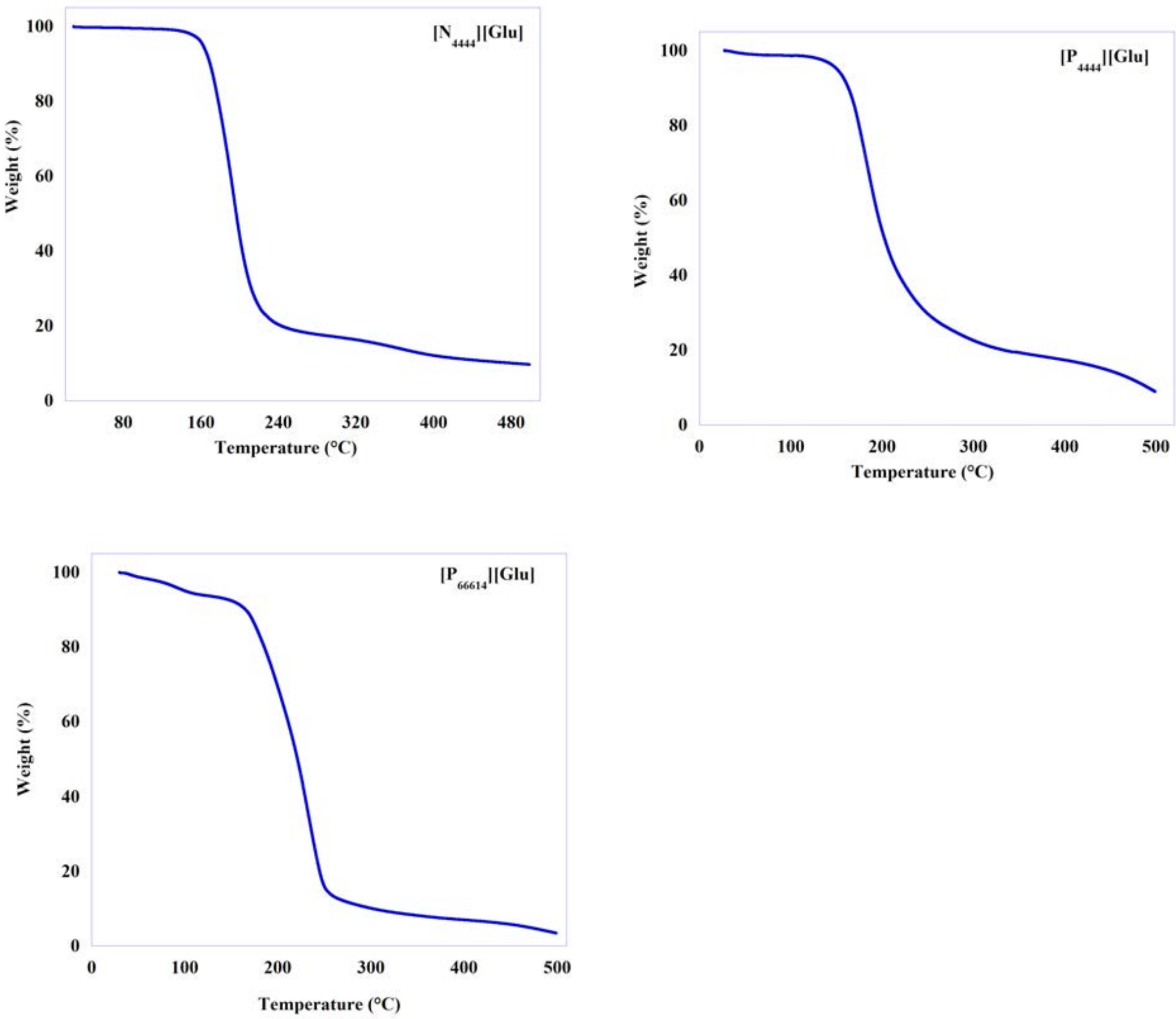


Figure S2. TGA traces for salts used.

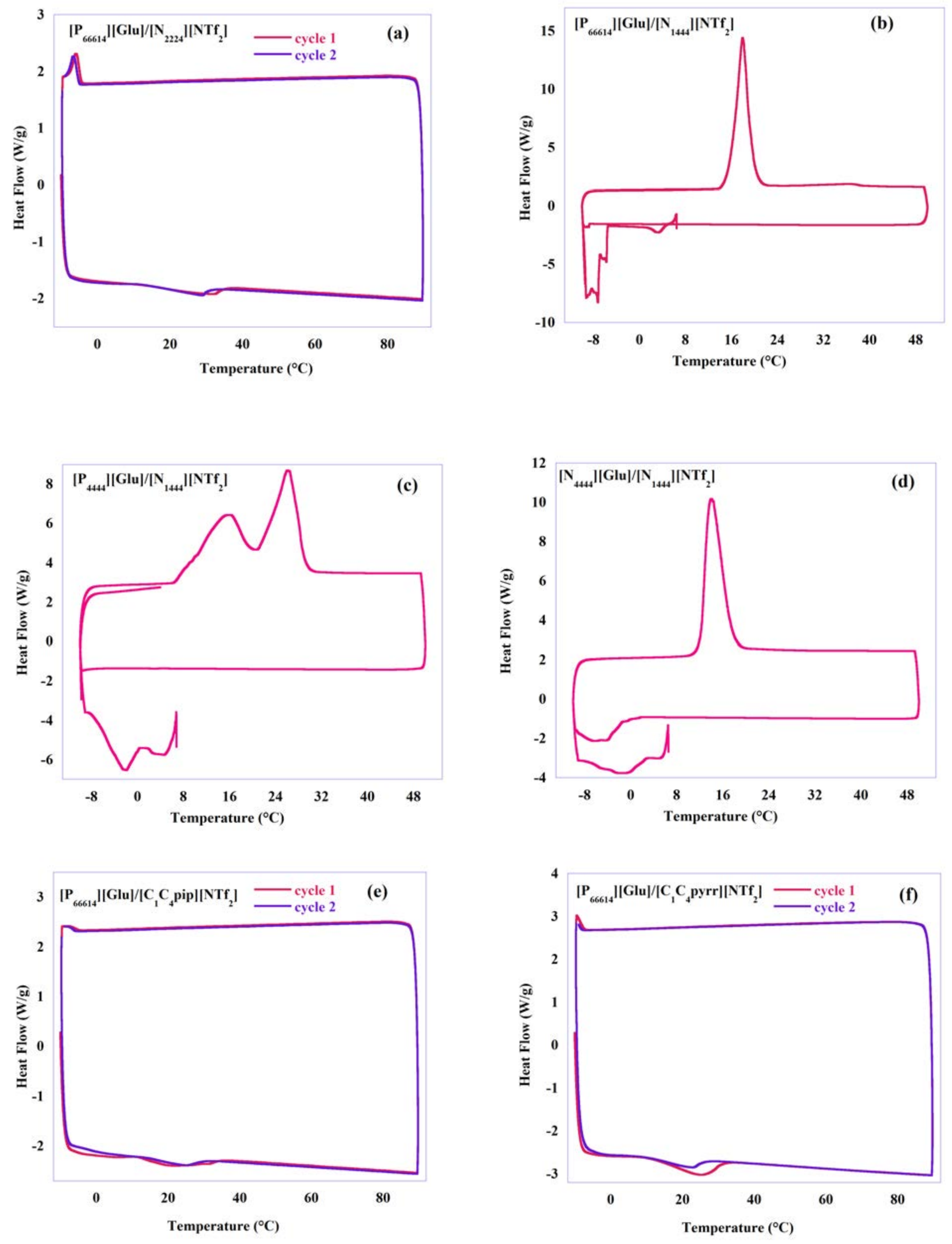


Figure S3. DSC thermograms obtained for gel phases. (**a**), (**e**) and (**f**) endothermic transition points downwards; (**b**)-(**d**) endothermic transition points upwards.

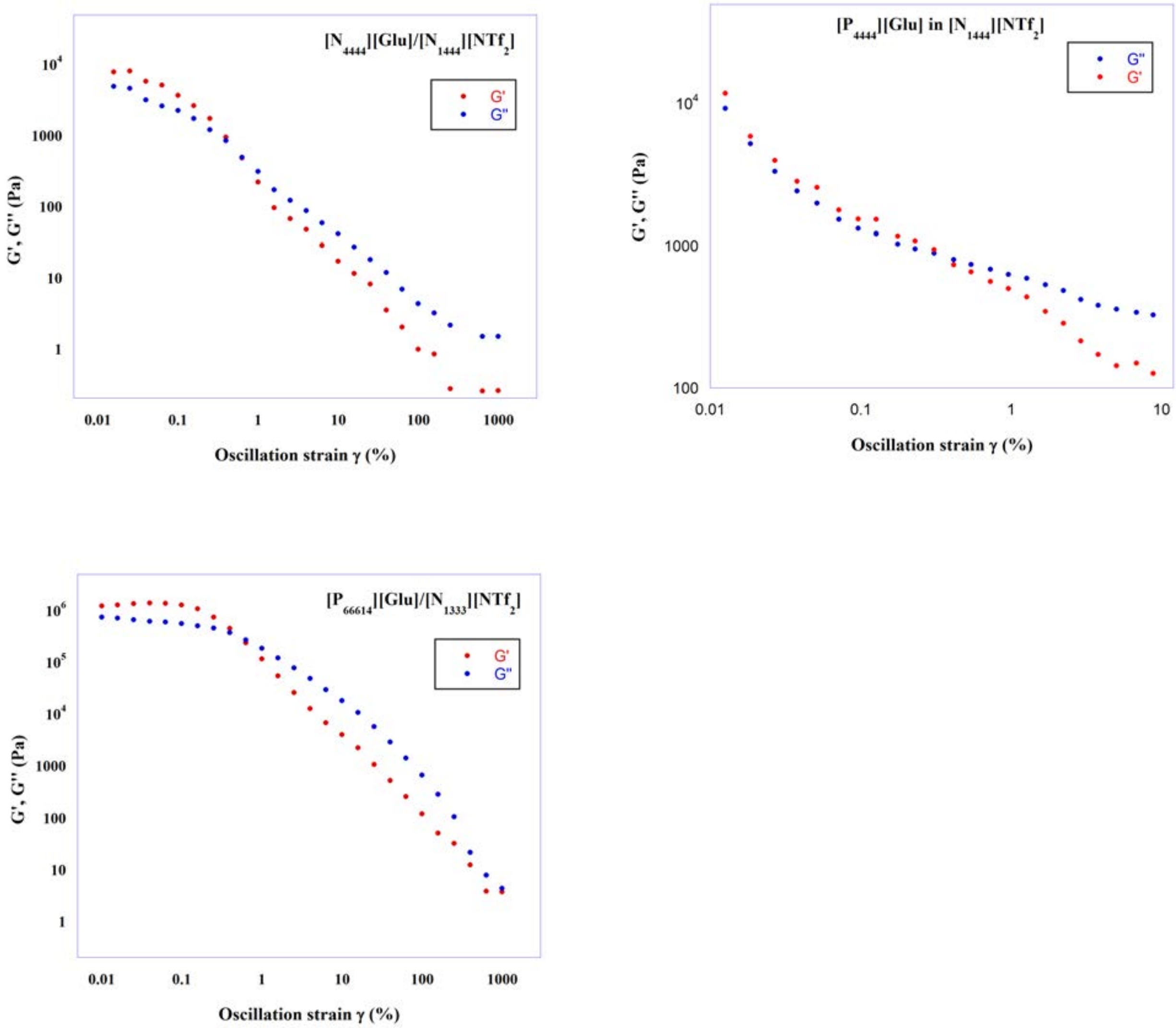
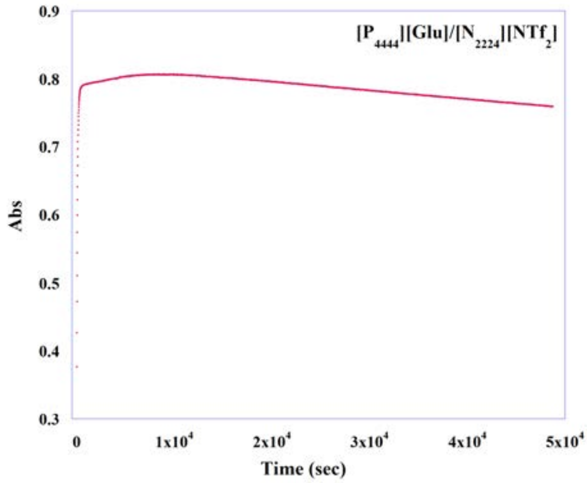
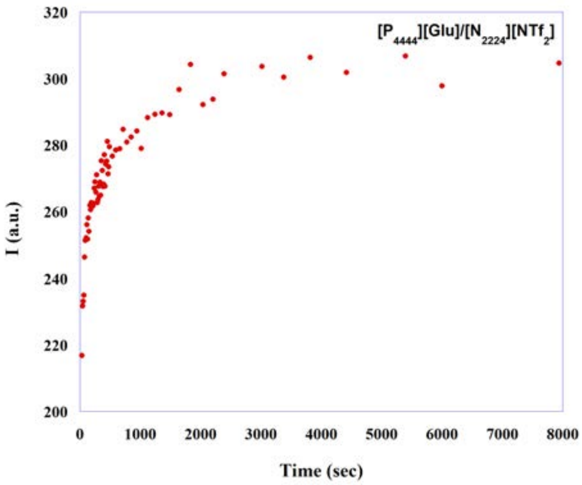
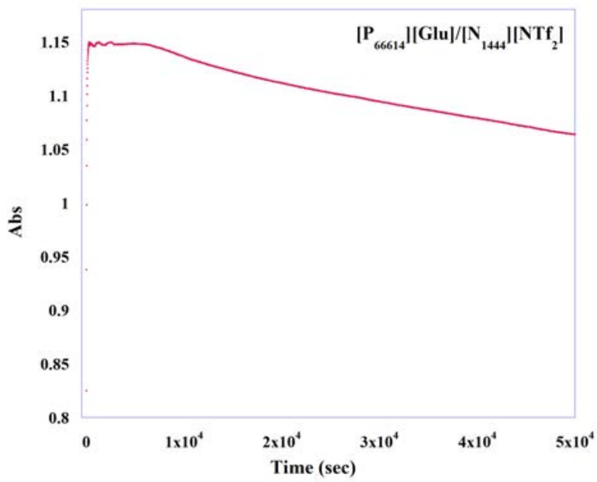
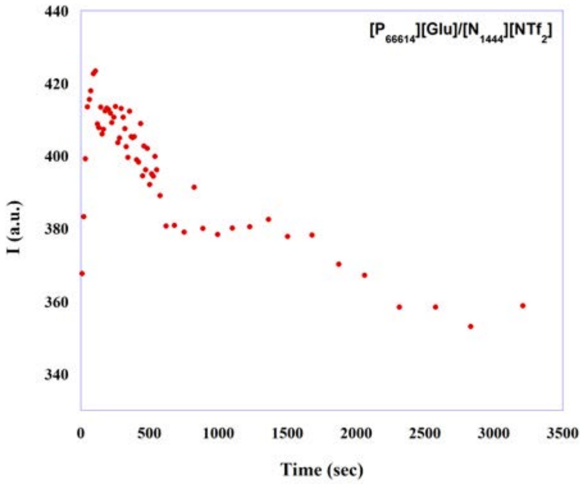


