Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Targeting adequate thermal stability and fire safety in selecting ionic liquid-based electrolytes for energy storage †

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† Electronic Supplementary Information (ESI) available

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SI-1: Synthesis of the electrolytes

The 1-butyl-3-methylimidazolium chloride was synthetized following this procedure. N-methylimidazole (99 %wt) was purchased from Sigma Aldrich and purified by distillation. Butylchloride (1.3 equivalent, Sigma Aldrich, 99 %wt) and N-methylimidazole (1 equivalent) were mixed without solvent at 70 °C during 3 days. The resulting IL was a white solid and was washed and recrystallized in toluene at 0 °C. Finally, this $[C_1C_4Im][Cl]$ was dried under primary vacuum at ambient temperature for 24 h. The chemical structure and the purity of the $[C_1C_4Im][Cl]$ were checked by ^1H and ^{13}C NMR. The 1-butyl-1-methylpyrrolidinium chloride (98 %) was purchased from Solvionic and used as received.

The NTf_2-based ILs were prepared by mixing 1 equivalent of the chloride IL with 1.1 equivalent of lithium bis(trifluoromethanesulfonylimide) ($LiNTf_2$) salt (Solvionic, 99.5 %wt, dried at 120 °C under high vacuum for 48 h) in water at ambient temperature for 24 hours. After several extractions with dichloromethane (Aldrich, 99.8 %), the absence of chloride anion was tested using silver nitrate. It was then filtered through silica, and the solvent was evaporated under vacuum. The NTf_2-based ILs $[C_1C_4Im][NTf_2]$ and $[PYR_{14}][NTf_2]$ were vacuum-dried at room temperature for 48 h under 10^{-5} mbars followed by a storage in an argon-filled glove box. The structure was checked by ^1H and ^{13}C liquid

NMR Bruker Avance 300 with probe BBO 5 mm at 27 °C, using deuterated dichloromethane as solvent. Standard 5 mm borosilicate NMR tubes were used. Chemical shifts were reported in ppm (singlet = s, doublet = d, and multiplet = m). Impurity levels of the ILs were then measured. Their water content was lower than 60 ppm (mass ratio), as assessed by Karl Fisher coulometric titration. The chloride content was lower than 0.5 % as shown by mass spectroscopy.

The electrolytes were prepared by adding $LiNTf_2$ (1 mol.L^{-1}) in a well stirred and dried IL at room temperature, and will be referred to as $[C_1C_4Im][Li][NTf_2]$ and $[PYR_{14}][Li][NTf_2]$. Finally the neat ILs and electrolytes were vacuum-dried at room temperature for 48 h under 10^{-5} mbars followed by storage in an argon-filled glove box.

SI-2: NMR characterisation of the ILs

$[C_1C_4Im][NTf_2]$

^{1}H NMR

δ = 0.990 (t, 3H, N-$(CH_2)_3$-C**H**$_3$), 1.395 (m, 1.99H, N-$(CH_2)_2$-C**H**$_2$-CH_3), 1.880 (m, 2.00H, N-CH_2-C**H**$_2$-), 3.949 (s, 2.98H, N-C**H**$_3$), 4.190 (t, 2.03H, N-C**H**$_2$-), 5.356 (s, CD_2Cl_2), 7.339 (s, 1.93H, N-C**H**=C**H**-N), 8.640 (s, 0.97H, N=C**H**-N)

^{13}C NMR

δ=13.321 (N-$(CH_2)_3$-**C**H_3), 19.649 (N-$(CH_2)_2$-**C**H_2-CH_3), 32.220 (N-CH_2-**C**H_2-), 36.601 (N-**C**H_3), 50.301 (N-**C**H_2-), 53.867 (m, CD_2Cl_2), 120.221 (m, N-$(SO_2$**C**$F_3)_2$), 122.760 (**C4**H), 124.101 (**C5**H), 136.079 (N=**C**H-N)

$[PYR_{14}][NTf_2]$

^{1}H NMR

δ = 1.013 (t, 3H, N-$(CH_2)_3$-C**H**$_3$), 1.4375 (m, 2.01H, N-$(CH_2)_2$-C**H**$_2$-CH_3), 1.770 (m, 2.21H, N-CH_2-C**H**$_2$-), 2.268 (m, 4H, N-CH_2-C**H**$_2$-C**H**$_2$-CH_2-N), 3.036 (s, 3.01H, N-**C**H_3), 3.298 (m, 2.04H, N-C**H**$_2$-), 3.506 (m, 4.05H, N-C**H**$_2$-CH_2-CH_2-C**H**$_2$-N), 5.368 (s, CD_2Cl_2)

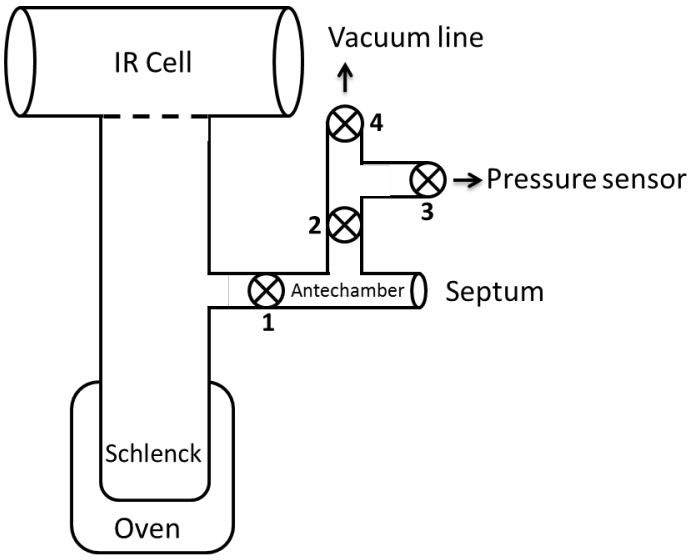
^{13}C NMR[1]

δ=13.674 (N-$(CH_2)_3$-**C**H_3), 19.908 (N-$(CH_2)_2$-**C**H_2-CH_3), 21.895 (N-CH_2-**C**H_2-**C**H_2-CH_2-N), 26.037 (N-CH_2-**C**H_2-), 48.877 (N-**C**H_2), 53.871 (m, CD_2Cl_2), 65.053 (N-**C**H_3 and N-**C**H_2-CH_2-CH_2-**C**H_2-N), 120.255 (quadruplet, N-$(SO_2$**C**$F_3)_2$)

