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# Aging effects on the properties of imidazolium, quaternary ammonium, pyridinium and pyrrolidinium-based ionic liquids used in fuel and energy production

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Ionic liquids are often cited for their excellent thermal stability, a key property for their use as solvents and in the chemical processing of biofuels. However, there has been little supporting data on the long term aging effect of temperature on these materials. Imidazolium, quaternary ammonium, pyridinium, and pyrrolidinium-based ionic liquids with the bis(trifluoromethylsulfonyl)imide and bis(perfluoroethylsulfonyl)imide anions were aged for 2520 hours (15 weeks) at 200°C in air to determine the effects of an oxidizing environment on their chemical structure and thermal stability over time. It was found that the minor changes in the cation chemistry could greatly affect the properties of the ILs over time.

**KEY WORDS:** ionic liquid, bis(trifluoromethylsulfonyl)imide, bis(perfluoroethylsulfonyl)imide, FT-IR, TGA, imidazolium, ammonium, pyrrolidinium, pyridinium, butonic acid

## **INTRODUCTION**

Discovered as recently as the late 1800s, ionic liquids (ILs) are a unique class of compounds that have emerged as a popular topic of research in the last several years. Ionic liquids are defined as ionic compounds whose melting points are below 100°C <sup>1</sup>. They are often comprised of bulky organic cations and organic or inorganic anions, such

as 1-butyl-3-methylimidazolium ( $[C_4mim]^+$ ), bis(trifluoromethylsulfonyl)imide ( $[Tf_2N]^-$ ) or hexafluorophosphate ( $[PF_6]^-$ ), although there are myriad other possible combinations of ions<sup>2</sup>. Properties attributed to this class of chemicals include ionic conductivity, negligible vapor pressure, non-flammability and high thermal stability. Ionic liquids, because of the aforementioned characteristics, are considered feasible candidates in numerous chemical applications such as heat transfer fluids used in concentrated solar power<sup>3</sup>, desulfurization<sup>4-5</sup>, dissolution of cellulose<sup>6-7</sup> and as solvents for chemical synthesis<sup>8-10</sup>.

In chemical processing, an ideal solvent will be compatible with common metals and stainless steel metals<sup>11</sup>, stable at high temperatures for long periods of time<sup>12</sup>, have low or negligible vapor pressure<sup>13-14</sup> to avoid costly pressure control apparatus, and have good thermal transport properties<sup>15-16</sup>. Ionic liquids have the potential to meet all these criteria, and with their “tunability” due to the large number of cation and anion combinations, they hold great promise as a common solvent of the future.

Especially as these compounds are considered for use in large-scale chemical processing schemes, their long term stability at higher temperatures is an important property that must be accurately determined. Some research has been done pertaining to the short-term effects of high temperatures on ionic liquids. It has been shown that the chemical nature of the anion predominantly determines the onset of thermal decomposition<sup>17</sup>, and in comparison with common IL anions, such as  $BF_4^-$ ,  $PF_6^-$ , and other halides, inclusion of the  $Tf_2N^-$  anion results in the greatest thermal stability<sup>18</sup>. In one particular study, Blake et. al performed a normal TGA experiment on  $[C_4mim][Tf_2N]$  at a constant ramp rate of 20°C/min to 500°C, and the onset of decomposition began at a

temperature >400°C. Other experiments, however, in which different temperatures (200°C, 300°C, and 375°C) were held constant for 120 minutes, revealed significant mass losses. Their conclusion was that simple TGA experiments cannot predict long-term thermal stability<sup>19</sup>, expressing the need for a long-term aging study.

The purpose of this study was to investigate the effect of long-term aging on the thermal stability and chemical structure of seven different ILs with common anions so as to explore their suitability for use at elevated temperatures for extended periods of time. This was accomplished by heating the ILs for 15 weeks at 200°C in an oxidizing environment and performing subsequent analyses on the aged chemicals. This data will help better assess the suitability of ionic liquids for long term performance in chemical processing at elevated temperatures.

## **EXPERIMENTAL**

### *Ionic Liquids*

Seven different ionic liquids were tested in this study. The chemicals and their respective abbreviations are:

1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>mim][Tf<sub>2</sub>N]

1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>mmim][Tf<sub>2</sub>N]

butyltrimethylammonium bis(trifluoromethylsulfonyl)imide [N<sub>4111</sub>][Tf<sub>2</sub>N]

1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>mpyrr][Tf<sub>2</sub>N]

4-dimethylamino n-butylpyridinium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N]

1-butyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide [C<sub>4</sub>mim][BETI]

1,1,1-trimethylammonium 1-butyonic acid bis(trifluoromethylsulfonyl)imide

$[N_{1114}CO_2][Tf_2N]$

$[C_4mim][Tf_2N]$ ,  $[C_4mmim][Tf_2N]$ ,  $[N_{4111}][Tf_2N]$ ,  $[C_4mpyrr][Tf_2N]$  were purchased as off the shelf chemicals from Ionic Liquid Technologies, Inc.  $[N_{1114}CO_2][Tf_2N]$  was purchased as a custom synthesis from Ionic Liquid Technologies, Inc.  $[C_4N_{11}pyr][Tf_2N]$  and  $[C_4mim][BETI]$  were synthesized by the following procedures:

$[C_4N_{11}pyr][Tf_2N]$

4-dimethylaminopyridine (0.409mol) was added to 100mL of chloroform and stirred until dissolved. Iodobutane was slowly added in 5% excess (0.430 mol) and stirred overnight. The chloroform was driven off by heating to 80°C and flowing air over the solution. An equimolar amount of bis(trifluoromethylsulfonyl)imide 80% aqueous solution (IoLiTec, Inc.) was added with an additional 20mL of DI H<sub>2</sub>O and allowed to stir overnight. The resulting ionic liquid was washed with DI H<sub>2</sub>O seven times was then bubbled with dry N<sub>2</sub> for 24 hours to help dry the ionic liquid.