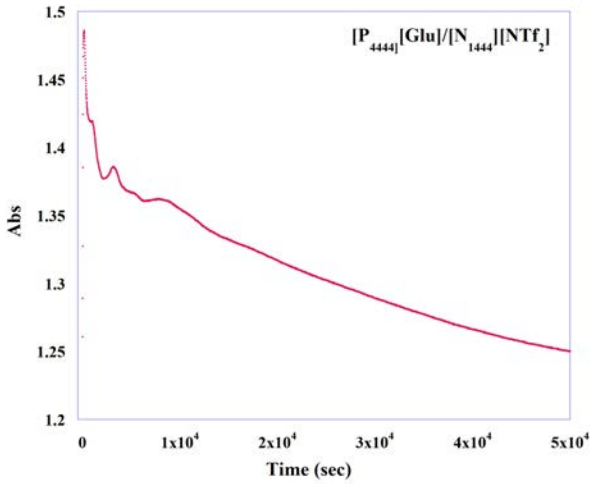
Figure S4. Strain sweep measurements performed at a frequency of 1 Hz and 25 °C for ILGs at 6.5 % wt of gelator.

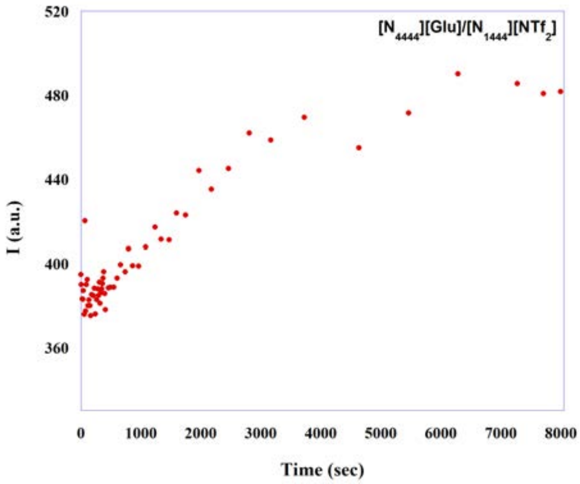

[P4444][Glu]/[N2224][NTf2]
Abs
Time (sec)


[P4444][Glu]/[N2224][NTf2]
I (a.u.)
Time (sec)


[P66614][Glu]/[N1444][NTf2]
Abs
Time (sec)


[P66614][Glu]/[N1444][NTf2]
I (a.u.)
Time (sec)


[P4444][Glu]/[N1444][NTf2]
Abs
Time (sec)


[N4444][Glu]/[N1444][NTf2]
I (a.u.)
Time (sec)

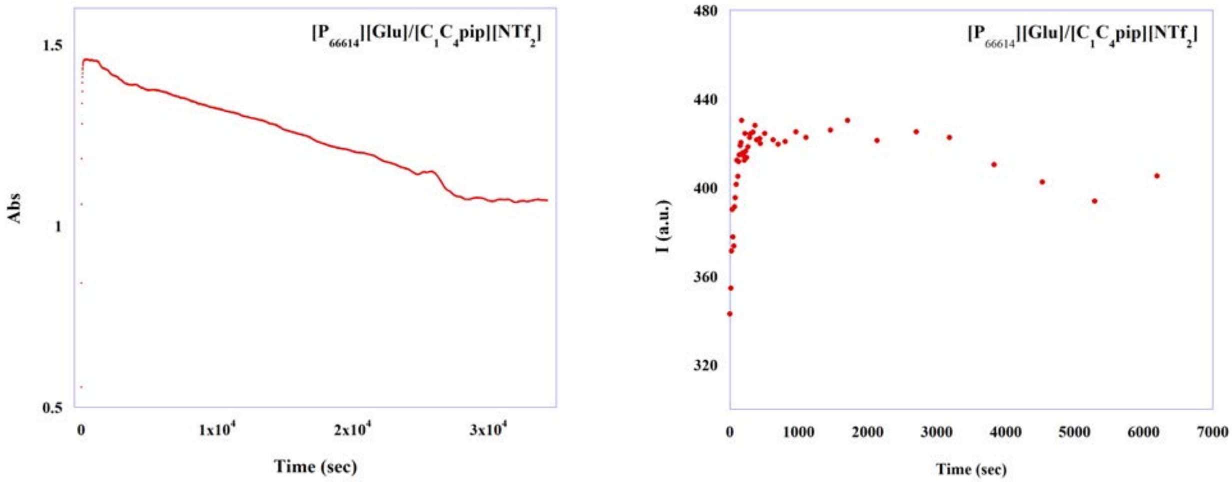
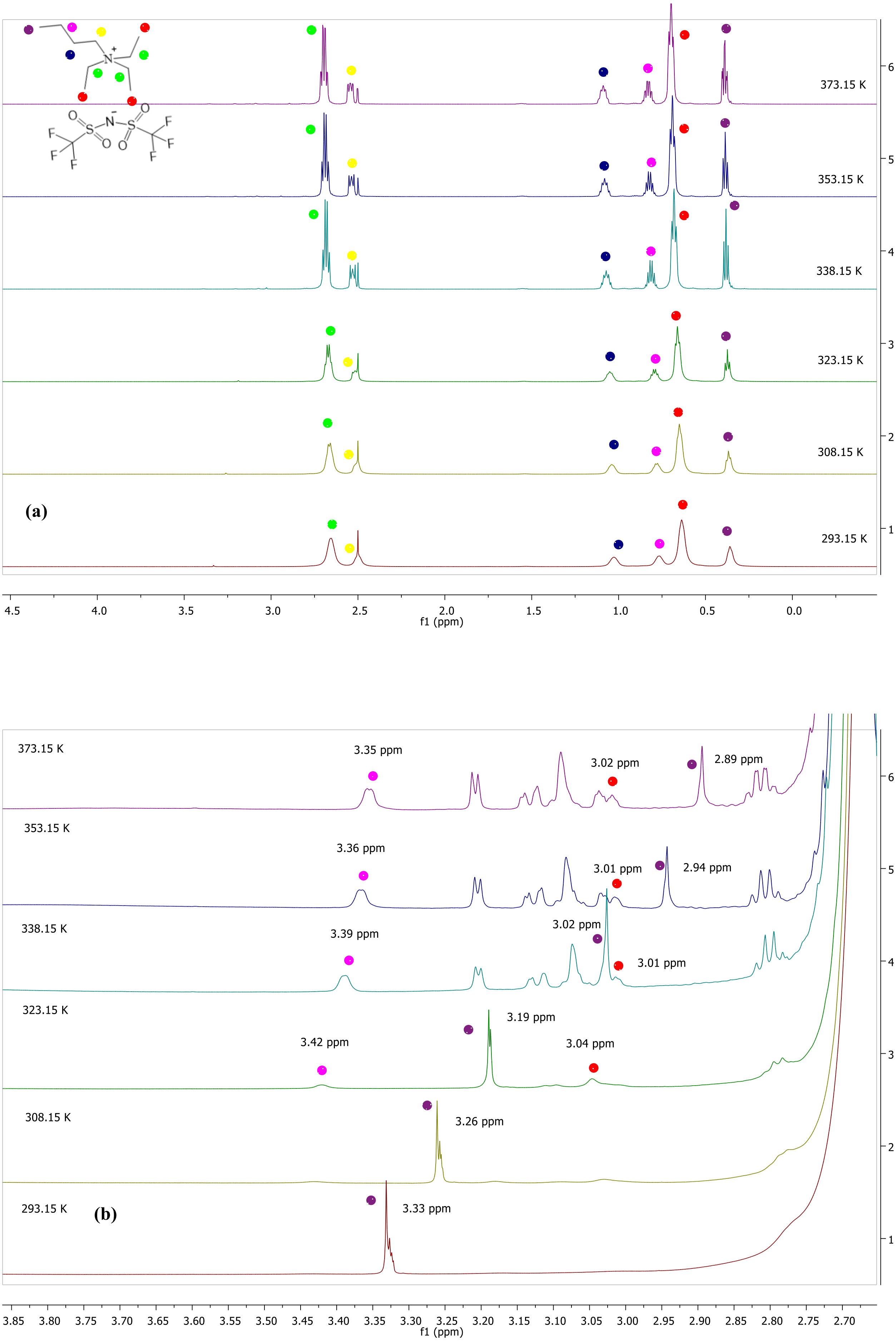
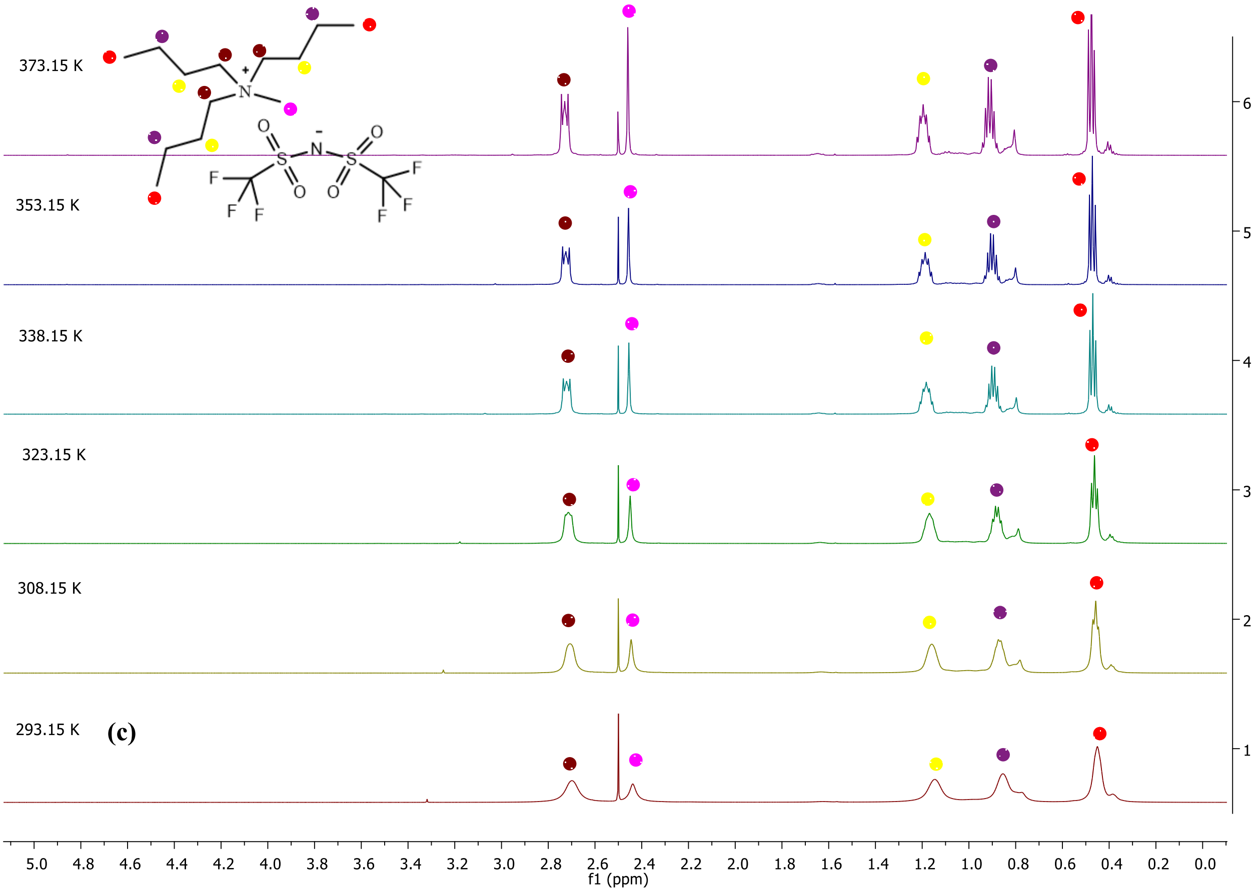