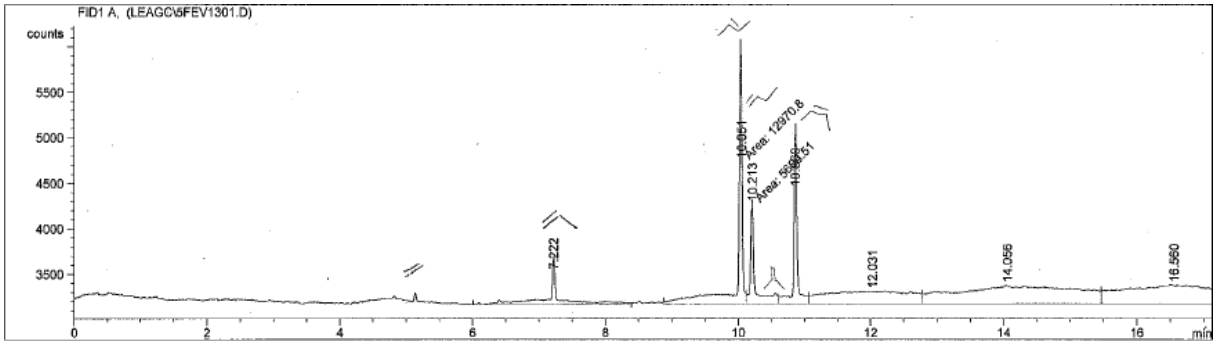
SI-3: Setup to analyse the decomposition products formed during thermal treatment of the electrolytes $[C_1C_4Im][Li][NTf_2]$ and $[PYR_{14}][Li][NTf_2]$ during 2 h at 350 °C

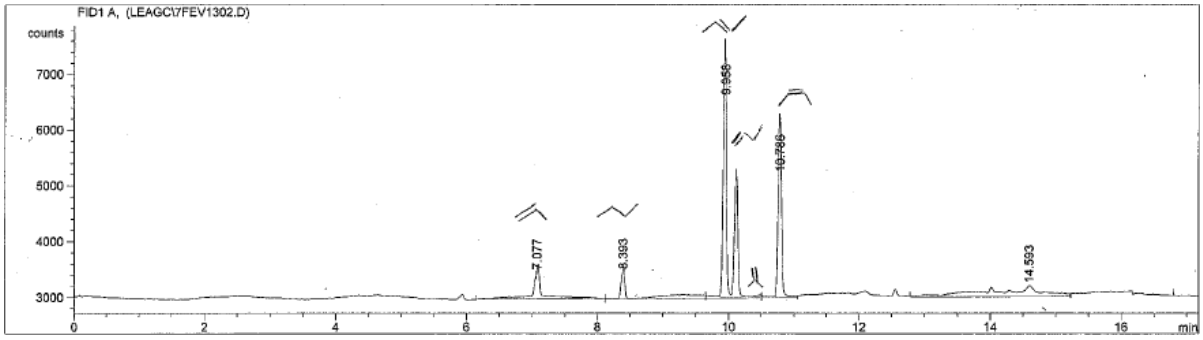
In the glove box, 3 mL of the electrolytes $[C_1C_4Im][Li][NTf_2]$ and $[PYR_{14}][Li][NTf_2]$ were introduced in an apparatus depicted below. They were dried under high vacuum (10^{-5} mbar) overnight before the experiment. A blank was collected for the Infrared (IR) spectra of the system using the connected IR cell. The entire system was put under vacuum, with 4 valves open. The reactor was then isolated closing valve 4. The solution was heated by a tubular oven at 10 °C.min^{-1} up to 350 °C. It was kept for 2 hours at this temperature while the pressure of the emitted gas was measured (by the pressure sensor). At the end of the two hours, valve 2 and 3 were closed and the system was cooled down to room temperature.

The system was disconnected from the vacuum line (at valve 4). The gaseous phase was analysed by infrared spectroscopy. Gas aliquots were taken up by closing valve 1 and introducing a syringe by the septum. To reproduce the analysis, the system was purged up to valve 1 (closing valve 1, open 4th and 2nd), gas was brought to the antechamber by closing valve 2 and opening 1 and taken through the septum. The gas samples were analysed by GC and GC-MS. After the gas phase analysis, the schlenk was disconnected from the IR cell in a glove box, and the liquid phase was analysed by ^{1}H, ^{13}C, ^{19}F and ^{7}Li liquid NMR, and by coupled GC-MS.

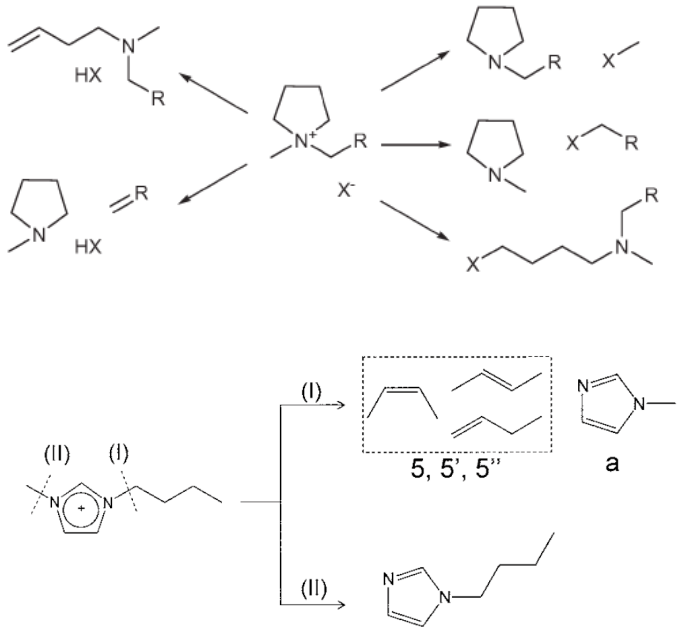


SI-4: GC chromatogram of $[C_1C_4Im][Li][NTf_2]$ (top) and $[PYR_{14}][Li][NTf_2]$ (bottom) on KCl on alumina column