$[C_4mim][BETI]$

A 1:1 molar ratio of 1-butyl-3-methylidazolium chloride (Aldrich) and Li bis(perfluoroethylsulfonyl)imide (3M) were mixed together and covered in 300mL of deionized water. The mixture was allowed to stir for 30 minutes after all salts were dissolved. The solution was allowed to settle into two phases. The organic phase was washed with DI water in a separatory funnel and allowed to settle for thirty minutes to

one hour. This process was repeated a minimum of three times. The organic phase was then bubbled with dry N<sub>2</sub> for 24 hours to help remove residual water and dry the IL. IC Anion analysis was completed to determine the level of residual chloride, which was undetectable by our testing methods.

Karl Fisher analysis indicated a final water content of 200 ppm for all ILs in this study.

They were not further dried prior to introduction to the aging oven.

### *Viscosity*

Viscosity was measured using the cone and plate method on a ThermoScientific Haake RheoStress 6000 with RheoWin software. A 1.0° carbon steel cone and flat plate was used. All measurements were conducted at 22°C and duplicated. The instrument was calibrated with the appropriate NIST standard for the viscosity window of the material.

### *Thermogravimetric Analysis*

All TGA experiments were conducted under a N<sub>2</sub> atmosphere using a Netzsch 209 F1 thermal gravimetric analyzer with single use Al crucibles at a ramp rate of 20°C/minute. The thermal analysis software (Proteus V5.2.0) calculates the thermal onset temperature based on the intersection of the baseline with the tangent, at the inflection point, of the decomposition rate.

### *ATR-FTIR*

All FT-IR experiments were conducted on a Nexus IS10 IR with diamond ATR SMART Accessory. Scans were repeated 32 times at a resolution of  $4\text{cm}^{-1}$ . The subtraction spectra of the data presented within the paper can be found within the Supplemental Information section.

## RESULTS AND DISCUSSION

The particular ILs included in this study were chosen for several reasons. Since the ultimate purpose of this research is to find a suitable heat transfer fluid to be implemented in solar thermal technology, corrosive ILs must be excluded<sup>20</sup>. Thus, ILs containing free halides or anions that could decompose to form free halides, such as  $\text{BF}_4^-$  or  $\text{PF}_6^-$ , were avoided<sup>8, 21</sup>. The anions studied, bis(trifluoromethylsulfonyl)imide ( $[\text{Tf}_2\text{N}]^-$ ) and perfluoroethylsulfonylimide ( $[\text{BETI}]^-$ ), were selected because research has not shown these to be corrosive yet they maintain high thermal stability<sup>18</sup>. The cations represent the range of common cations found in the literature and the addition of the butonic acid cation, which. Approximately 50mL of each IL was added to in a Pyrex beaker and placed in an oven at  $200^\circ\text{C}$ . Once a week an aliquot was taken from the sample and observations of changes in the IL were recorded. It is assumed that at  $200^\circ\text{C}$  effects from water in the IL will be negligible<sup>22-23</sup>, but the effects of oxygen on degradation of the IL could have significant impact<sup>24</sup>. Further studies will be completed to compare the effects of an oxygen free environment with these results.

### *Qualitative Observations and Rheological Measurements*

Physical observations of the ILs throughout the aging process are summarized in Table 2, and pictures representing the ILs before aging and after 15 weeks of aging are presented in Figure 1. The average viscosity measurements of the ILs at room temperature are reported in Table 3. All of the ILs tested experienced a change in color almost immediately after exposure to heat. The cause of this change in color is still unknown, in some ILs it is suspected to be a result of carbonization<sup>25</sup>. Based only on physical appearance, the imidazolium cations ([C<sub>4</sub>mim] and [C<sub>4</sub>mmim]) were the most resistant to degradation during the aging process. The imidazolium based ILs had increase in viscosity and minimal deposition of solids on the insides of the beakers, less than 5%. [C<sub>4</sub>mim] had slightly less solid formation than [C<sub>4</sub>mmim] and the [Tf<sub>2</sub>N] anion had less solids formation and was less viscous than the [BETI]. This is also confirmed by the viscosity measurements. All ILs increased in viscosity, but the imidazolium based ILs had the lowest increase of all seven ILs tested. The viscosity of [C<sub>4</sub>mmim][Tf<sub>2</sub>N] more than doubled over the course of the experiment, while the [C<sub>4</sub>mim][Tf<sub>2</sub>N] and [C<sub>4</sub>mim][BETI] increased less than 17%, disproving the previous theory that methyl blocking of the C-2 proton could help increase thermal stability of the cation.<sup>3</sup>

The two quaternary ammonium ILs, [N<sub>4111</sub>] and [N<sub>1114</sub>CO<sub>2</sub>] performed poorly during the aging process. The [N<sub>4111</sub>] gradually increased solids content throughout the aging process until approximately 50% of the remaining material was in solid form. During the first 5 weeks of this process the viscosity remained relatively unchanged, but increased significantly by week 10 when a greater amount of solids had formed. By 15 weeks, the IL resembled a sludge with a measured viscosity 4X the original value. The addition of the carboxylic acid group further destabilized the quaternary ammonium



anion. Initially the removed aliquots had no observable change in appearance other than color and a slight formation of solids, but after week one the IL began to form crystals once the aliquot was cooled to room temperature. The IL measured viscosity decreased by half after one week and the IL continued to become more viscous and solid-like where the remaining liquid was very light in color with a chunky solid. Eventually, [N<sub>1114</sub>CO<sub>2</sub>][Tf<sub>2</sub>N] dried to a loose, black powder.