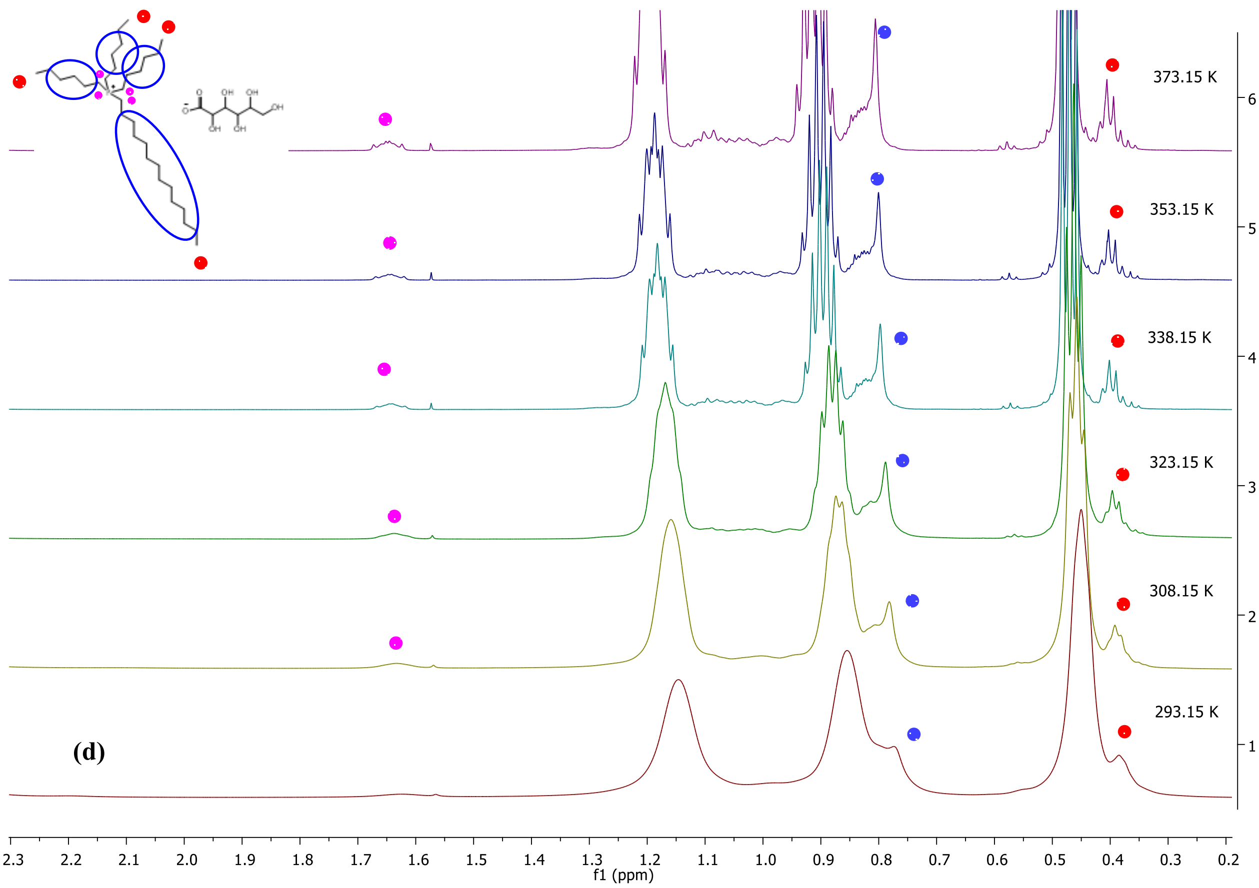
Figure S5. Plots of the opacity and I_{RLS} as a function of the time for ILGs at 6.5% wt of gelator.



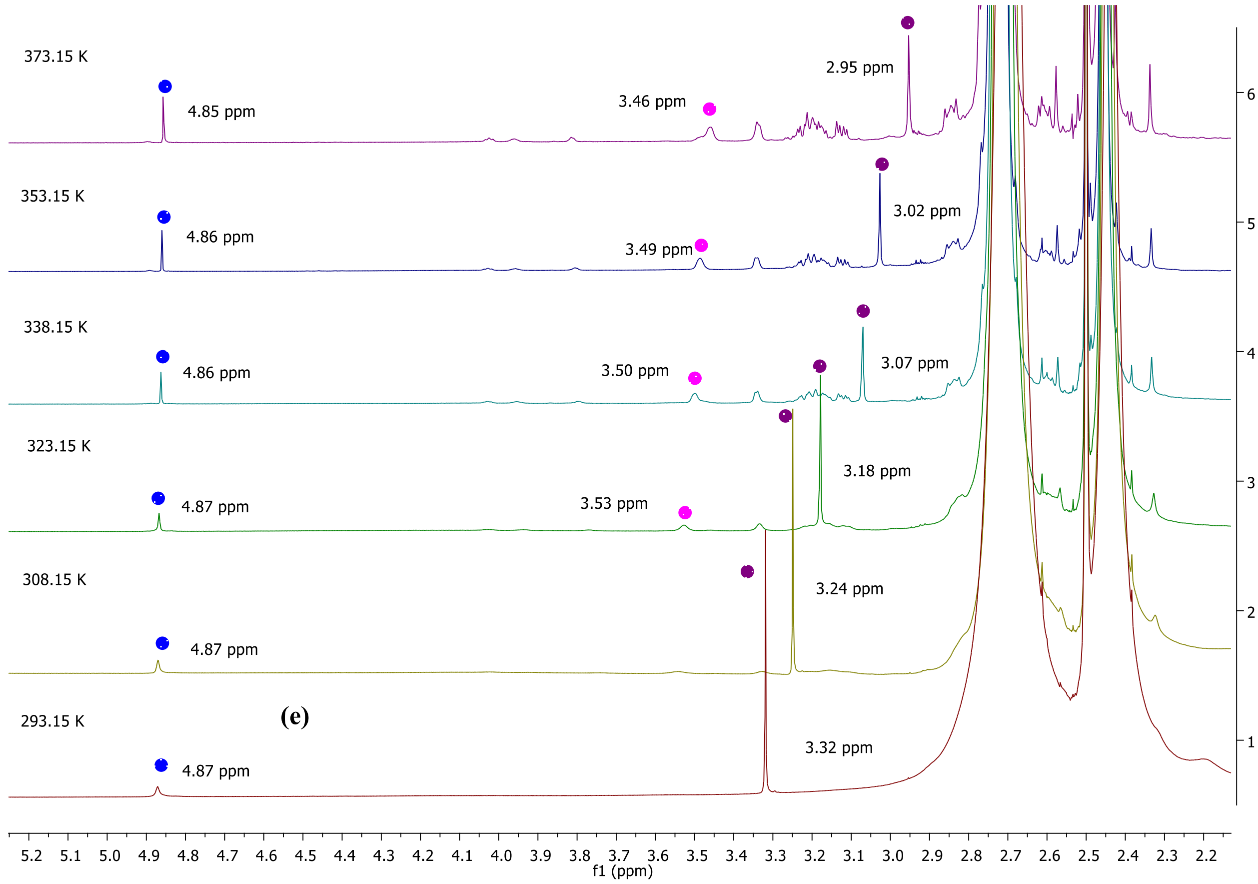
(a)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
(b)
3.35 ppm
3.02 ppm
2.89 ppm
3.36 ppm
3.01 ppm
2.94 ppm
3.39 ppm
3.02 ppm
3.01 ppm
3.42 ppm
3.19 ppm
3.04 ppm
3.26 ppm
3.33 ppm
3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10 3.05 3.00 2.95 2.90 2.85 2.80 2.75 2.70
f1 (ppm)

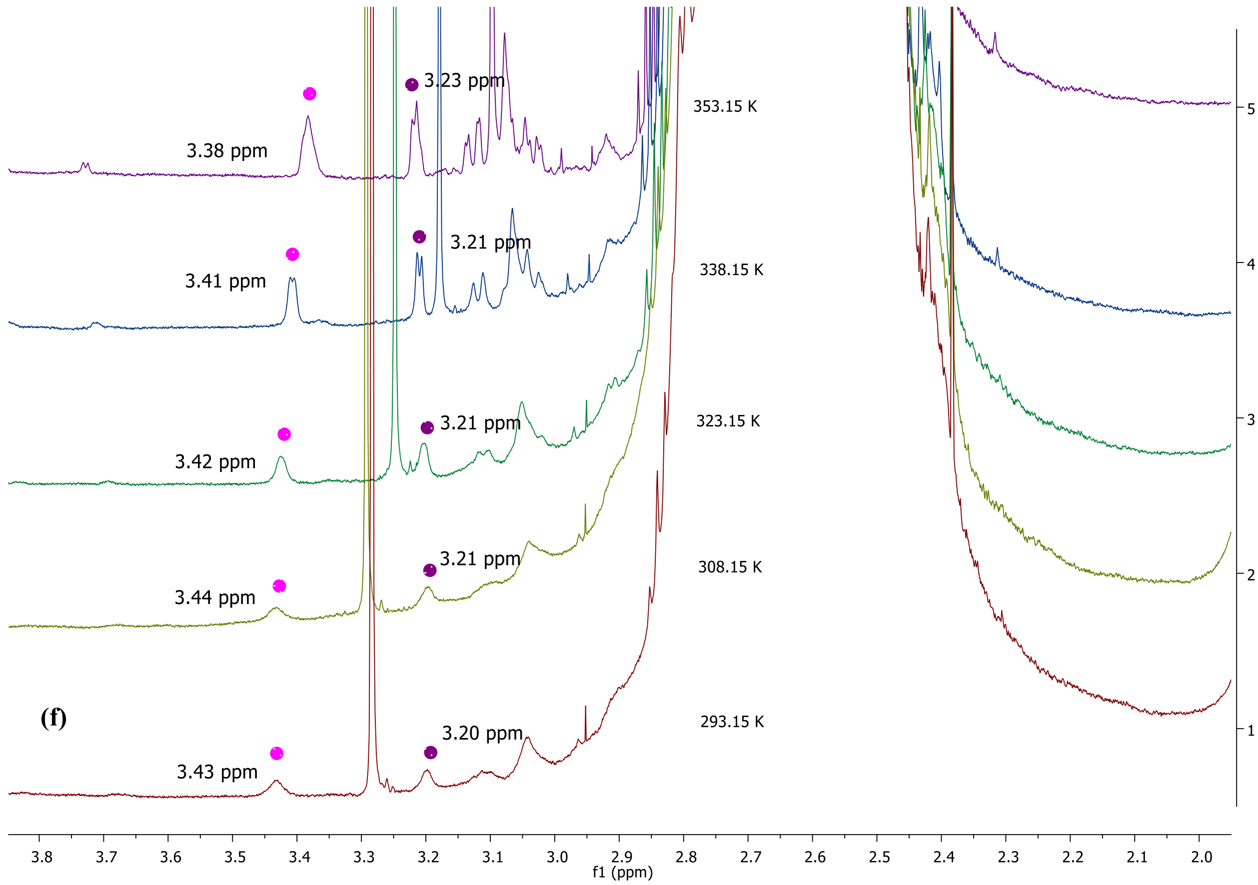


373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
(c)
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f1 (ppm)