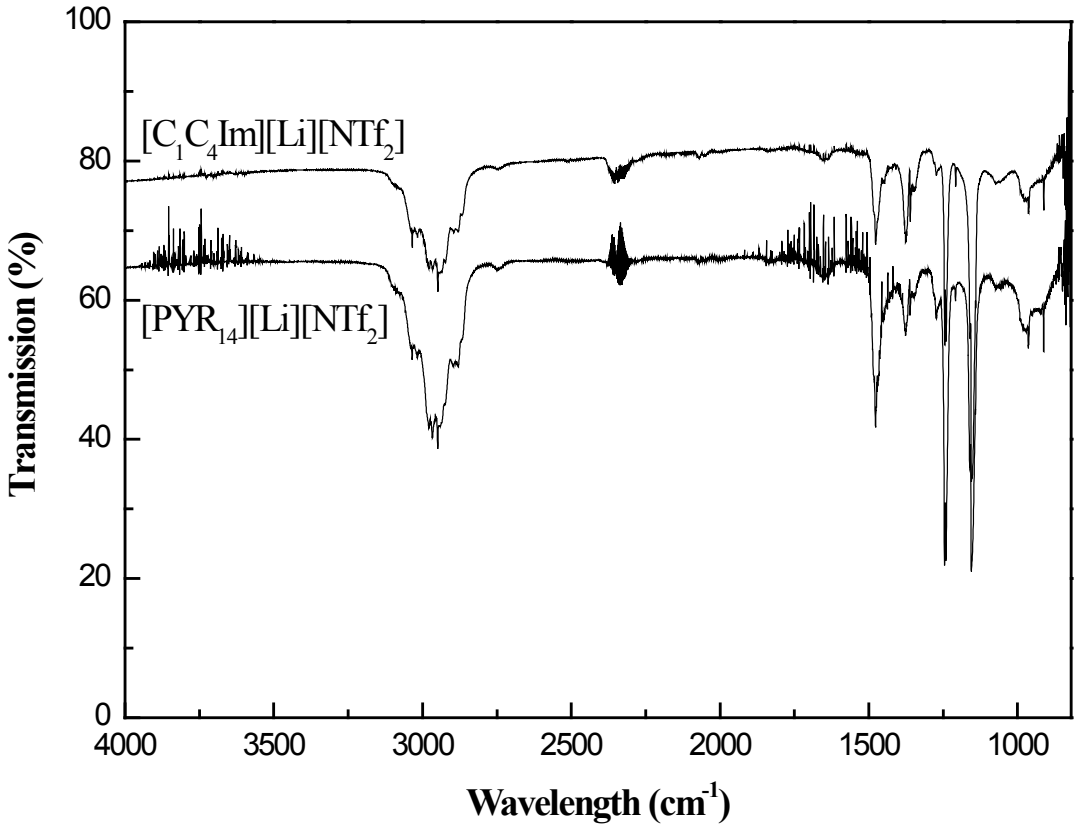




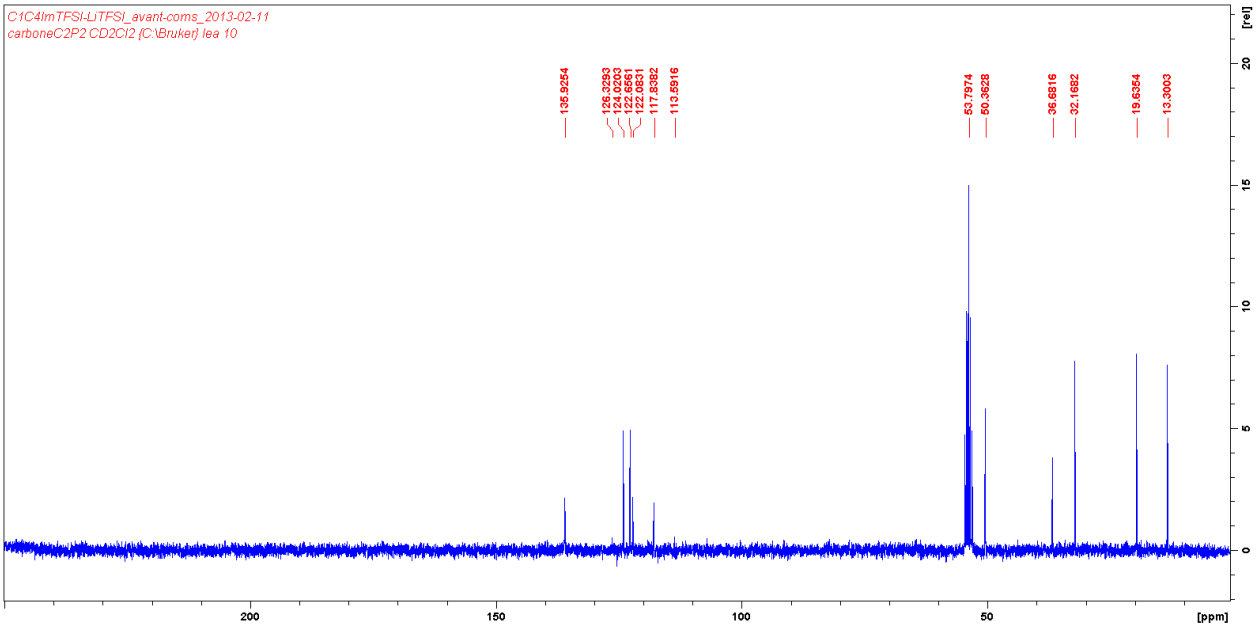
SI-5: Decomposition mechanisms of imidazolium and pyrrolidinium cations [2,3]

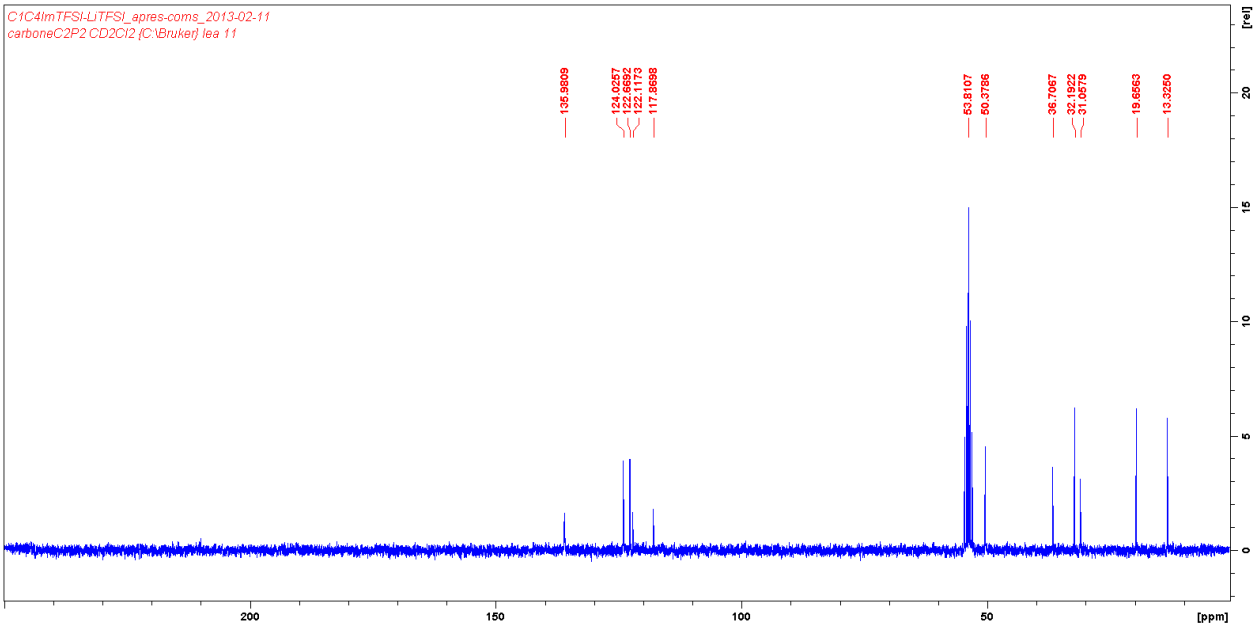


SI-6: Infrared spectra of electrolytes gas phase (after blank subtraction)