[C<sub>4</sub>mpyr][Tf<sub>2</sub>N] gradually increased in solids formation during the aging process. As more solids formed, the remaining liquid became lighter in color. The viscosity decreased slightly from the neat IL, following the the same trend as [N<sub>4111</sub>][Tf<sub>2</sub>N]. After 15 weeks a gummy, thick solid remained. [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N] was the only IL to not have any loose solid formation during the aging process. However, the IL slowly became more and more viscous until it formed a hard tar on the bottom of the beaker that could not be removed.

### *Thermophysical Properties*

Samples from the aliquots were taken to determine if changes were occurring in the decomposition temperatures of the ILs as they age. The change in decomposition temperatures, reported as 5% weight loss at 20°C/min heating rate, are found in Figure 2. The decomposition temperature fluctuated for [C<sub>4</sub>mim][Tf<sub>2</sub>N] and overall decreased from 434°C to 427°C at week 15. [C<sub>4</sub>mmim][T<sub>2</sub>N] had a slightly larger decrease in decomposition temperature, from 443°C to 435°C. The decomposition temperature of [C<sub>4</sub>mim][BETI] also decreased approximately 10°C, from 414°C to 404°C over the fifteen week time period.

[N<sub>4111</sub>][Tf<sub>2</sub>N] had a steady decrease in decomposition temperature from 424°C to 405°C, The decomposition temperature for [N<sub>1114</sub>CO<sub>2</sub>][Tf<sub>2</sub>N] fluctuated erratically, but followed a general upward trend from 330°C to 389°C as the IL became completely solid. Although [C<sub>4</sub>mpyr][Tf<sub>2</sub>N] underwent considerable physical changes, the decomposition temperature of the IL remained approximately 420°C. The largest and most distinct change in decomposition temperature profile was with [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N]. The decomposition temperature decreased each week from the highest of all ILs tested, 460°C to 404°C. This temperature decrease mirrored the increase in viscosity that occurred in the IL until the tar was formed.

### *Chemical Changes*

FT-IR ATR was completed on the ILs throughout the aging process in attempts to determine chemical changes that were occurring in the IL and correlate them to changes in the physical properties of the IL. There are no major observable changes to the IR spectra of [C<sub>4</sub>mim][Tf<sub>2</sub>N] and [C<sub>4</sub>mmim][Tf<sub>2</sub>N] over the course of aging. They are represented in Figure 3 and Figure 4, respectively. The figures show representative spectra of the neat IL and the IL after 15 weeks of aging at 200°C. One minor change is decrease in intensity of the weak peak at 950 cm<sup>-1</sup>, which is representative of alkene groups. This evidence may support the opening of the imidazole ring during the aging process. These chemical observations are supported by the physical observations of the IL described above and attest to the long term thermal stability of the ILs. These chemical observations are supported by the physical observations of the IL described in Table 2.

The IR spectra of  $[N_{4111}][Tf_2N]$  remains unchanged during the 15 week aging process. The spectrum gives no indication of chemical changes that result in the formation of solids in the aged IL. Attempts to isolate the solids and study them independently were inconclusive due to the quantity of materials available. The IR spectra of  $[C_4mpyrr][Tf_2N]$  in Figure 6 also remains unchanged over the 15 week aging period, while the physical appearance of the IL undergoes drastic changes during the time period. In Figures 3-6 the IR signal of the  $[Tf_2N]$  anion is so dominate that it overshadows the chemical absorbance signal for structural changes that are occurring in the cation of the IL. A previous report by Wooster et al.<sup>26</sup> describes some potential decomposition mechanisms of pyrrolidinium based ILs. Possible pathways for decomposition include the Hoffman elimination, which will result in protonated anions and terminal alkenes and the reverse alkylation reaction. These pathways are also applicable to the imidizolium<sup>27</sup> and quaternary ammonium ILs<sup>28</sup>.

Contrary to the previously described ILs, in Figure 7 the IR spectra of  $[C_4N_{11}pyr][Tf_2N]$  undergoes many changes during the aging process that mirror the physical observations previously described. Starting at two weeks aging time, a decrease is seen in the signal at  $1560\text{cm}^{-1}$  attributed to C-C stretching in the aromatic ring, but a slight growth in peaks at  $1530\text{cm}^{-1}$ . During the aging process there is a decrease in the cluster of peaks at about  $2930\text{cm}^{-1}$  attributed to the  $sp^3$  C-H stretch but a growth of peaks is seen clustered around  $3350\text{cm}^{-1}$  assigned to  $sp^2$  C-H stretch. There is also a loss of the peak at  $942\text{cm}^{-1}$  and the emergence of the peak at  $997\text{cm}^{-1}$ . This evidence supports the ring opening of the pyridinium and polymerization of the system and is further backed by the physical observations.

The FT-IR structure of  $[N_{1114}CO_2][Tf_2N]$  in Figure 8 undergoes more changes than any of the other ILs described in this work. After nine weeks the peaks at  $1710\text{cm}^{-1}$  (carbamate C=O stretch<sup>29</sup>) have completely disappeared and a broad peak at  $3160\text{cm}^{-1}$  (sp<sup>2</sup> C-H stretch<sup>30</sup> or broad amide N-H<sup>29</sup>) has emerged. The peak at  $3160\text{cm}^{-1}$  continues to strengthen before weakening and disappearing. During this time, a broad hump centered at  $1610\text{cm}^{-1}$ , also attributed to the aliphatic amine, emerges and the peaks defining the  $[Tf_2N]$  slowly decrease in intensity. This evidence would indicate an initial polymerization of the cation structure before further decomposition.