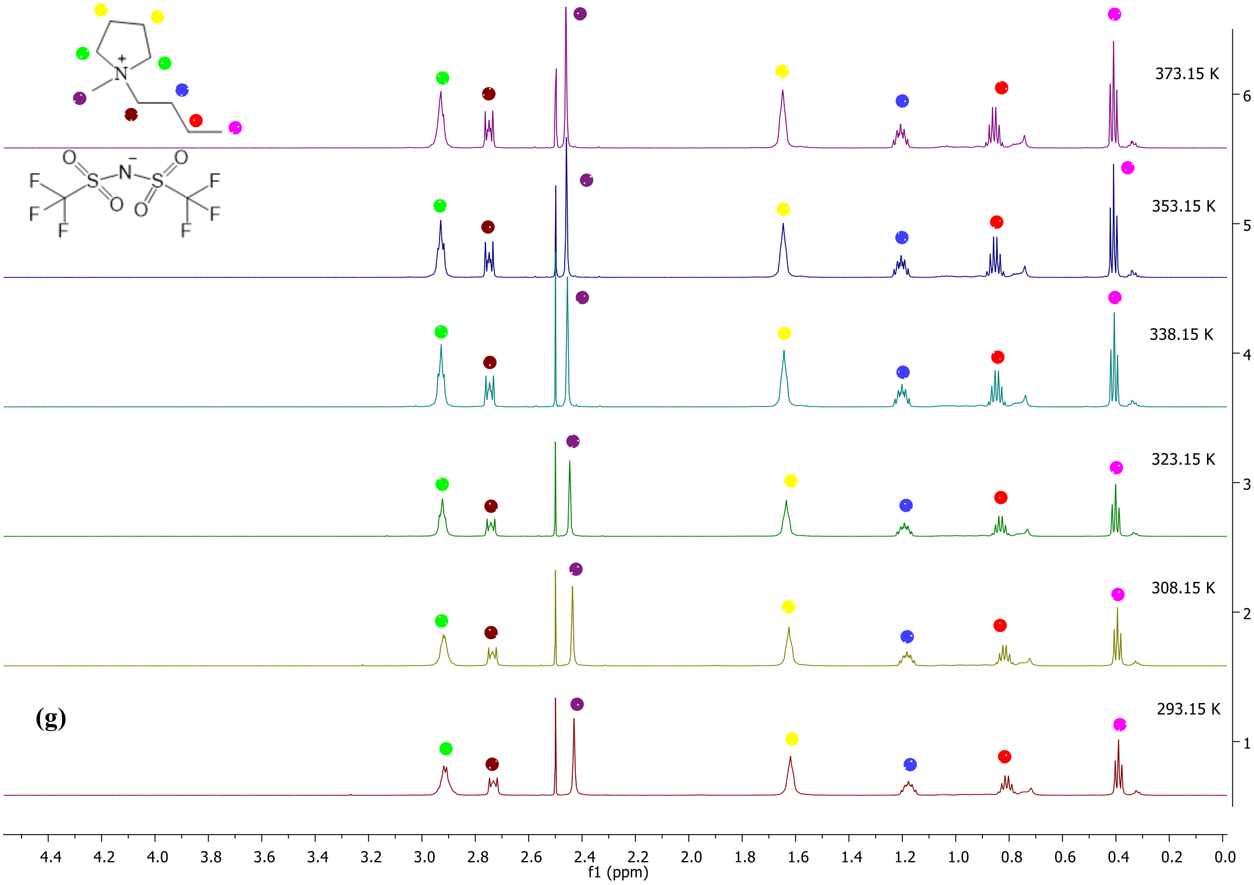


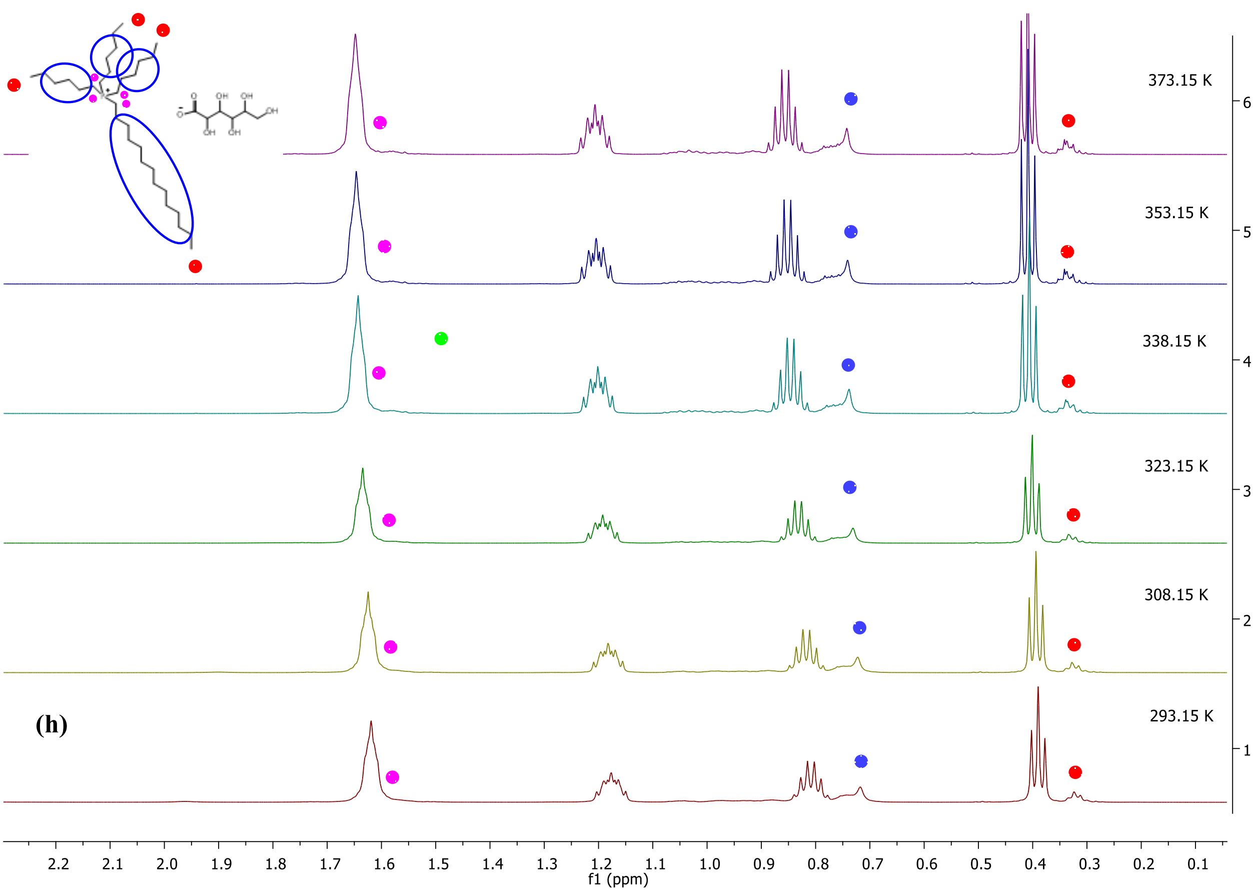
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
(d)
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2
f1 (ppm)

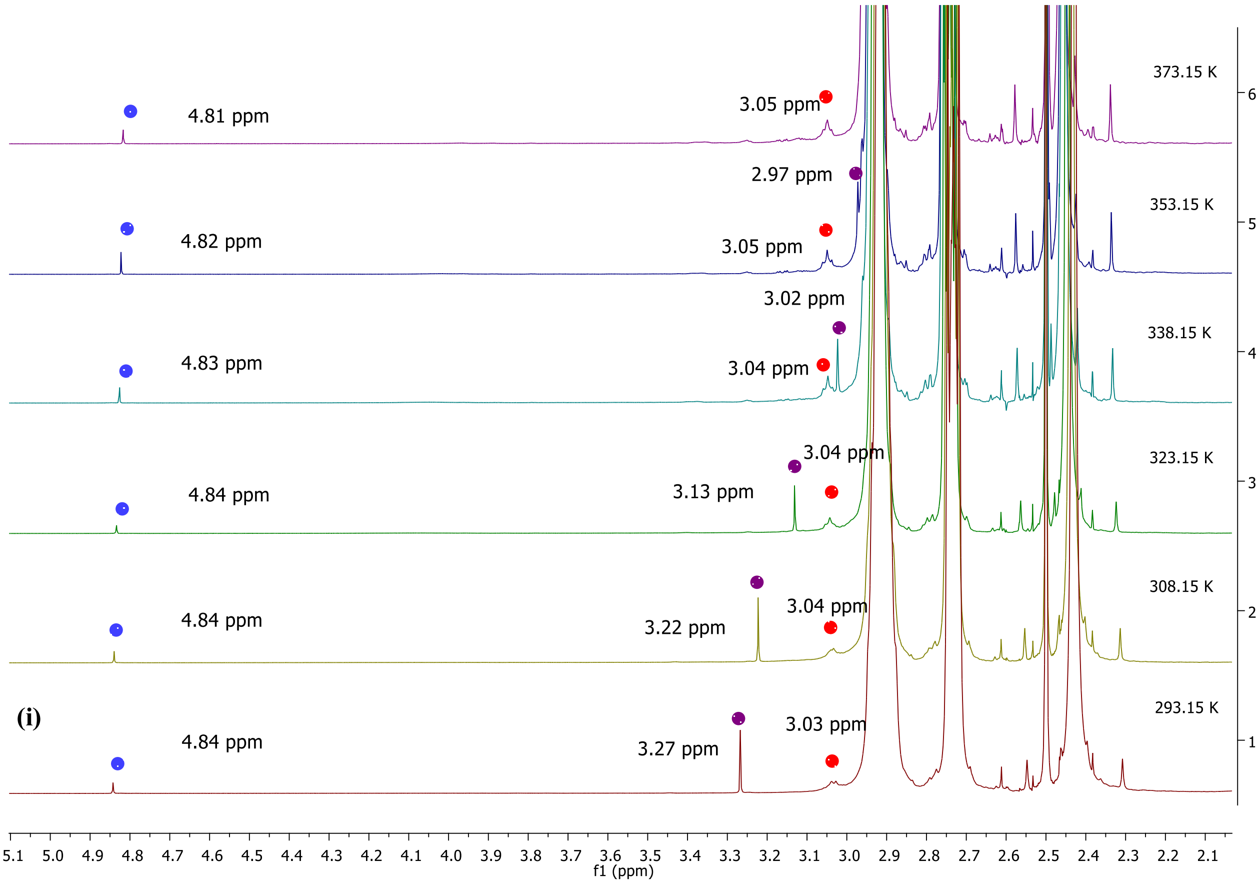

373.15 K
4.85 ppm
3.46 ppm
2.95 ppm
353.15 K
4.86 ppm
3.49 ppm
3.02 ppm
338.15 K
4.86 ppm
3.50 ppm
3.07 ppm
323.15 K
4.87 ppm
3.53 ppm
3.18 ppm
308.15 K
4.87 ppm
3.24 ppm
293.15 K
(e)
4.87 ppm
3.32 ppm
f1 (ppm)