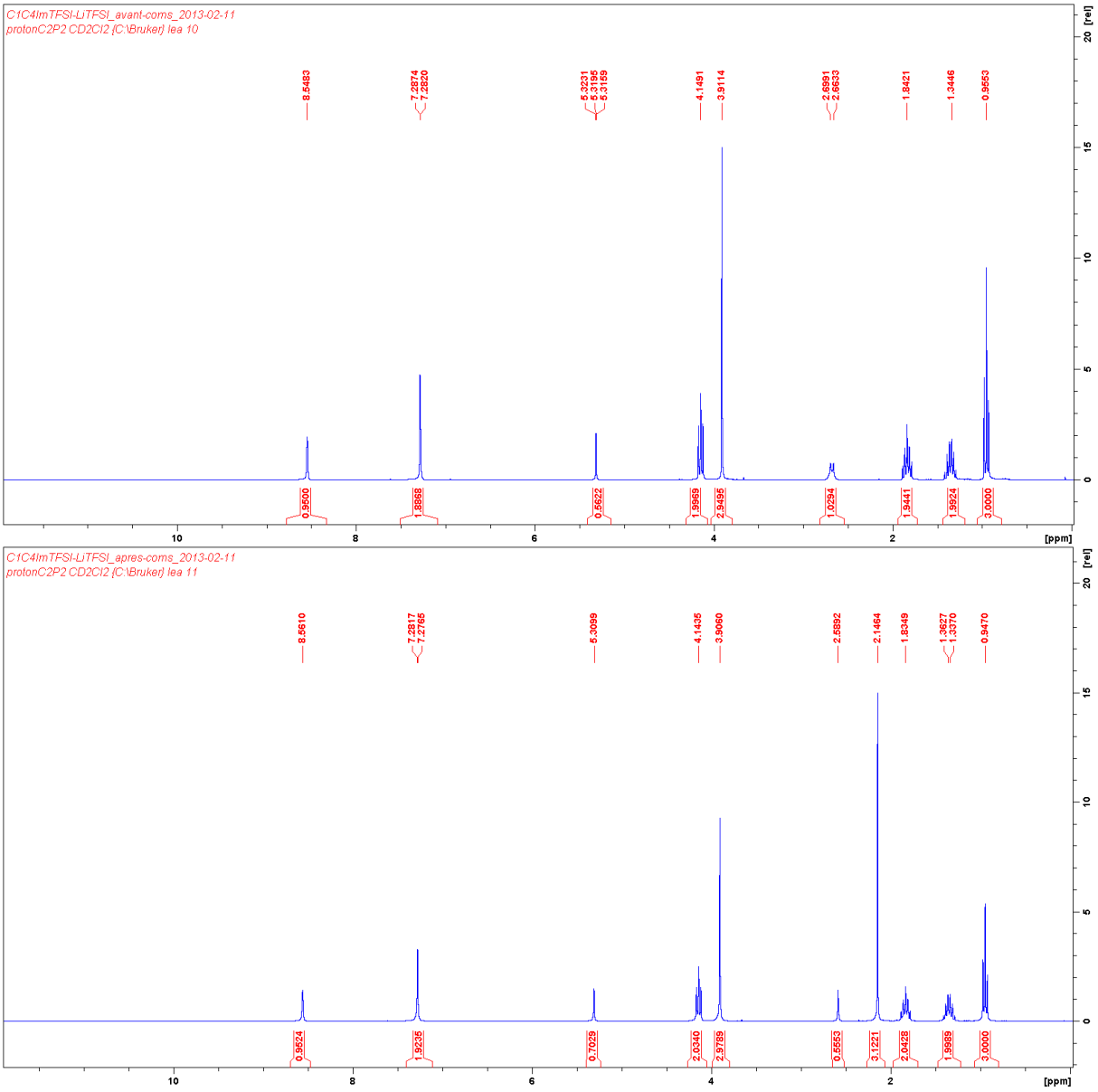


SI-7: Liquid phase study by ^{1}H, ^{13}C, ^{19}F and ^{7}Li solution NMR

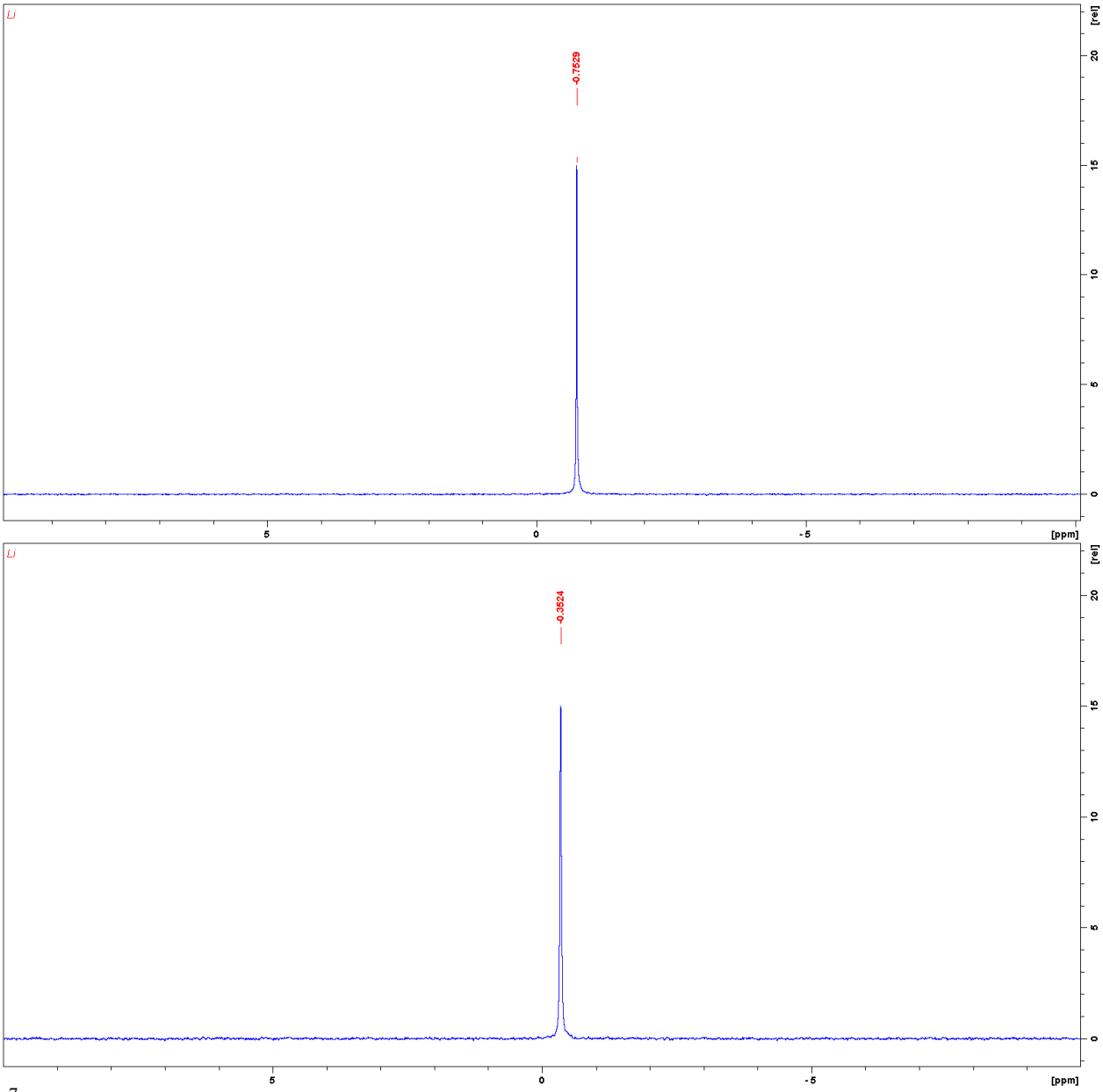




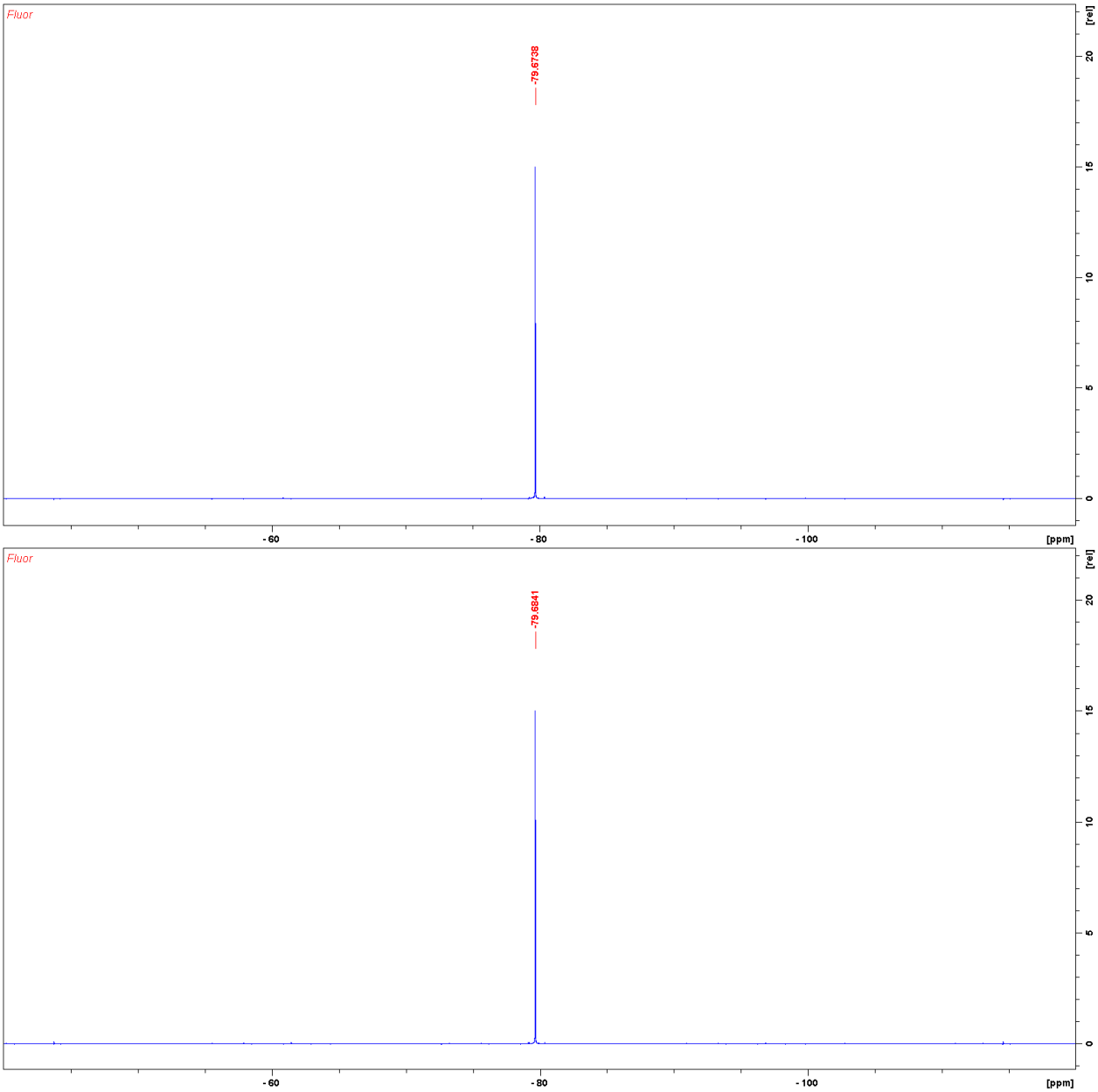