The FT-IR spectra for  $[C_4mim][BETI]$  before and after 15 weeks aging in Figure 9 remains relatively unchanged with the appearance of the weak peak at  $2340\text{cm}^{-1}$ , which can be assigned to a tertiary amine<sup>31</sup>. When comparing the absorption signals mainly attributed to the anions  $[Tf_2N]$  and  $[BETI]$ ,  $[BETI]$  displays a sharp absorbance at  $970\text{cm}^{-1}$  (CCCC stretch<sup>30</sup>) with a decrease in intensity of the signal at approximately  $1050\text{cm}^{-1}$ , due to the S-N-S antisymmetric stretch, a C-C stretch, and NCH<sub>3</sub> twisting<sup>32</sup>. This also corresponds with an inverse in intensity of the peaks at approximately  $1210\text{cm}^{-1}$  and  $1160\text{cm}^{-1}$ , the latter due to the CF<sub>3</sub> antisymmetric stretch and the former due to the CF<sub>3</sub> symmetric stretch<sup>32</sup>.

## CONCLUSIONS

The high thermal stability of ionic liquids has been one of the most frequently cited beneficial properties for their use as solvents, heat transfer fluids, and chemical process media. However, testing is typically completed under dynamic conditions and in an inert atmosphere. This leads to a potential misrepresentation of the actual “thermal

stability” limits of the fluids. We tested seven different [Tf<sub>2</sub>N] and [BETI] ILs at a temperature of 200°C in air, far below their determined decomposition point. It was found that the physical appearance rapidly changed, while solids began to form as soon as after one week of exposure. While relatively small changes were seen in the decomposition temperatures of the ionic liquids, the physical appearance and properties of the materials changes significantly. After over 2000 hours of treatment at low temperatures, three of the ILs, [N<sub>1114</sub>CO<sub>2</sub>][Tf<sub>2</sub>N], [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N], and [C<sub>4</sub>mpyrr][Tf<sub>2</sub>N], had completely polymerized or solidified. The remaining four ILs had solids formation and a noticeable change in viscosity that could potentially significantly impact the operational performance of the fluid.

It was also found that the minor changes in the cation chemistry could greatly change the properties of the ILs over time. The addition of one methyl group in the C-2 position slightly increased the solids formation in the IL, although both [C<sub>4</sub>mim][Tf<sub>2</sub>N] and [C<sub>4</sub>mmim][Tf<sub>2</sub>N] performed similarly. The quaternary ammonium group formed large amounts of solids, but did retain some liquid, similar to the imidazoliums, but the addition of a butonic acid group to the quaternary ammonium in [N<sub>1114</sub>CO<sub>2</sub>][Tf<sub>2</sub>N] destabilized the IL. The butyl substituted pyrrolidium and pyridium groups produced tar-like products under aging. All of which indicate that the selection of the cation and cation ligand substitution is just as important as the selection of the anion in ILs for high temperature systems. This also suggests that ILs should be tested under process conditions prior to use to ensure stability during operation and to prevent adverse effects to the operating system and chemical process.

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Table 1. Decomposition temperatures of the neat (unaged) ILs reported at two heating rates in a TGA.

| Ionic Liquid  | Temp at 10°C/min    |            | Temp at 20°C/min    |            |
|---|---------------------|------------|---------------------|------------|
|   | Decomposition onset | 5% wt loss | Decomposition onset | 5% wt loss |
| [C <sub>4</sub> mim][Tf <sub>2</sub> N]                 | 443                 | 413        | 454                 | 434        |
| [N <sub>4111</sub> ][Tf <sub>2</sub> N]                 | 435                 | 404        | 447                 | 424        |
| [C <sub>4</sub> mmim][Tf <sub>2</sub> N]                | 459                 | 430        | 464                 | 443        |
| [C <sub>4</sub> mpyr][Tf <sub>2</sub> N]                | 436                 | 406        | 450                 | 420        |
| [C <sub>4</sub> N <sub>11</sub> pyr][Tf <sub>2</sub> N] | 465                 | 440        | 489                 | 460        |
| [N <sub>1114</sub> CO <sub>2</sub> ][Tf <sub>2</sub> N] | 379                 | 324        | 397                 | 330        |
| [C <sub>4</sub> mim][BETI]                              | 418                 | 392        | 437                 | 414        |

Table 2: Observations of physical changes in ionic liquids from week to week after constant exposure to 200°C in air. NC = no change

| Week | [C <sub>4</sub> mim]   | [N <sub>4111</sub> ]  | [C <sub>4</sub> mmim]                | [C <sub>4</sub> mpyrr]                                | [C <sub>4</sub> N <sub>11</sub> pyr]              | [N <sub>1114</sub> CO <sub>2</sub> ]                                     | [C <sub>4</sub> mim][BETI]    |
|------|--|---|--------------------------------------|---|---|--|-------------------------------|
| 0    | light yellow liquid  | colorless liquid  | colorless liquid                     | yellow liquid   | bright orange liquid                              | colorless liquid   | colorless liquid              |
| 1    | brown liquid   | brown liquid  | brown liquid                         | brown liquid  | brown liquid                                      | light brown liquid, black solid formation                                | brown liquid                  |
| 5    | small amount of very small black solid particles in brown liquid | small black solid particles in brown liquid                     | more viscous, slight solid formation | increased solid formation, liquid is more transparent | increasingly viscous brown liquid                 | crystallized upon cooling to room temperature forming a dark brown solid | slightly more viscous, darker |
| 10   | NC   | greater quantity of black solid material present in dark liquid | NC                                   | black, wet, clumpy solid with clear liquid            | oily appearance, incredibly viscous, almost solid | Dry, black, chunky solid   | NC                            |
| 15   | NC   | clumpy, wet, black solid formations present in dark liquid      | Increased solids formations          | thick, gummy black solid                              | thick, hard, slightly sticky, tarlike             | very dry, black, loose solid particles                                   | NC                            |