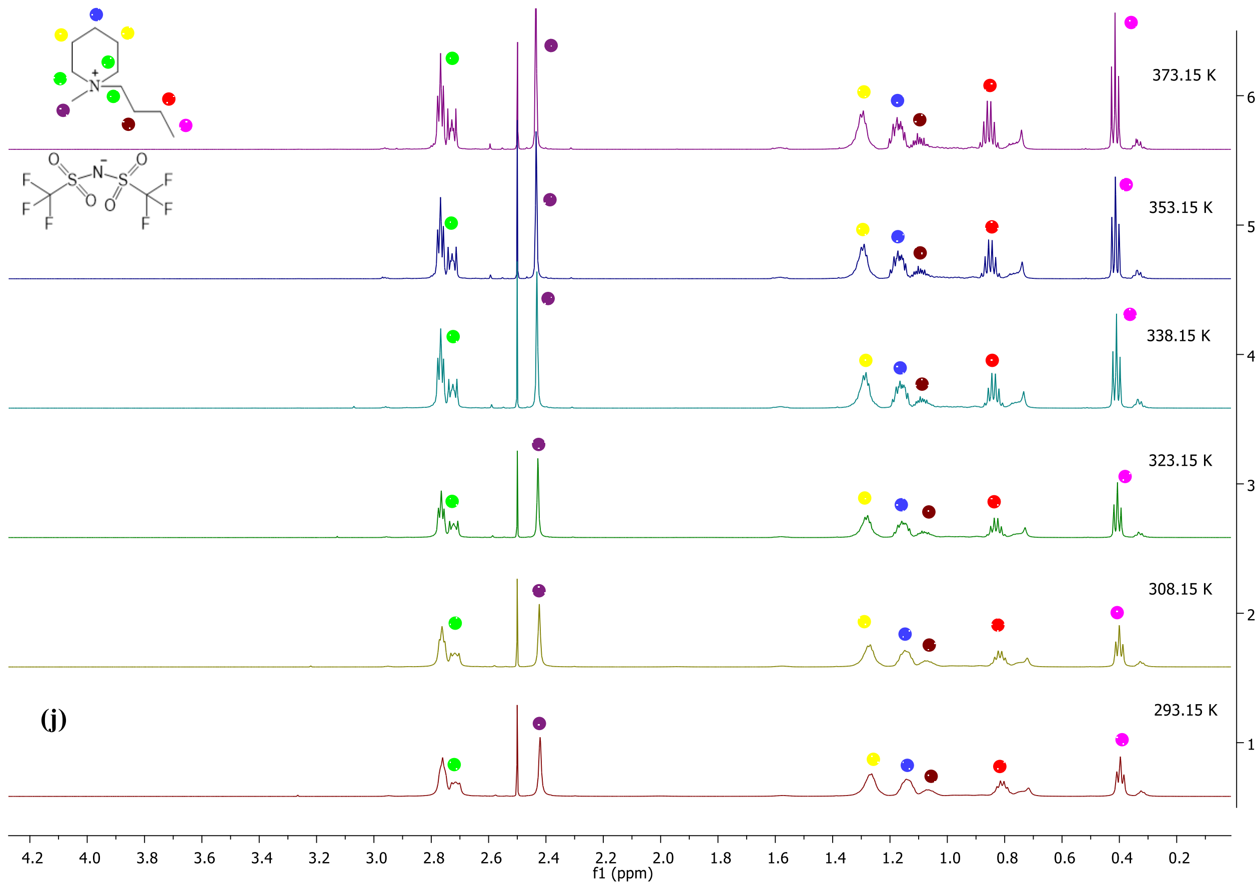


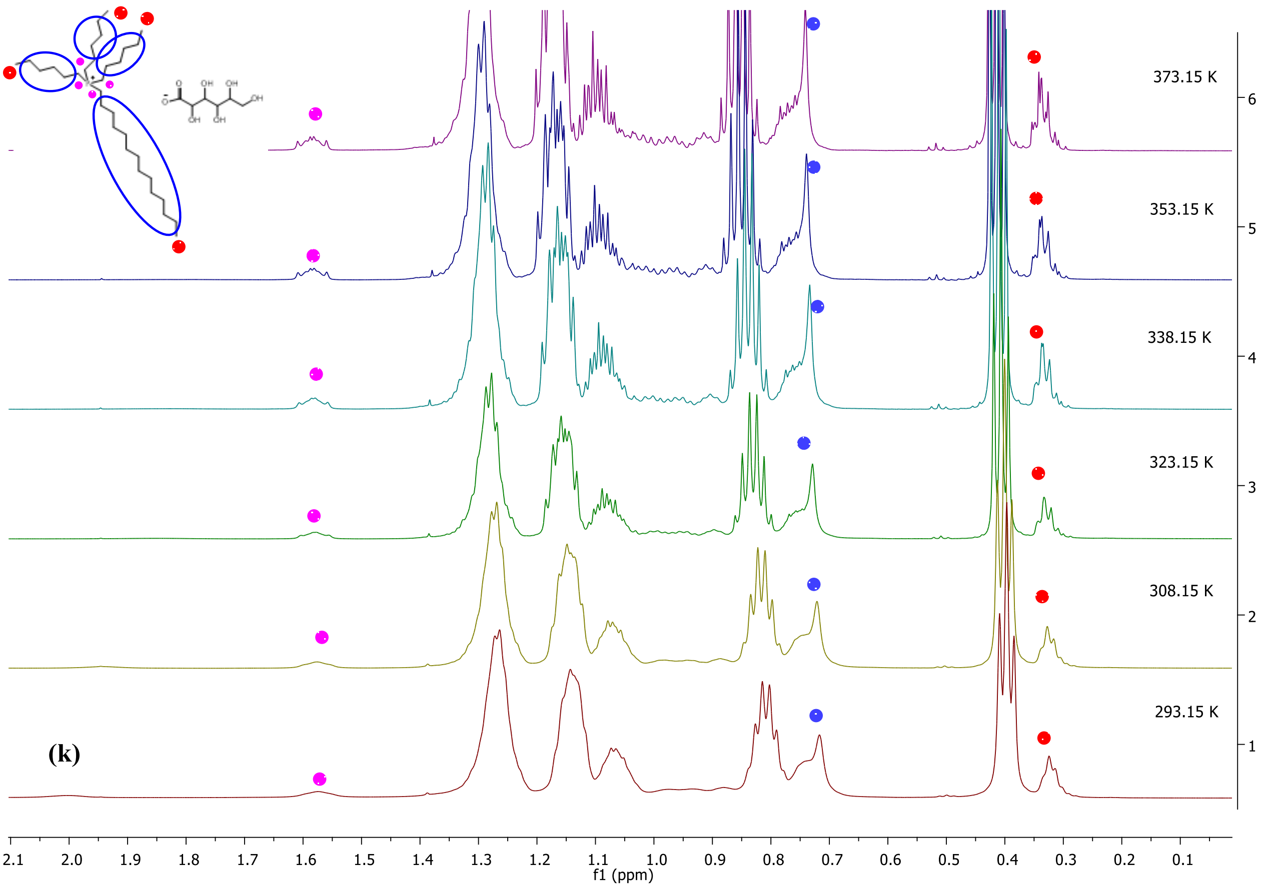
(f)
3.38 ppm
3.23 ppm
353.15 K
3.41 ppm
3.21 ppm
338.15 K
3.42 ppm
3.21 ppm
323.15 K
3.44 ppm
3.21 ppm
308.15 K
3.43 ppm
3.20 ppm
293.15 K
f1 (ppm)


(g)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
f1 (ppm)


(h)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
f1 (ppm)


(i)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
4.81 ppm
4.82 ppm
4.83 ppm
4.84 ppm
4.84 ppm
4.84 ppm
3.05 ppm
2.97 ppm
3.05 ppm
3.02 ppm
3.04 ppm
3.04 ppm
3.13 ppm
3.22 ppm
3.04 ppm
3.27 ppm
3.03 ppm
f1 (ppm)


(j)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
f1 (ppm)


(k)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
f1 (ppm)

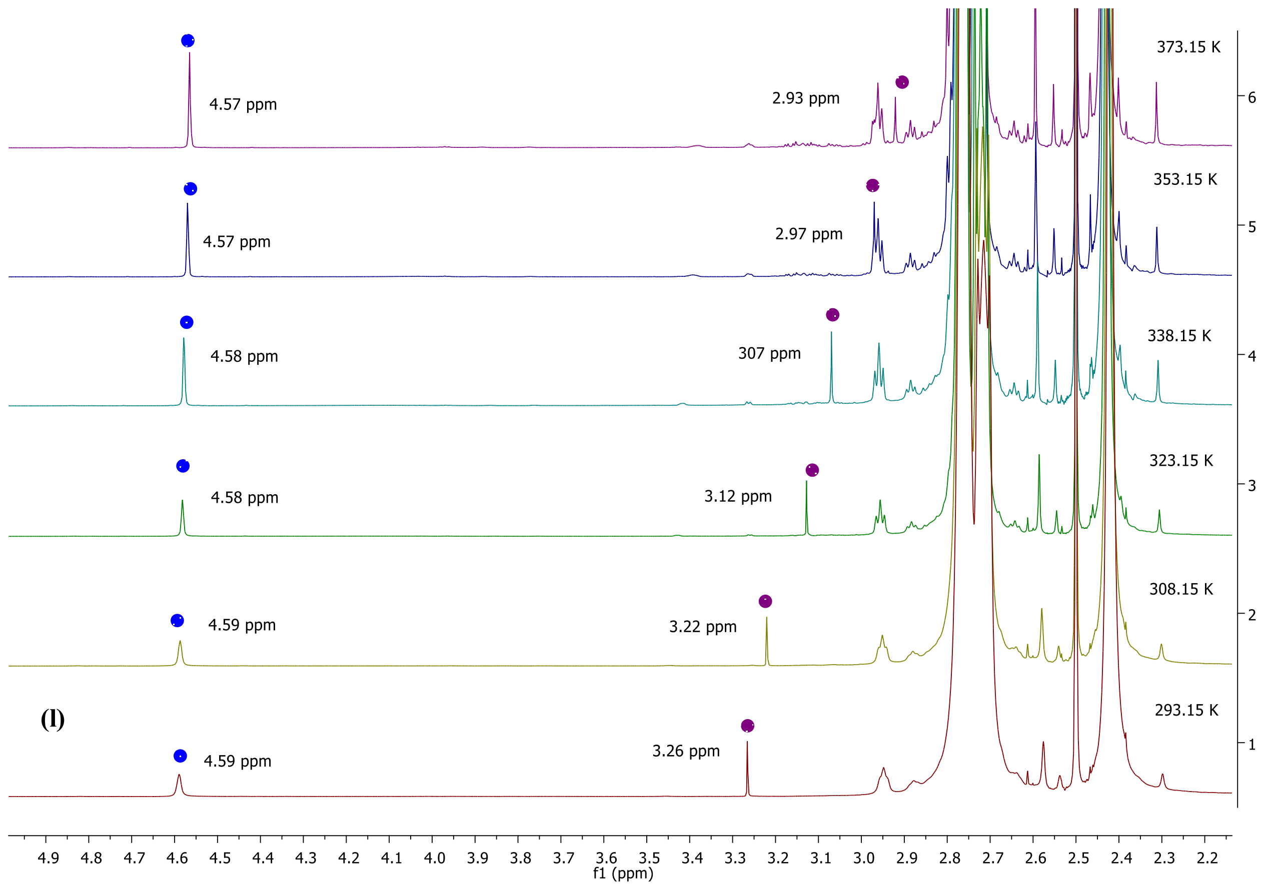

(l)
373.15 K
353.15 K
338.15 K
323.15 K
308.15 K
293.15 K
4.57 ppm
4.57 ppm
4.58 ppm
4.58 ppm
4.59 ppm
4.59 ppm
2.93 ppm
2.97 ppm
307 ppm
3.12 ppm
3.22 ppm
3.26 ppm
f1 (ppm)

Figure S6. ^{1}H NMR spectra of ILGs at 6.5% wt as a function of temperature for: **(a) [P$_{4\,4\,4\,4}$][Glu]/[N$_{2\,2\,2\,4}$][NTf$_2$]**; **(b) [P$_{4\,4\,4\,4}$][Glu]/[N$_{2\,2\,2\,4}$][NTf$_2$]** enlarged region between 2.60-3.85 ppm; (**c**) **[P$_{6\,6\,6\,14}$][Glu]/[N$_{1\,4\,4\,4}$][NTf$_2$]**; (**d**) **[P$_{6\,6\,6\,14}$][Glu]/[N$_{1\,4\,4\,4}$][NTf$_2$]** enlarged region between 0.2-2.3 ppm; (**e**) **[P$_{6\,6\,6\,14}$][Glu]/[N$_{1\,4\,4\,4}$][NTf$_2$]** enlarged region between 2.2-5.2 ppm; **(f) [P$_{6\,6\,6\,14}$][Glu]/[N$_{2\,2\,2\,4}$][NTf$_2$]** enlarged region between 2.0-3.8 ppm; (g) **[P$_{6\,6\,6\,14}$][Glu]/[C$_1$C$_4$pyrr][NTf$_2$]**; (h) **[P$_{6\,6\,6\,14}$][Glu]/[C$_1$C$_4$pyrr][NTf$_2$]** enlarged region between 0.1-2.2 ppm; (i) **[P$_{6\,6\,6\,14}$][Glu]/[C$_1$C$_4$pyrr][NTf$_2$]** enlarged region between 2.1-5.1 ppm; (j) **[P$_{6\,6\,6\,14}$][Glu]/[C$_1$C$_4$pip][NTf$_2$]**; (k) **[P$_{6\,6\,6\,14}$][Glu]/[C$_1$C$_4$pip][NTf$_2$]** enlarged region between 0.1-2.1 ppm; (l) **[P$_{6\,6\,6\,14}$][Glu]/[C$_1$C$_4$pip][NTf$_2$]** enlarged region between 2.2-4.9 ppm.

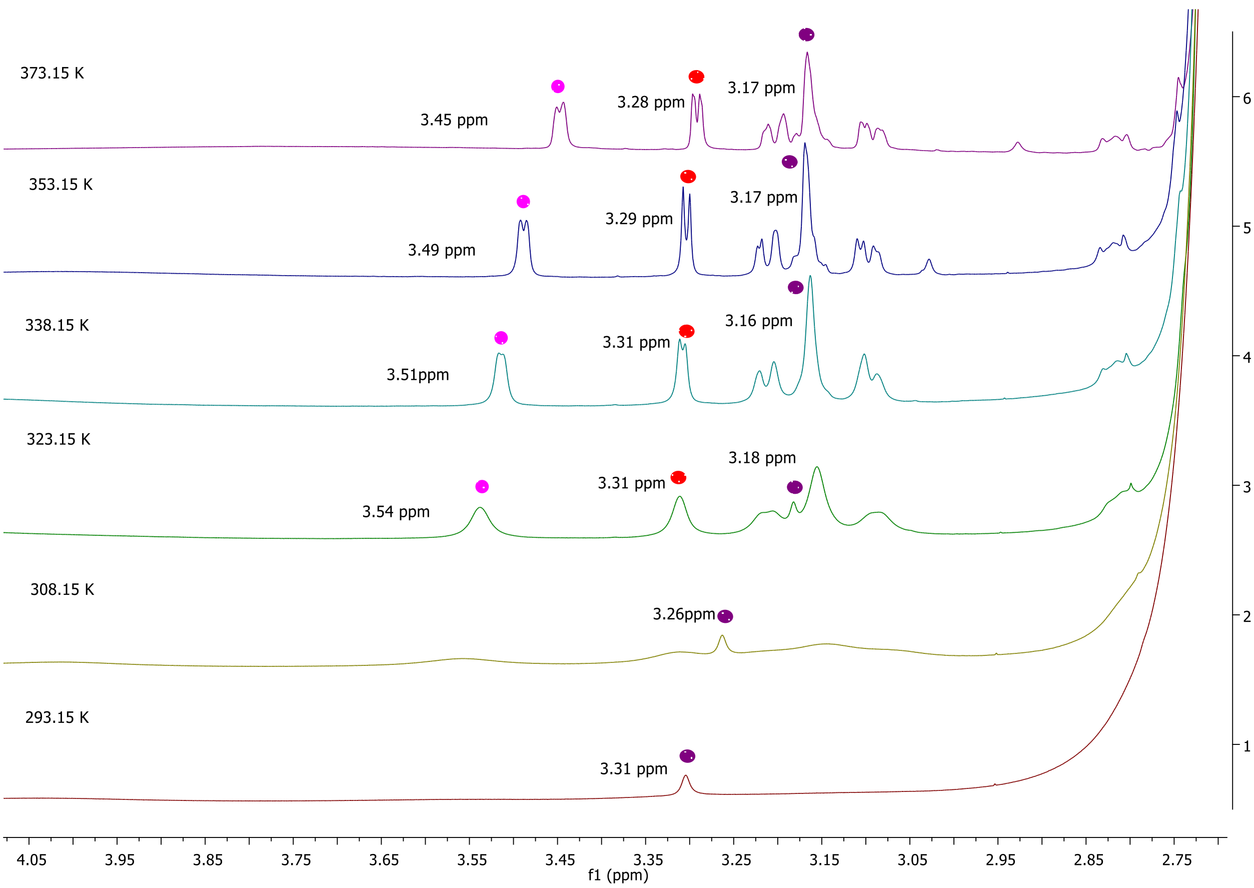
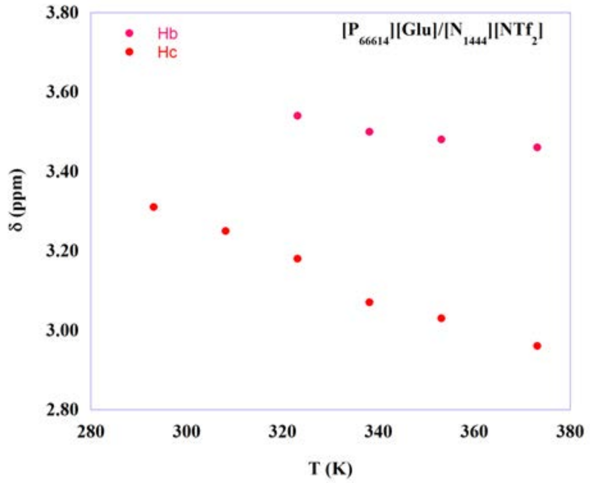
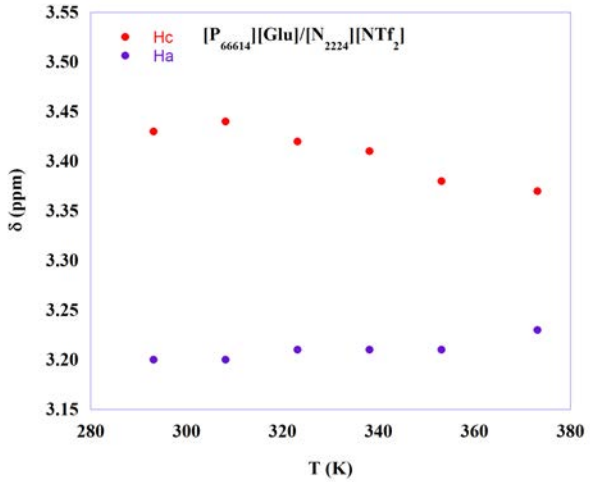