^{13}C NMR spectra of $[C_1C_4Im][Li][NTf_2]$ before (top) and after (bottom) thermal treatment



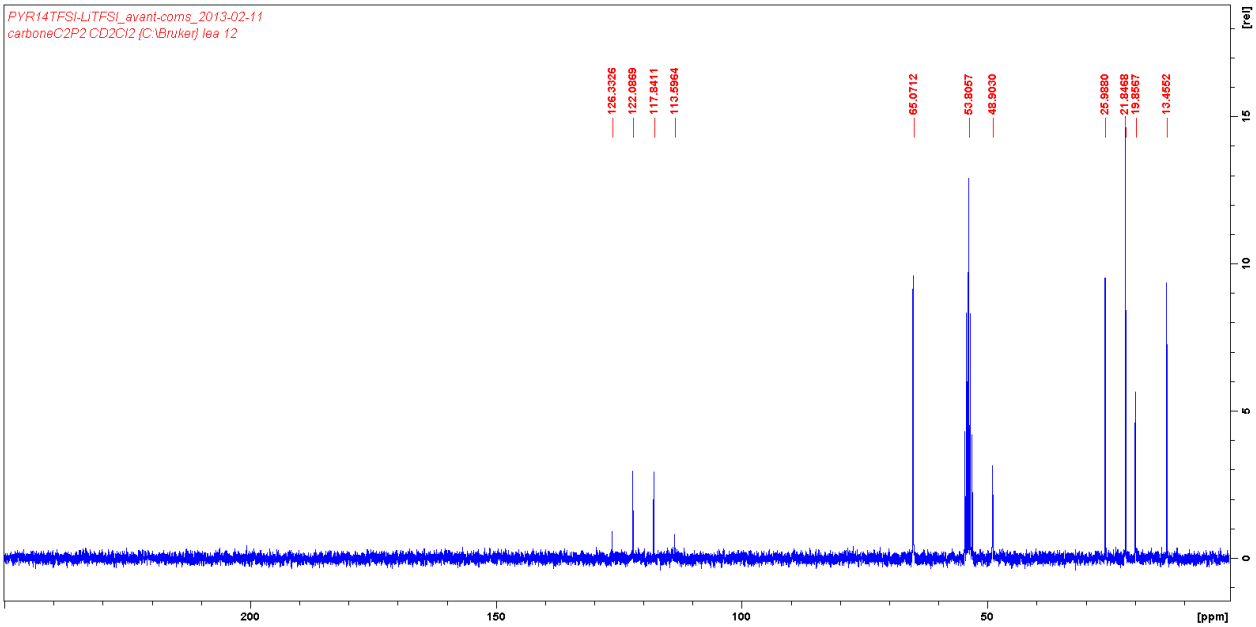
^{1}H NMR spectra of $[C_1C_4Im][Li][NTf_2]$ before (top) and after (bottom) thermal treatment