Table 3. Average viscosity of the ILs as a function of aging time at 200°C, as measured at 22°C, in cP.

| Week      | [C <sub>4</sub> mim] | [N <sub>4111</sub> ] | [C <sub>4</sub> mmim] | [C <sub>4</sub> mpyr] | [C <sub>4</sub> N <sub>11</sub> pyr] | [N <sub>1114</sub> CO <sub>2</sub> ] | [C <sub>4</sub> mim][BETI] |
|-----------|----------------------|----------------------|-----------------------|-----------------------|--------------------------------------|--------------------------------------|----------------------------|
| <b>0</b>  | 54.6                 | 112.5                | 108.4                 | 88.8                  | 91.1                                 | 2050                                 | 127.4                      |
| <b>1</b>  | 59.6                 | 111.2                | 122.0                 | 81.6                  | 134.2                                | 984.1                                | 134.7                      |
| <b>5</b>  | 58.6                 | 117.5                | 143.0                 | NM                    | 441.8                                | solid                                | 147.3                      |
| <b>10</b> | 60.6                 | 196.7                | 150.6                 | 555.8                 | 9133                                 | solid                                | 149.2                      |
| <b>15</b> | 62.7                 | 417.1                | 227.5                 | 778.9                 | solid                                | solid                                | 148.9                      |

\*NM = not measured, inadequate amount of sample to get representative viscosity measurement

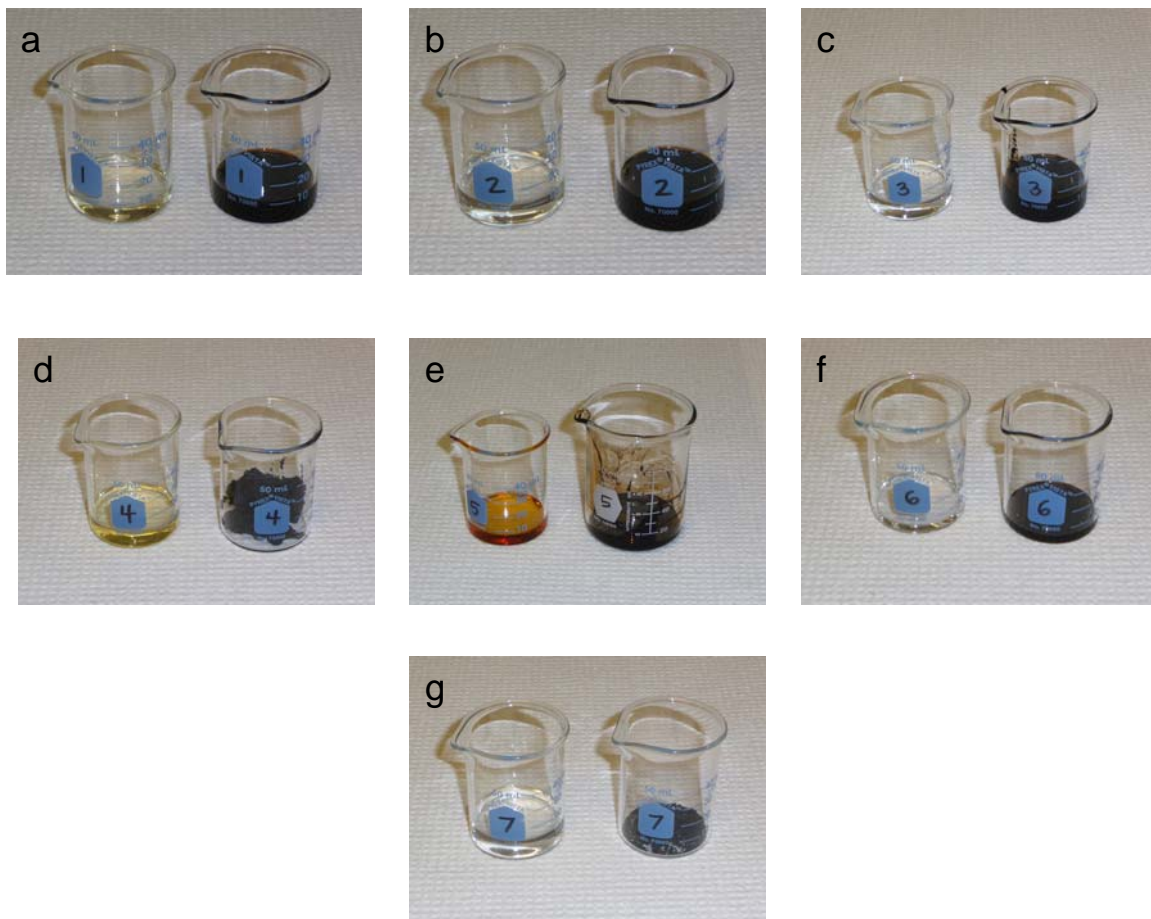


Figure 1: Side by side comparison of ionic liquids after 2520 hours (15 weeks) and in the neat (unaged) condition. (a)  $[C_4mim][Tf_2N]$ , (b)  $[N_{4111}][Tf_2N]$ , (c)  $[C_4mmim][Tf_2N]$ , (d)  $[C_4mpyr][Tf_2N]$ , (e)  $[C_4N_{11}pyr][Tf_2N]$ , (f)  $[C_4mim][BETI]$ , (g)  $[N_{1114}CO_2][Tf_2N]$ .