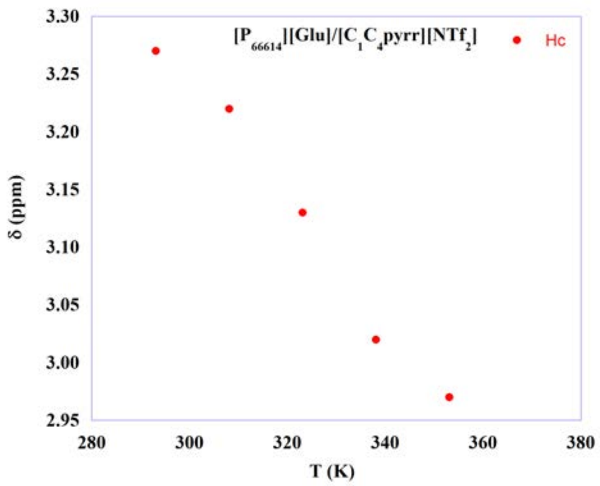
Figure S7. Enlarged region of ^{1}H NMR spectra of **[P$_{4\,4\,4\,4}$][Glu]/[N$_{1\,4\,4\,4}$][NTf$_2$]** at 3.0 % wt as a function of temperature.



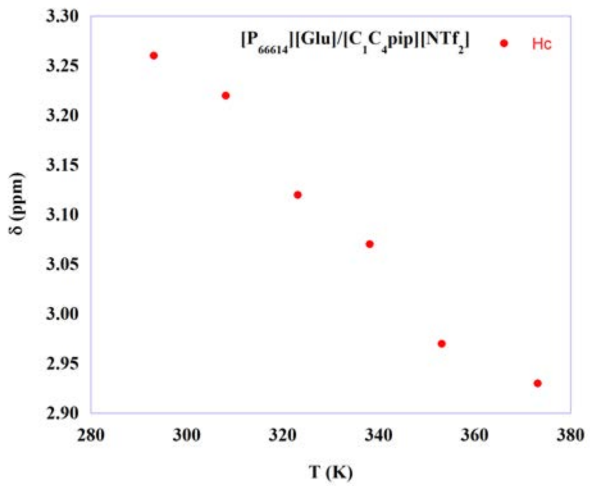
[P66614][Glu]/[N1444][NTf2]
Hb
Hc
δ (ppm)
T (K)



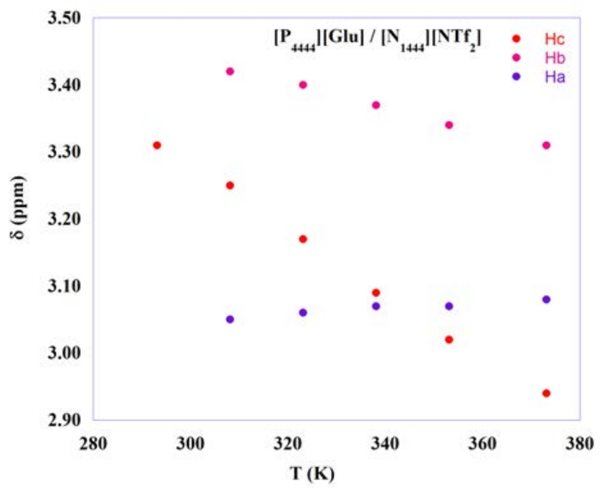
[P66614][Glu]/[N2224][NTf2]
Hc
Ha
δ (ppm)
T (K)



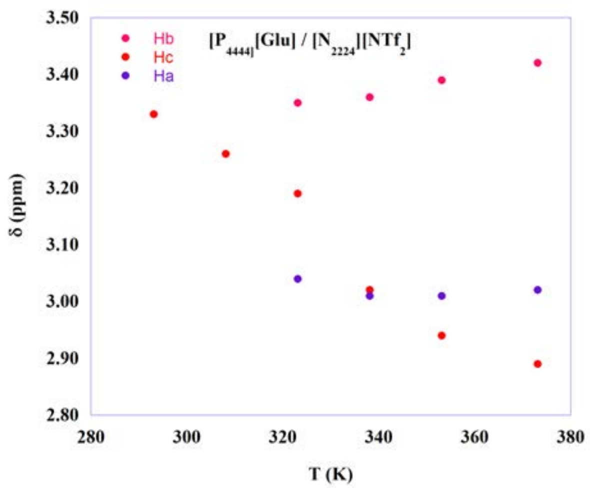
[P66614][Glu]/[C1C4pyrr][NTf2]
Hc
δ (ppm)
T (K)



[P66614][Glu]/[C1C4pip][NTf2]
Hc
δ (ppm)
T (K)



[P4444][Glu] / [N1444][NTf2]
Hc
Hb
Ha
δ (ppm)
T (K)



[P4444][Glu] / [N2224][NTf2]
Hb
Hc
Ha
δ (ppm)
T (K)

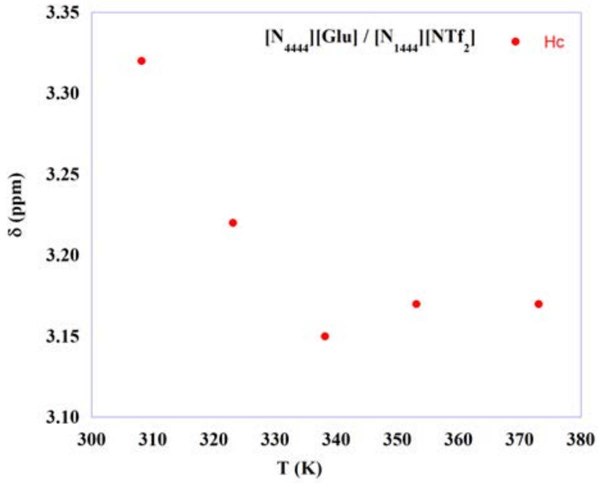


Figure S8. Changes in chemical shift as a function of the temperature for the ILGs.

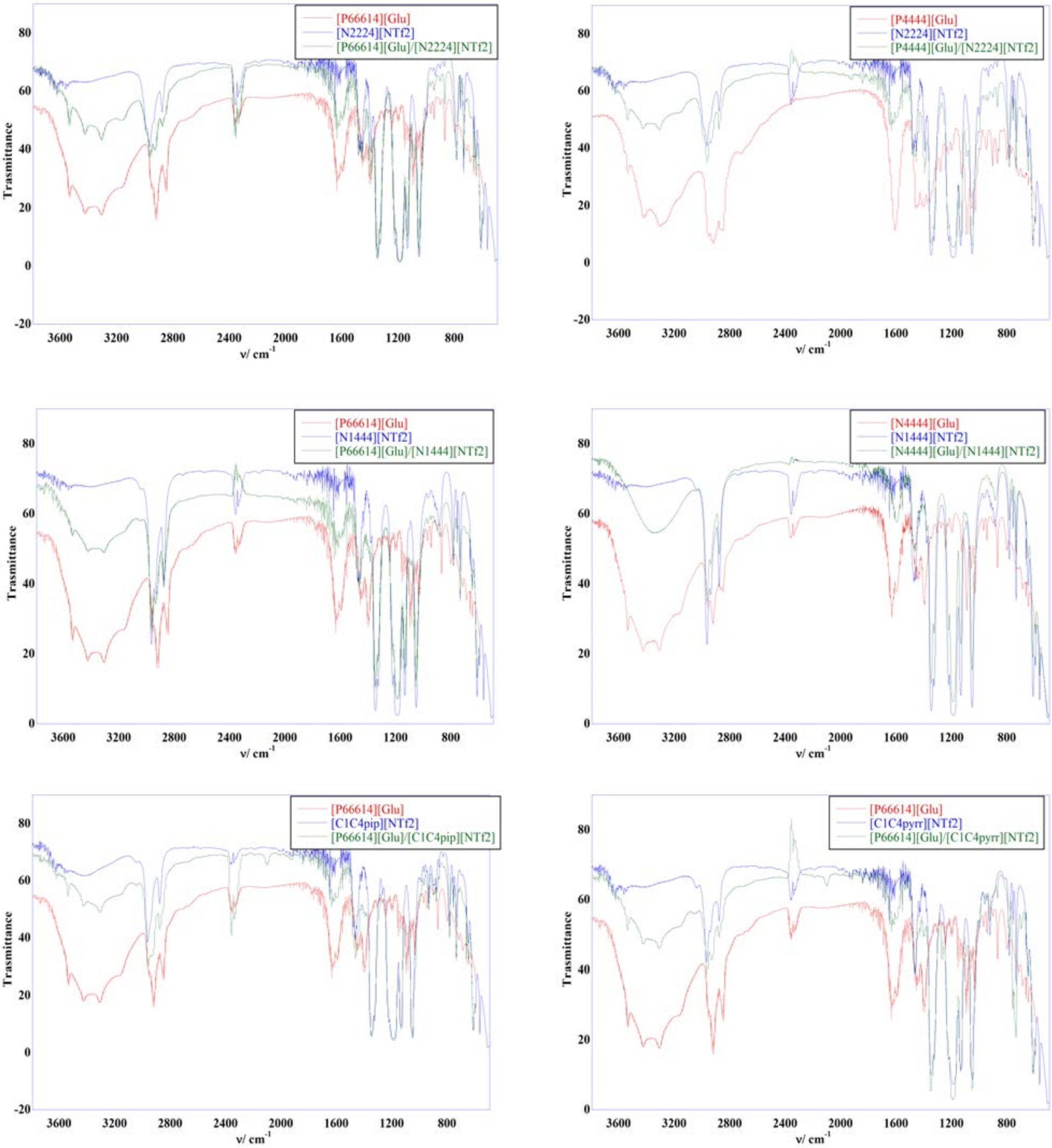
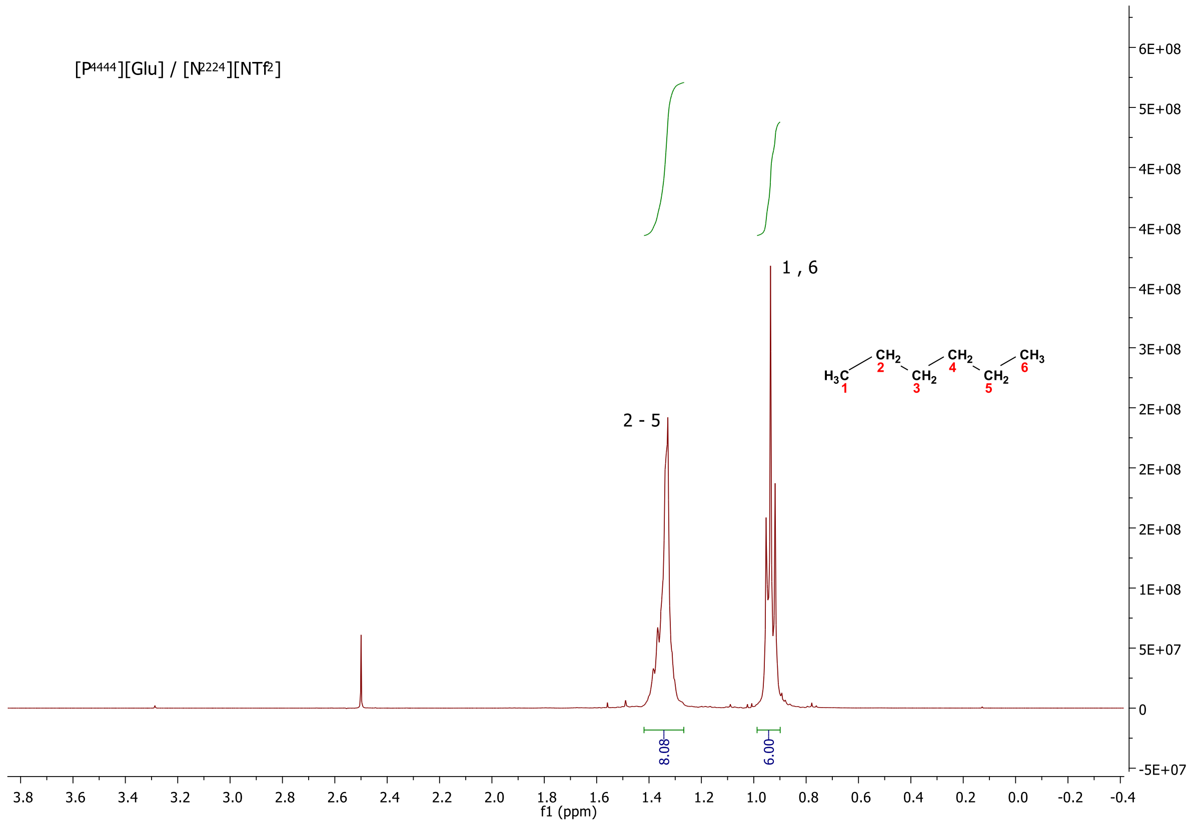


Figure S9. FT-IR spectra for neat gelator, ionic liquid and corresponding ILG at 6.5 % wt of gelator.