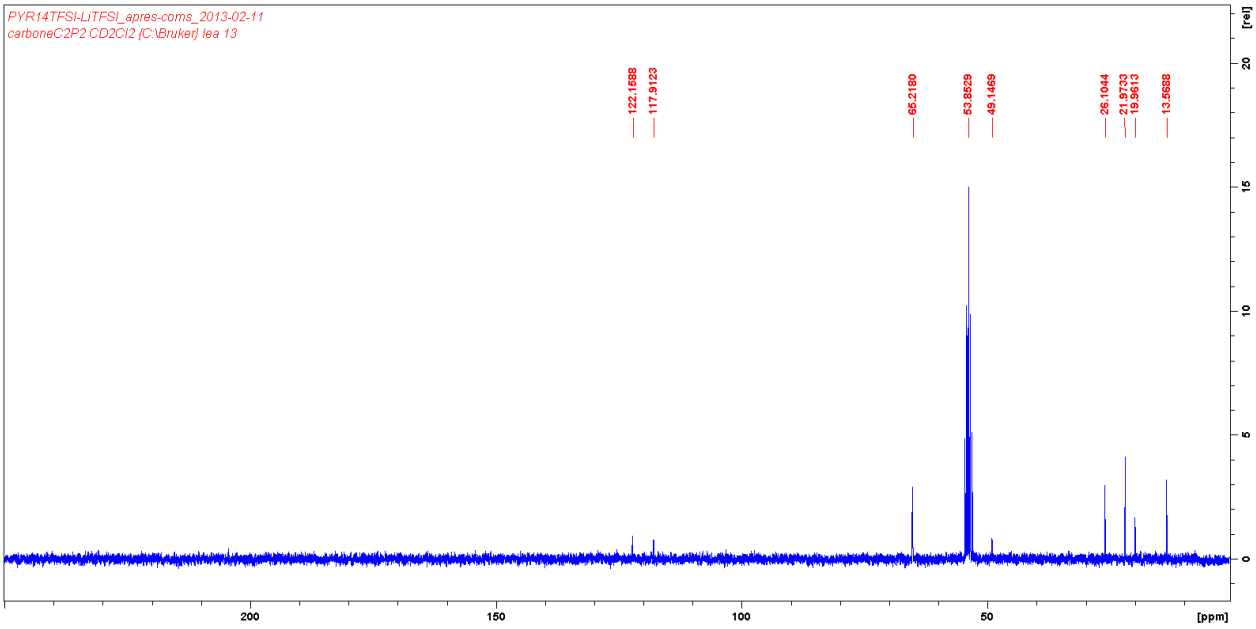


^{7}Li NMR spectra of $[C_1C_4Im][Li][NTf_2]$ before (top) and after (bottom) thermal treatment

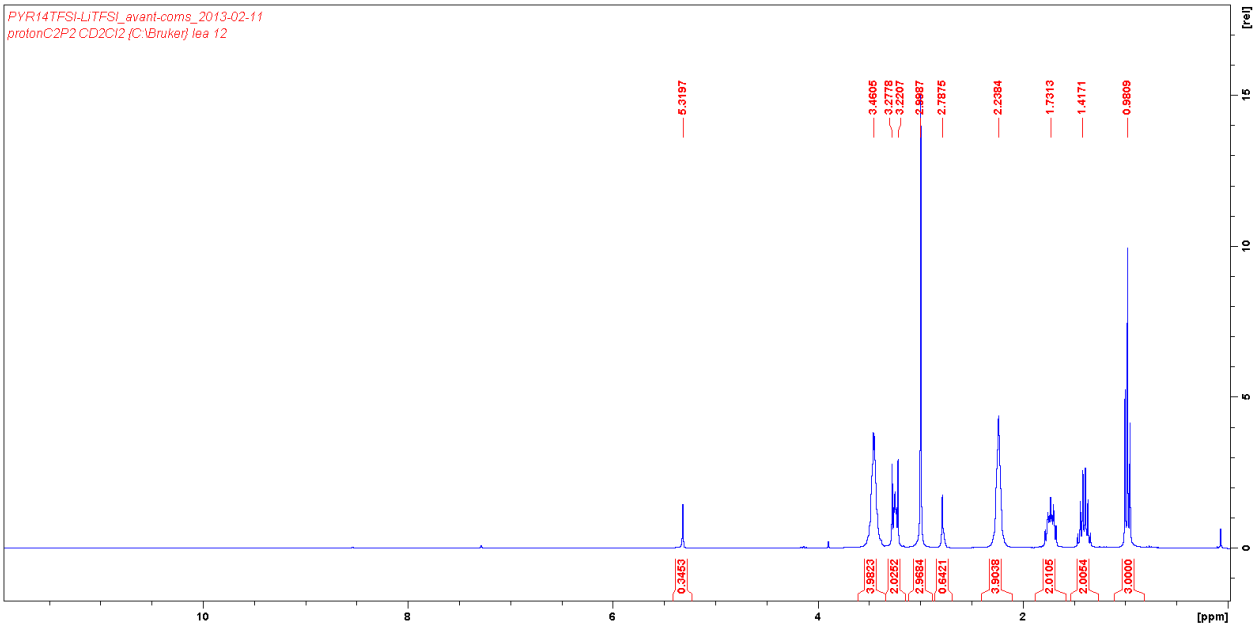


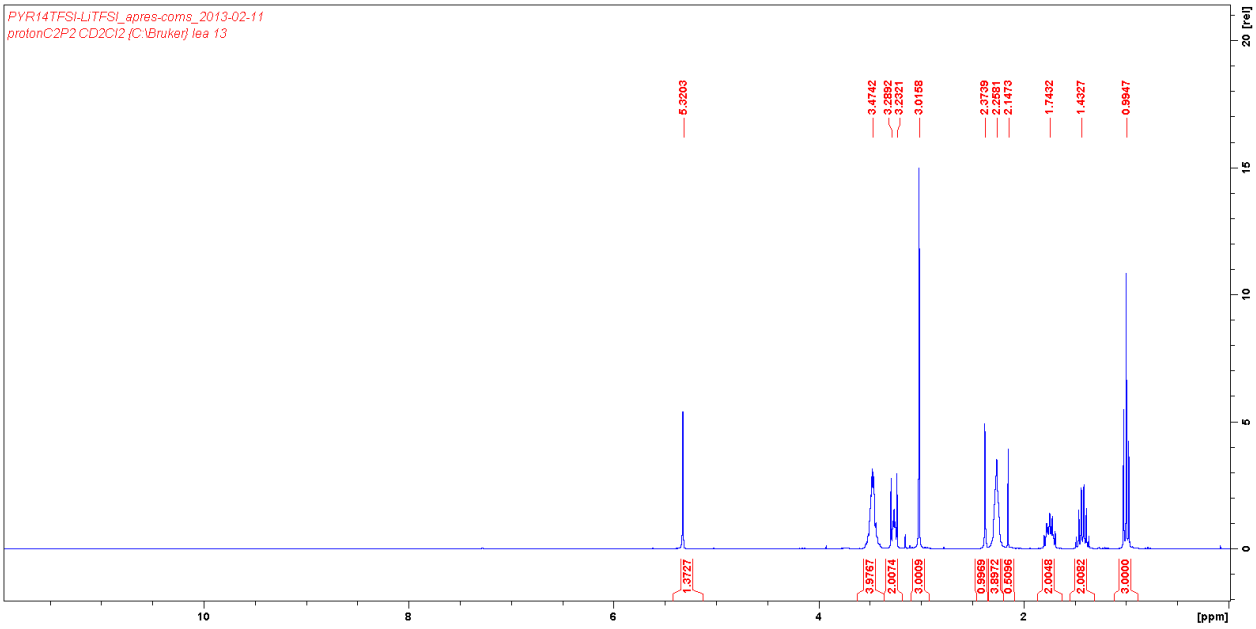
^{19}F NMR spectra of $[C_1C_4Im][Li][NTf_2]$ before (top) and after (bottom) thermal treatment