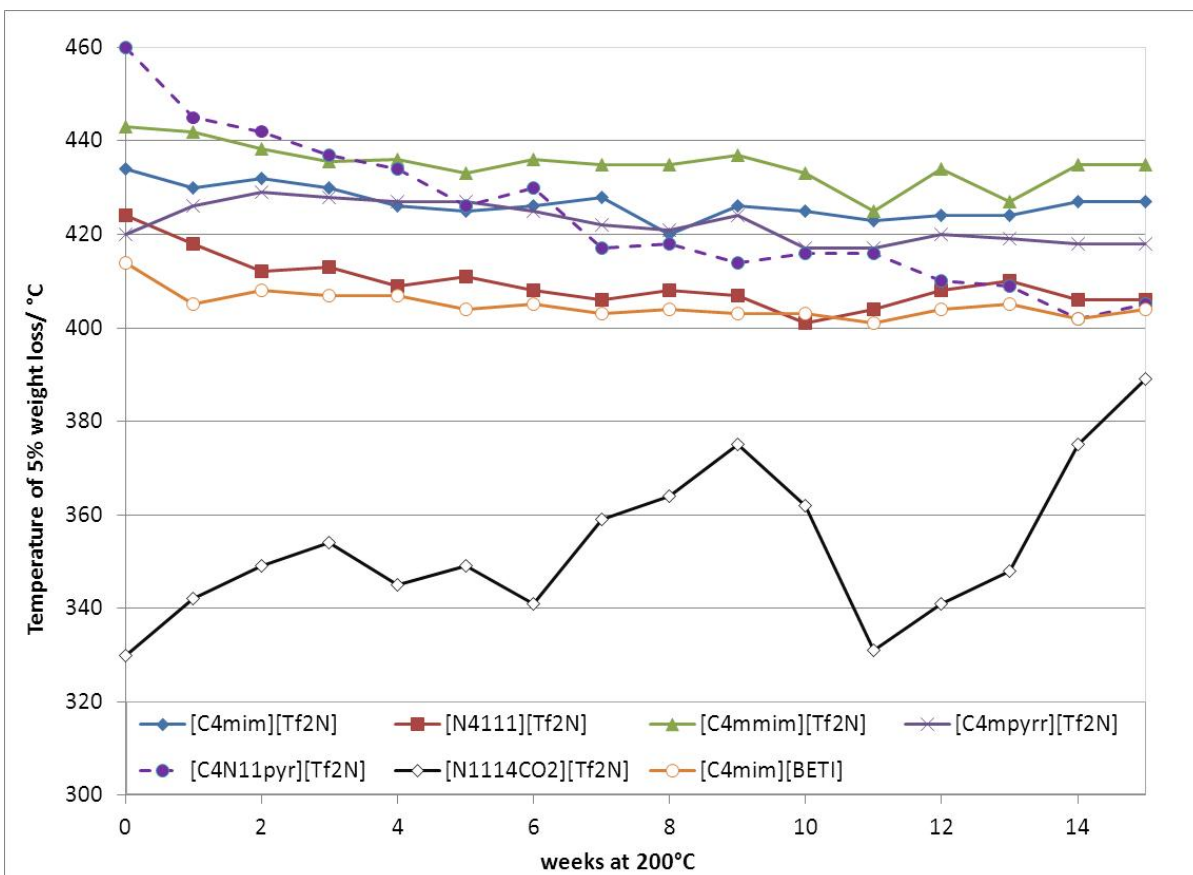


Figure 2: Change in measured decomposition temperature in a TGA as a result of long-term aging at 200°C, reported as 5%wt loss.