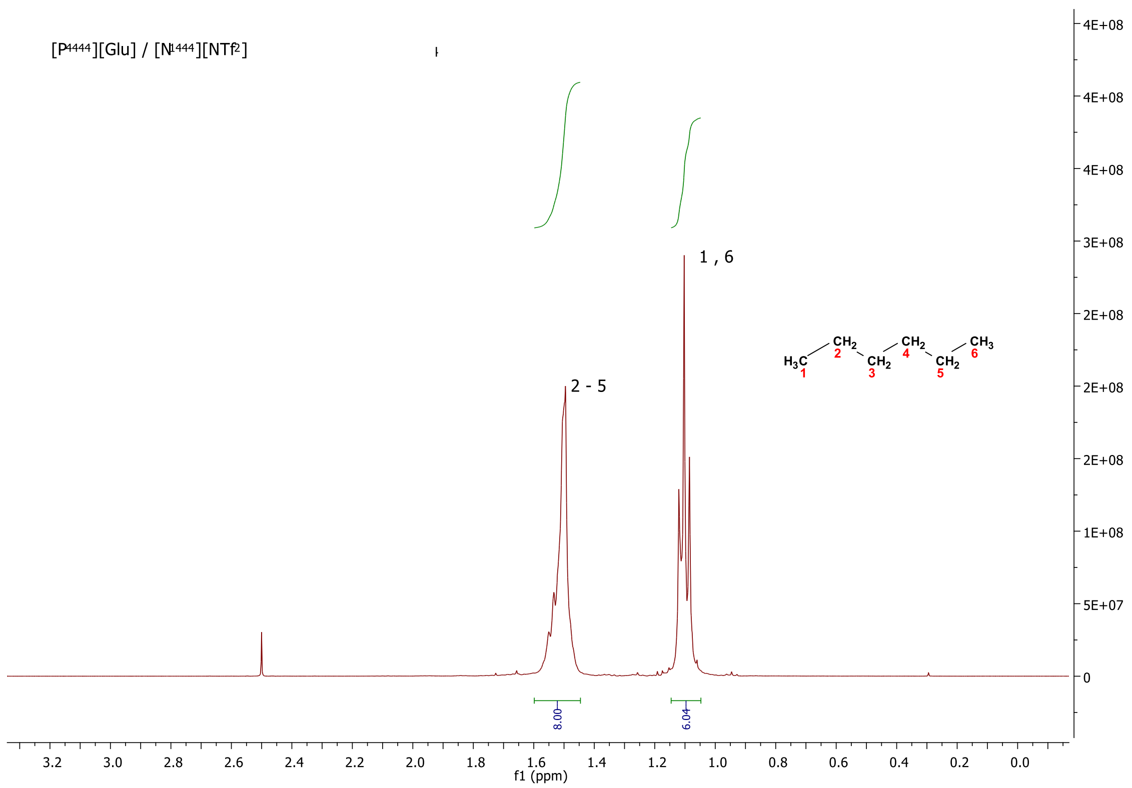
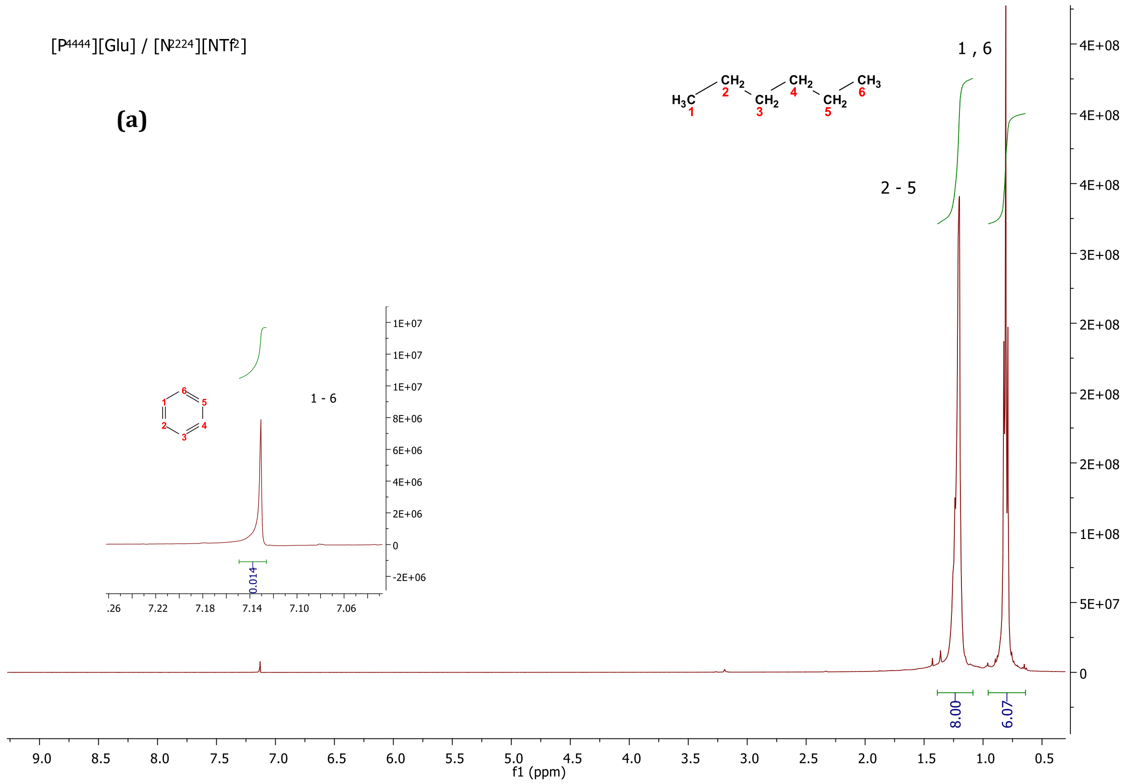
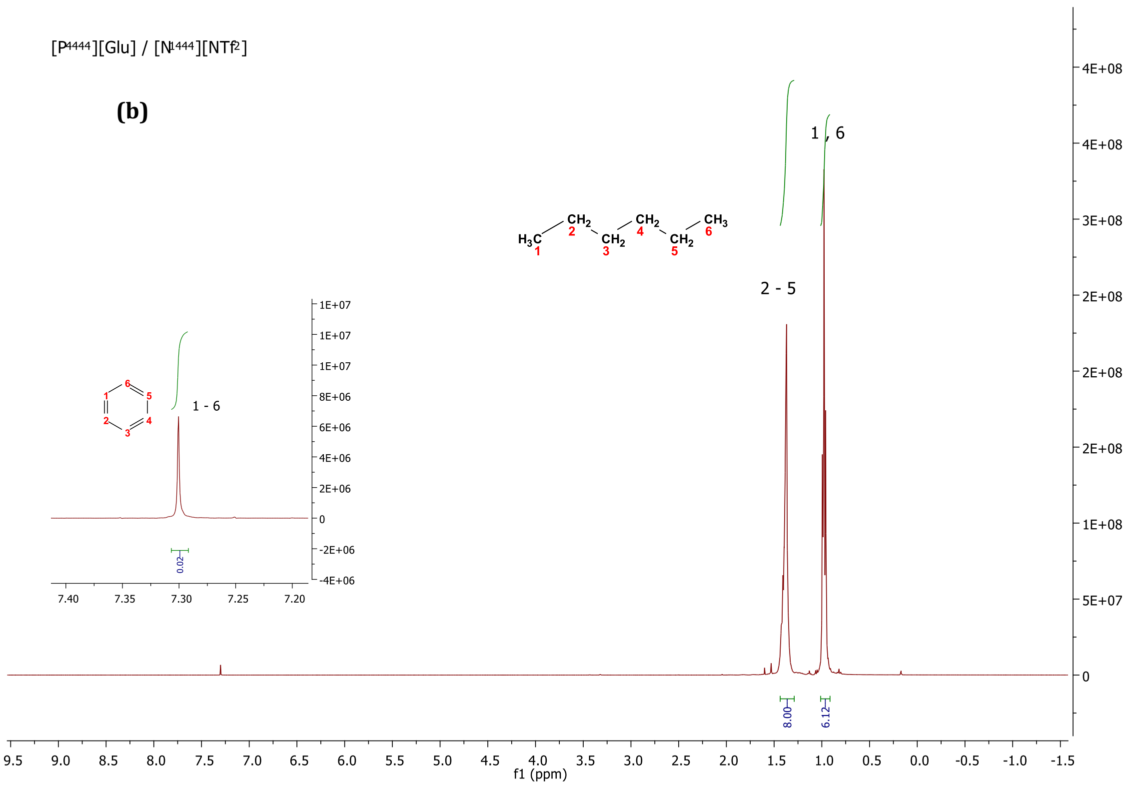


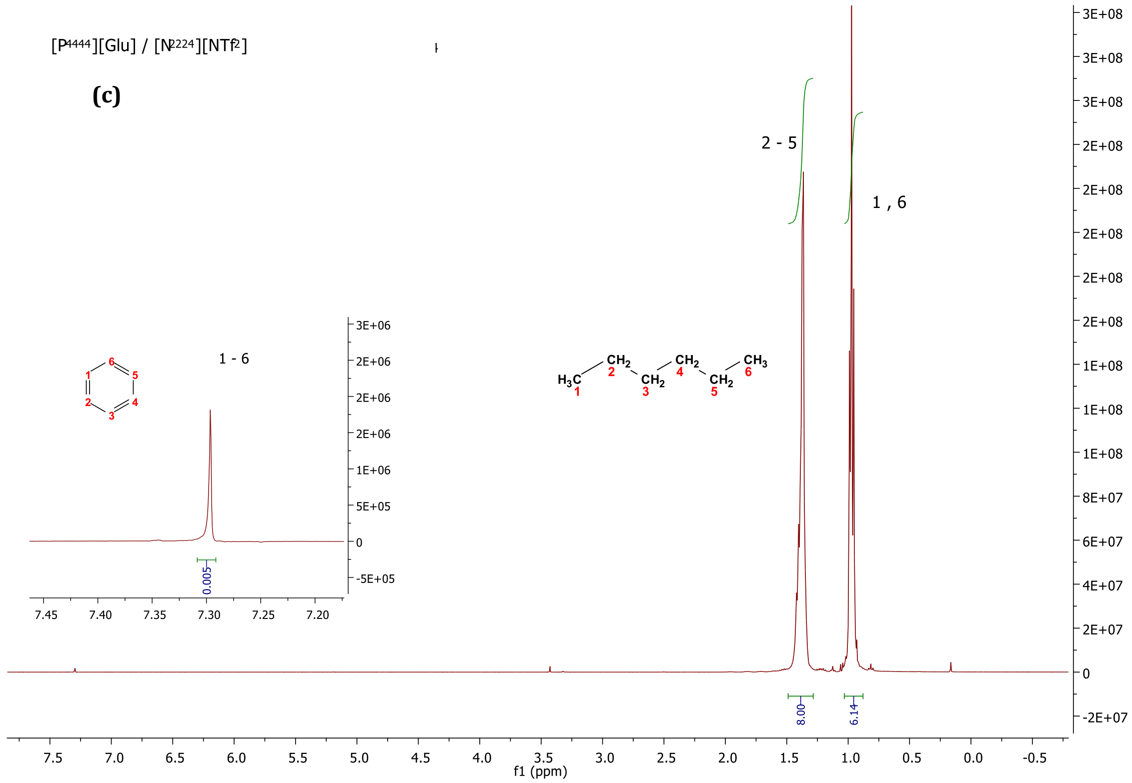
Figure S10. [1]H NMR spectra of hexane solution after 7h of contact time with **[P4444][Glu]/[N2224][NTf2]** (top) and **[P4444][Glu]/[N1444][NTf2]** (bottom).