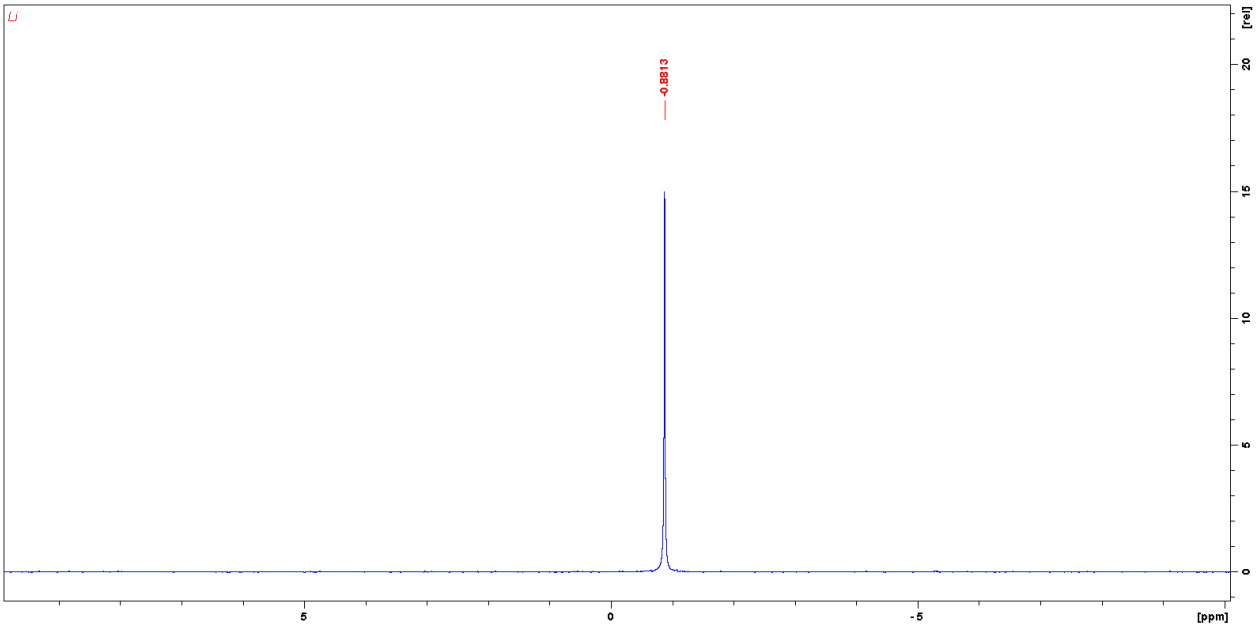


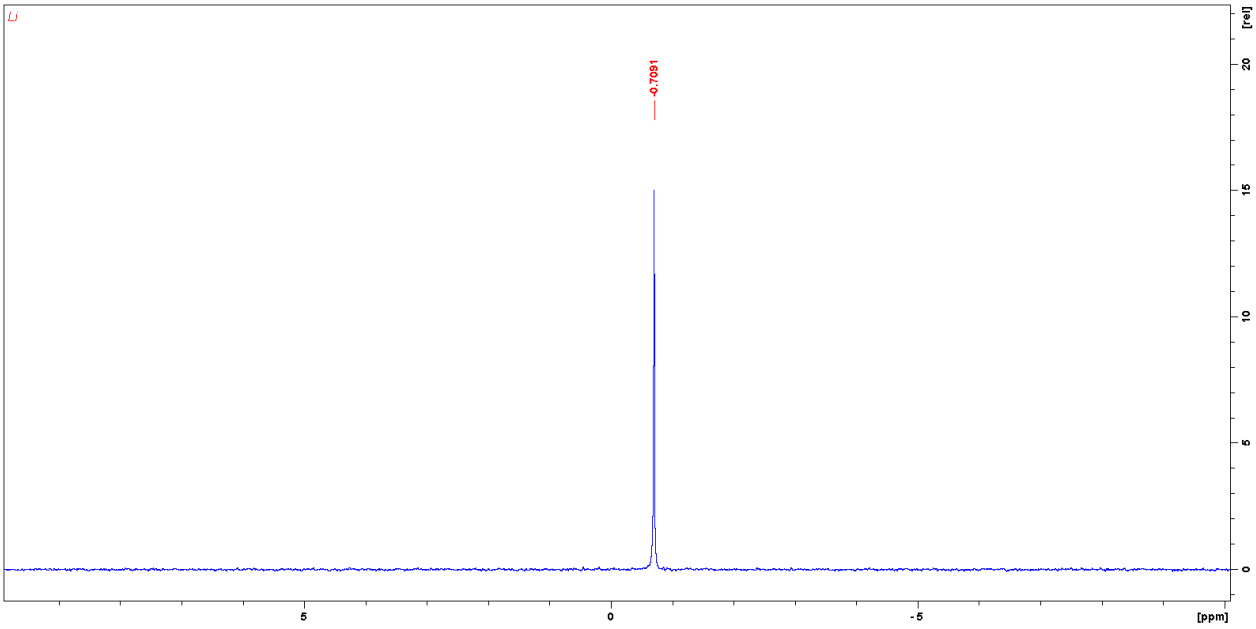
^{13}C NMR spectra of [PYR$_{14}$][Li][NTf$_2$] before (top) and after (bottom) thermal treatment