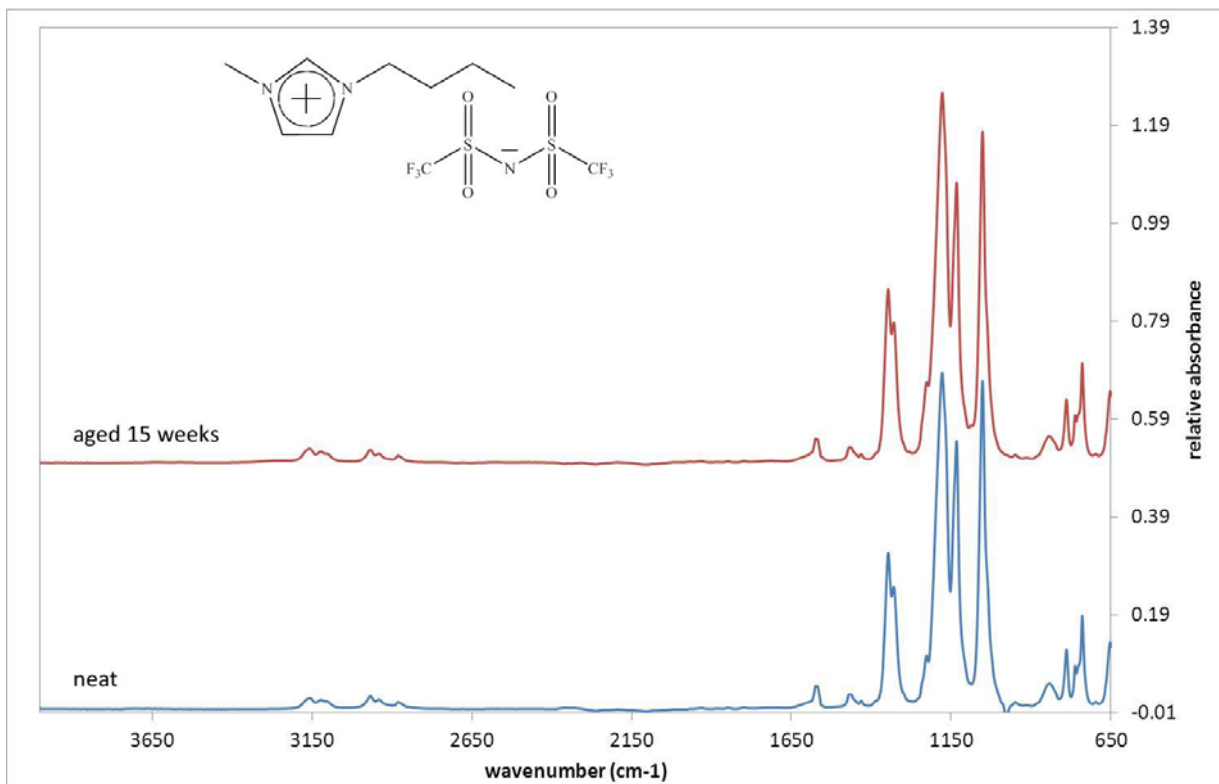


Figure 3: FT-IR spectra of [C<sub>4</sub>mim][Tf<sub>2</sub>N] before and after 15 weeks aging at 200°C.

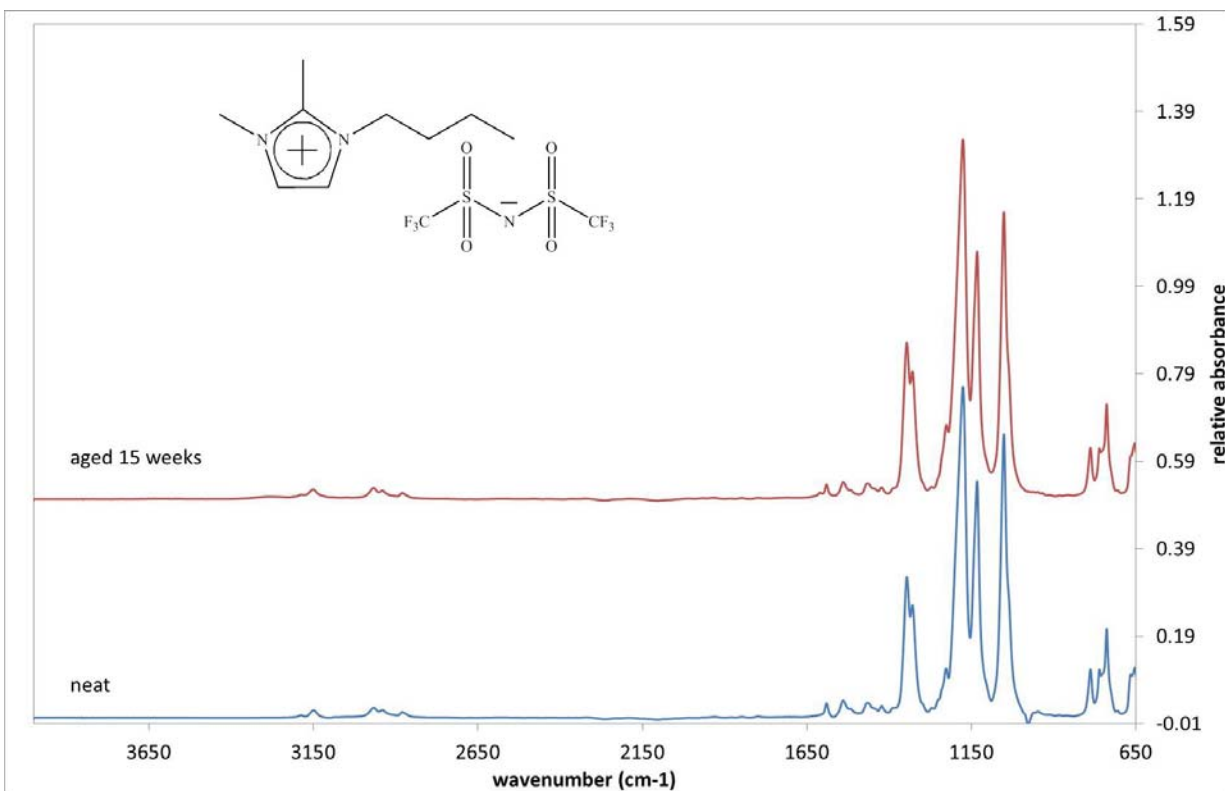


Figure 4: FT-IR spectra of [C<sub>4</sub>mmim][Tf<sub>2</sub>N] before and after 15 weeks aging at 200°C.