[P4444][Glu] / [N2224][NTf2]
(a)
1 , 6
2 - 5
1 - 6
8.00
6.07
0.014
f1 (ppm)



[P4444][Glu] / [N1444][NTf2]
(b)
1 , 6
2 - 5
1 - 6
8.00
6.12
0.02
f1 (ppm)



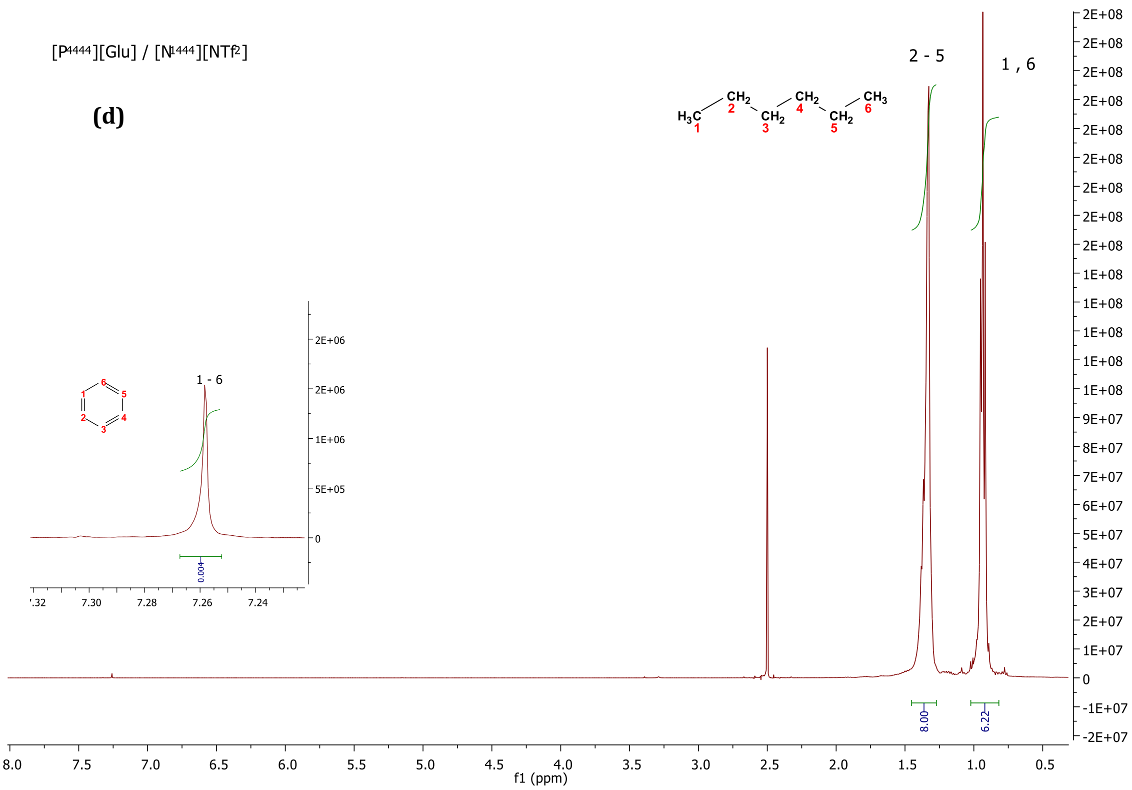


Figure S11. [1]H NMR spectra of hexane solution of benzene at **(a)** - **(b)** 2000 ppm and **(c)** – **(d)** 500 ppm after 7h of contact time with **[P4444][Glu]/[N2224][NTf2]** or **[P4444][Glu]/[N1444][NTf2]** (inset spectra are intensity expanded to observe trace amount of benzene).

Table S1. Gelation tests performed in conventional solvents for the gelators used.

Solvent	C (wt%)	$[P_{6\,6\,6\,14}]$[Glu]	$[P_{4\,4\,4\,4}]$[Glu]	$[N_{4\,4\,4\,4}]$[Glu]
methanol	1 - 3	SC	SC	SC
ethanol	1 - 3	SC	SC	SC
1-propanol	1 - 3	SC	SC	SC
2-propanol	1 - 3	SC	SC	SC
butanol	1 - 3	SC	SC	SC
pentanol	1 - 3	SC	SC	SC
hexanol	1 - 3	SC	SC	SC
octanol	1 - 3	SC	SC	SC
distilled water	1 - 3	SC	SC	SC
sea water	1 - 3	SC	SC	SC
1,3-propanediol	1 - 3	SC	SC	SC
triethylene glycol	1 - 3	SC	SC	SC
n-hexane	1 - 3	I	I	I
n-heptane	1	I	I	I
cyclohexane	1	SC	SC	SC
petroleum ether	1	SC	I	I
R-limonene	0.5 - 1	I	I	I
ethyl lactate	1 - 3	S	S	S
olive oil	1 - 5	S	S	S
sweet corn oil	1 - 5	S	S	S
mixed seeds oil	1 - 5	I	I	I
silicon oil	1 - 5	I	S	I
paraffin oil	1 - 5	PG	S	I
engine oil	1 - 5	S	S	S
diesel	1 - 5	S	I	I

S= soluble after heating; I= insoluble; SC= soluble without heating; PG= gel like precipitate.

Table S2. Stretching frequencies corresponding to gelator ($\nu_{gelator}$) and ILGs (ν_{ILG}) and changes in stretching frequencies ($\Delta\nu$) on going from gelator to gel phase.

Ionogel	$\nu_{gelator}$ / cm^{-1}	ν_{ILG} / cm^{-1}	$\Delta\nu$ / cm^{-1}
[$P_{6\,6\,6\,14}$][Glu]/[$N_{1\,4\,4\,4}$][NTf_2]	3540	3540	0
	3428	3428	3
	3306	3314	-8
	3161	3166	-5
	1618	1618	12
	1448	1462	-14
	1398	1348	50
[$P_{6\,6\,6\,14}$][Glu]/[$N_{2\,2\,2\,4}$][NTf_2]	3540	3540	0
	3431	3428	3
	3306	3314	-8
	3161	3166	-7
	1630	1621	9
	1448	1460	-12
	1398	1352	46
[$P_{6\,6\,6\,14}$][Glu]/[C_1C_4pyrr][NTf_2]	3540	3545	-5
	3431	3428	3
	3306	3311	-5
	3161	3166	-5
	2930	2969	-39
	2860	2883	-23
	1630	1628	2
	1448	1467	-19
	1398	1353	45
[$P_{6\,6\,6\,14}$][Glu]/[C_1C_4pip][NTf_2]	3540	3545	-5
	3431	3428	3
	3306	3311	-5
	3161	3166	6
	2930	2964	-34
	2860	2880	-20
	1630	1621	9
	1448	1469	-21

	1398	1354	44
[$P_{4\,4\,4\,4}$][Glu]/[$N_{1\,4\,4\,4}$][NTf_2]	3572	3629	-57
	3552	3554	-2
	3416	3433	-17
	3300	3312	-12
	3158	3166	-8
	2929	2970	-41
	2862	2870	-8
	1613	1638	-25
[$P_{4\,4\,4\,4}$][Glu]/[$N_{2\,2\,2\,4}$][NTf_2]	3572	3631	-59
	3552	3545	7
	3416	3432	-16
	3300	3311	-11
	3158	3167	-9
	1613	1632	-19
[$N_{4\,4\,4\,4}$][Glu]/[$N_{1\,4\,4\,4}$][NTf_2]	3566		
	3444	3344	-22
	3322		
	2977	2977	0
	2933	2877	56
	2855		
	1638	1596	42
	1602		
	1447	1463	-16
	1397	1353	44

Table S3. Adsorption efficiency (AE)[a] of sulphur compounds on ILGs at 6.5% wt of gelator and corresponding ILs at 20 °C.

Adsorbent	AE (%) T		AE (%) BT		AE (%) DBT	
	t = 24 h	t = 48 h	t = 24 h	t = 48 h	t = 24 h	t = 48 h
$[N_{2\,2\,2\,4}][NTf_2]$	83.7	87.0	56.2	56.9	57.2	54.7
$[P_{4\,4\,4\,4}][Glu]/[N_{2\,2\,2\,4}][NTf_2]$	49.5	60.4	57.7	67.2	46.8	68.0
$[P_{4\,4\,4\,4}][Glu]/[N_{2\,2\,2\,4}][NTf_2]$ (30 °C)	47.2	60.9				
$[N_{1\,4\,4\,4}][NTf_2]$	12.0	53.2	47.2	53.3	49.9	73.8
$[N_{4\,4\,4\,4}][Glu]/[N_{1\,4\,4\,4}][NTf_2]$	22.9	86.4	45.0	52.8	27.5	46.2
$[P_{4\,4\,4\,4}][Glu]/[N_{1\,4\,4\,4}][NTf_2]$	40.6	82.4	41.2	53.8	26.5	46.5
$[P_{4\,4\,4\,4}][Glu]/[N_{1\,4\,4\,4}][NTf_2]$ (30 °C)	57.6	65.3				

[a]AE values were reproducible within ± 2 %.

Table S4. Adsorption efficiency (AE)[a] of sulphur compounds on **$[P_{4\,4\,4\,4}][Glu]/[N_{2\,2\,2\,4}][NTf_2]$** at 6.5% wt of gelator as a function of the time at 20 °C.

T		BT		DBT	
Time (h)	**AE (%)**	**Time (h)**	**AE (%)**	**Time (h)**	**AE (%)**
2	8.2	1	14.2	1	18.7
4	21.3	2	15.6	2	18.3
6	32.8	3	19.8	3	17.6
7	33.7	5.5	23.8	4	29.1
8	42.1	6	30.7	6	37.8
16	50.9	7.5	36.7	7.5	38.8
19	49.8	9	39.5	8	40
22	47.9	15	41.6	15	39.4
24	48.8	18	40.3	18	41.4
		21	47.8	21	46.1
		24	57.7	24	46.8

[a]AE values were reproducible within ± 2 %.

Table S5. Adsorption efficiency (AE)[a] of sulphur compounds on **[P$_{4444}$][Glu]/[N$_{1444}$][NTf$_2$]** at 6.5% wt of gelator as a function of the time at 20 °C.

T		BT		DBT	
Time (h)	**AE (%)**	**Time (h)**	**AE (%)**	**Time (h)**	**AE (%)**
1	0	1	26.8	1	6.9
2	10.5	2	27.0	2	5.2
3	22.5	3	25.9	3	9.3
4	23.8	4	24.4	4	17
6	22.6	5	24.2	6	17
8	21.6	6	28.2	8	18.6
9	24.5	7	30.3	9	19.7
15	29	8	31.7	16	27.0
17	27.8	9	31.0	19	29.4
19	32.2	15	32.6	22	27.5
22	36.9	17	36.3	24	26.5
24	40.6	19	40.0		
		23	45.0		
		24	41.0		

[a]AE values were reproducible within ± 2 %.

Table S6. Adsorption efficiency (AE)[a] of sulphur compounds on ILGs at 6.5% wt of gelator, using solution of single components (C = 1500 ppm) or mixed solutions (C = 1500 ppm), at 20 °C.

	[P$_{4444}$][Glu]/[N$_{2224}$][NTf$_2$]			**[P$_{4444}$][Glu]/[N$_{1444}$][NTf$_2$]**		
	AE (%)			**AE (%)**		
	T	BT	DBT	T	BT	DBT
Single	42.6	54.5	51.2	42.6	54.5	51.2
Mix	58.1	78.0	78.2	15.0	58.1	55.7

[a]AE values were reproducible within ± 2 %.

Table S7. Adsorption efficiency (AE)[a] of sulphur compounds on ILGs at 6.5% wt of gelator, as a function of concentration of sulphur compounds, at 20 °C.

	$[P_{4\,4\,4\,4}][Glu]/[N_{2\,2\,2\,4}][NTf_2]$			**$[P_{4\,4\,4\,4}][Glu]/[N_{1\,4\,4\,4}][NTf_2]$**		
$C_{T,BT,DBT}$(ppm)	**AE (%)**			**AE (%)**		
	T	BT	DBT	T	BT	DBT
900	51.3	53.9	54.0	0	25.7	34.3
1500	58.1	78.0	78.2	15.0	58.1	55.7
2250	62.2	72.8	72.9	31.5	68.3	73.2
3000	67.4	76.9	81.2	56.2	72.6	71.4

[a]AE values were reproducible within ± 2 %.

Table S8. Adsorption efficiency (AE)[a] of sulphur compounds on ionic liquid gels, at 6.5% wt of gelator, as a function of fuel volume (C = 1500 ppm), at 20 °C.

	$[P_{4\,4\,4\,4}][Glu]/[N_{2\,2\,2\,4}][NTf_2]$			**$[P_{4\,4\,4\,4}][Glu]/[N_{1\,4\,4\,4}][NTf_2]$**		
***V* (μL)**	**AE (%)**			**AE (%)**		
	T	BT	DBT	T	BT	DBT
300	68.1	84.0	84.2	27.0	52.1	51.0
400	69.1	80.6	82.5	26.0	53.1	56.2
500	58.1	78.0	78.2	15.0	58.1	55.7
700	43.4	46.6	60.6	0	50.2	50.2

[a]AE values were reproducible within ± 2 %.

Table S9. Adsorption efficiency (AE)[a] of sulphur compounds (C = 1500 ppm) on ILGs, at 6.5% wt of gelator, as a function of vial diameter, at 20 °C.

	$[P_{4\,4\,4\,4}][Glu]/[N_{2\,2\,2\,4}][NTf_2]$			**$[P_{4\,4\,4\,4}][Glu]/[N_{1\,4\,4\,4}][NTf_2]$**		
***d* (cm)**	**AE (%)**			**AE (%)**		
	T	BT	DBT	T	BT	DBT
0.5	58.1	78.0	78.2	15.0	58.1	55.7
1	13.8	46.0	47.2	10	40.8	42.6

[a]AE values were reproducible within ± 2 %.

Table S10. Adsorption efficiency (AE)[a] of sulphur compounds (C = 1500 ppm) on ILGs, at 6.5% wt of gelator, using different ways of use, at 20 °C.

$[P_{4444}]$[Glu]/ $[N_{2224}][NTf_2]$			**$[P_{4444}]$[Glu]/$[N_{1444}][NTf_2]$**		
AE (%)			**AE (%)**		
T	BT	DBT	T	BT	DBT
58.1	78.0	78.2	15.0	58.1	55.7

[a]AE values were reproducible within ± 2 %.

Table S11. Adsorption efficiency (AE)[a] of sulphur compounds (C = 1500 ppm) on ILGs, at 6.5% wt of gelator, after different cycles of reuse, at 20 °C.

	$[P_{4444}]$[Glu]/ $[N_{2224}][NTf_2]$			**$[P_{4444}]$[Glu]/$[N_{1444}][NTf_2]$**		
	AE (%)			**AE (%)**		
	T	BT	DBT	T	BT	DBT
I cycle	58.1	78.0	78.7	15.0	58.1	55.7
II cycle	26.5	36.2	36.2	25.5	42.0	40.2
III cycle	32.0	31.1	31.4	24.4	38.7	41.3
IV	23.3	17.0	16.3	19.2	31.9	34.5
				22.4	15.5	16.3

[a]AE values were reproducible within ± 2 %.