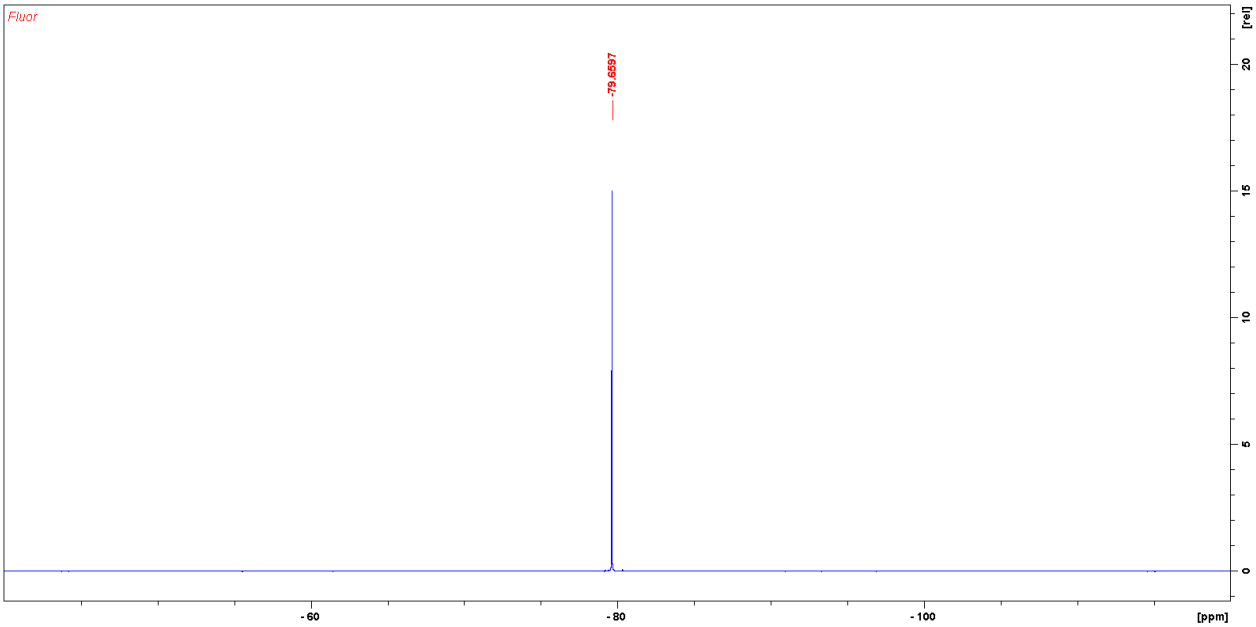


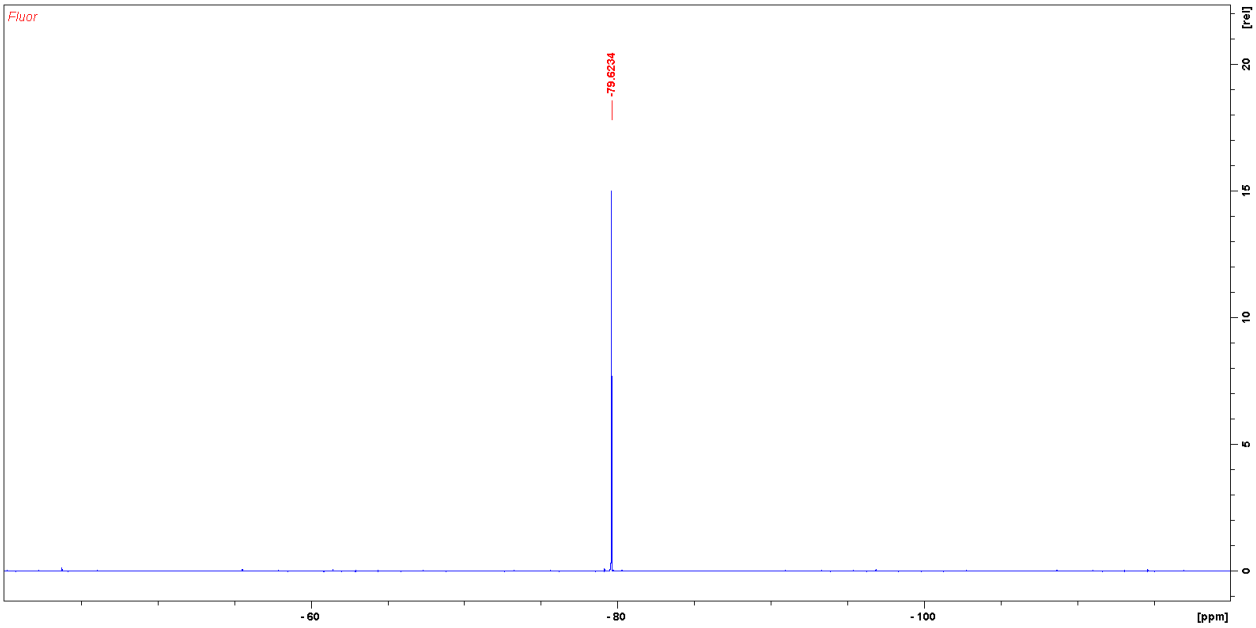
^{1}H NMR spectra of $[PYR_{14}][Li][NTf_2]$ before (top) and after (bottom) thermal treatment





^{7}Li NMR spectra of $[C_1C_4Im][Li][NTf_2]$ before (top) and after (bottom) thermal treatment





^{19}F NMR spectra of $[C_1C_4Im][Li][NTf_2]$ before (top) and after (bottom) thermal treatment

SI-8 Data validation from the Tewarson tests

It is a routine practice in the lab where the Tewarson apparatus is used to check validity of data from the calculation of mass balance regarding main elements contained in the test samples.

	$[C_1C_4Im][NTf_2]$	$[PYR_{14}][NTf_2]$	$[C_1C_4Im][Li][NTf_2]$	$[PYR_{14}][Li][NTf_2]$
Initial mass (g)	59,3	51,3	61,9	65,1
Residual mass (g)	8,6	2,9	9,2	4,8
		% of element in the residue		
Carbon	49,8	60,9	50,1	55,6
Fluorine	8,7	9,9	11,1	10,1
Sulphur	5,5	7,1	4,4	3,2
		Mass of residue (g)		
Carbon	4,28	1,77	4,61	2,67
Fluorine	0,75	0,29	1,02	0,48
Sulphur	0,47	0,21	0,40	0,15
		Conversion efficiency without residue (%)		
Carbon	66	92,5	59,1	69,3
Fluorine	73,5	76,1	81,3	65,6
Sulphur	86,9	98,2	91,8	89,7
		Conversion efficiency with residue (%)		
Carbon	91,5	103,6	88,6	84,3
Fluorine	78,2	78,2	86,9	68,1
Sulphur	92,1	100,9	95,8	91,1

Carbon and sulphur balance examination

Carbon and sulphur recovery efficiencies from sample content into identified carbonated or S-containing species (in flue gas) or as C or S content (in solid residues) lied in between 84% and 103 % for carbon and 91 % to 101 % for sulphur respectively. This confirmed to our experience (several thousand test runs with the *Tewarson Apparatus*) that no special concern in the performance of the experiments and related data computations appeared. From dedicated analysis of fire calorimetry accuracy analysis, we know that, at lab scale, errors in yields of energy and product releases may be in the order of some 5 to 10%. Accuracy varies according to complexity of test samples (decreasing with complexity of structure and number of hetero-atom in test molecules) and operating conditions. Such error levels keep however quite reasonable for fire safety engineering purposes, owing to complexity of fire phenomena.

Fluorine balance examination

Observed conversion efficiency is thought reasonable, although classically lower than for carbon and sulphur mass balances. Although latest standards for the sampling and measurements are applied routinely (by use of ISO standards developed by ISO TC92 SC3 Committee: *Fire Threat to People and the Environment*), we are confronted here to

potentially non identified species in the flue gas, or absorption issues in apparatus hood and ducting system and/or sampling line.

References

1. J. Golding, S. Forsyth, D. R. MacFarlane, M. Forsyth and G. B. Deacon, *Green Chem.*, 2002, **4**, 223-229.
2. T. J. Wooster, K. M. Johanson, K. J. Fraser, D. R. MacFarlane and J. L. Scott, *Green Chem.*, 2006, **8**, 691-696.
3. H. Ohtani, S. Ishimura and M. Kumai, *Anal. Sci.*, 2008, **24**, 1335-1340.