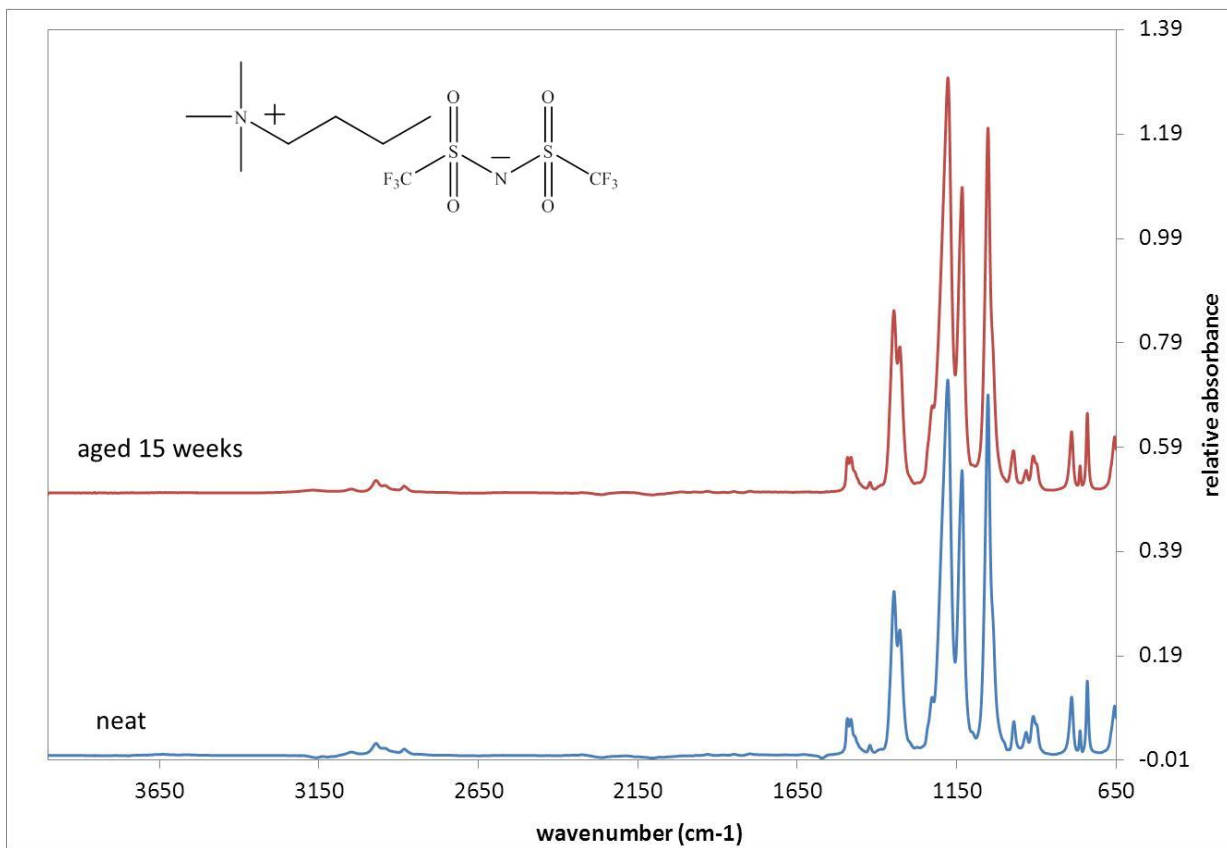


Figure 5: FT-IR spectra of [N<sub>4111</sub>][Tf<sub>2</sub>N] before and after 15 weeks aging at 200°C.

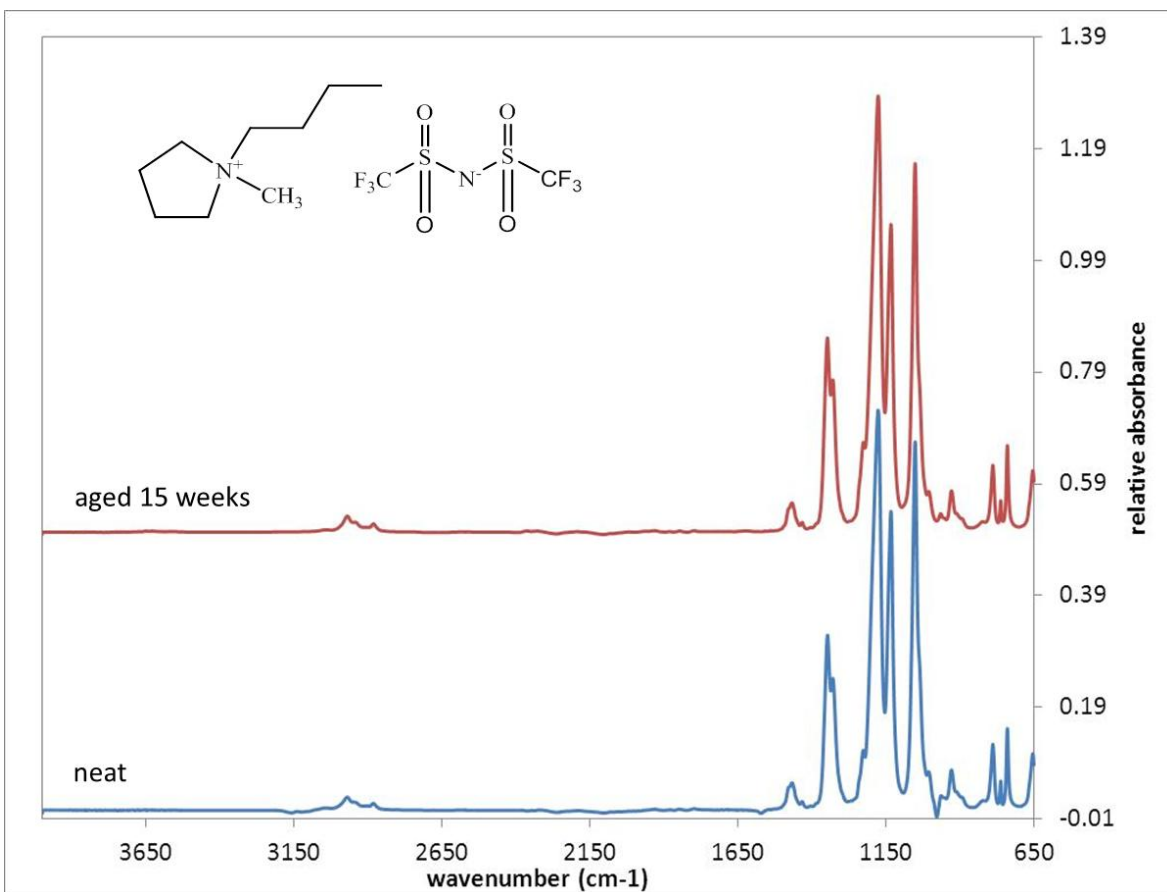


Figure 6: FT-IR spectra of [C<sub>4</sub>mpyrr][Tf<sub>2</sub>N] before and after 15 weeks aging at 200°C.

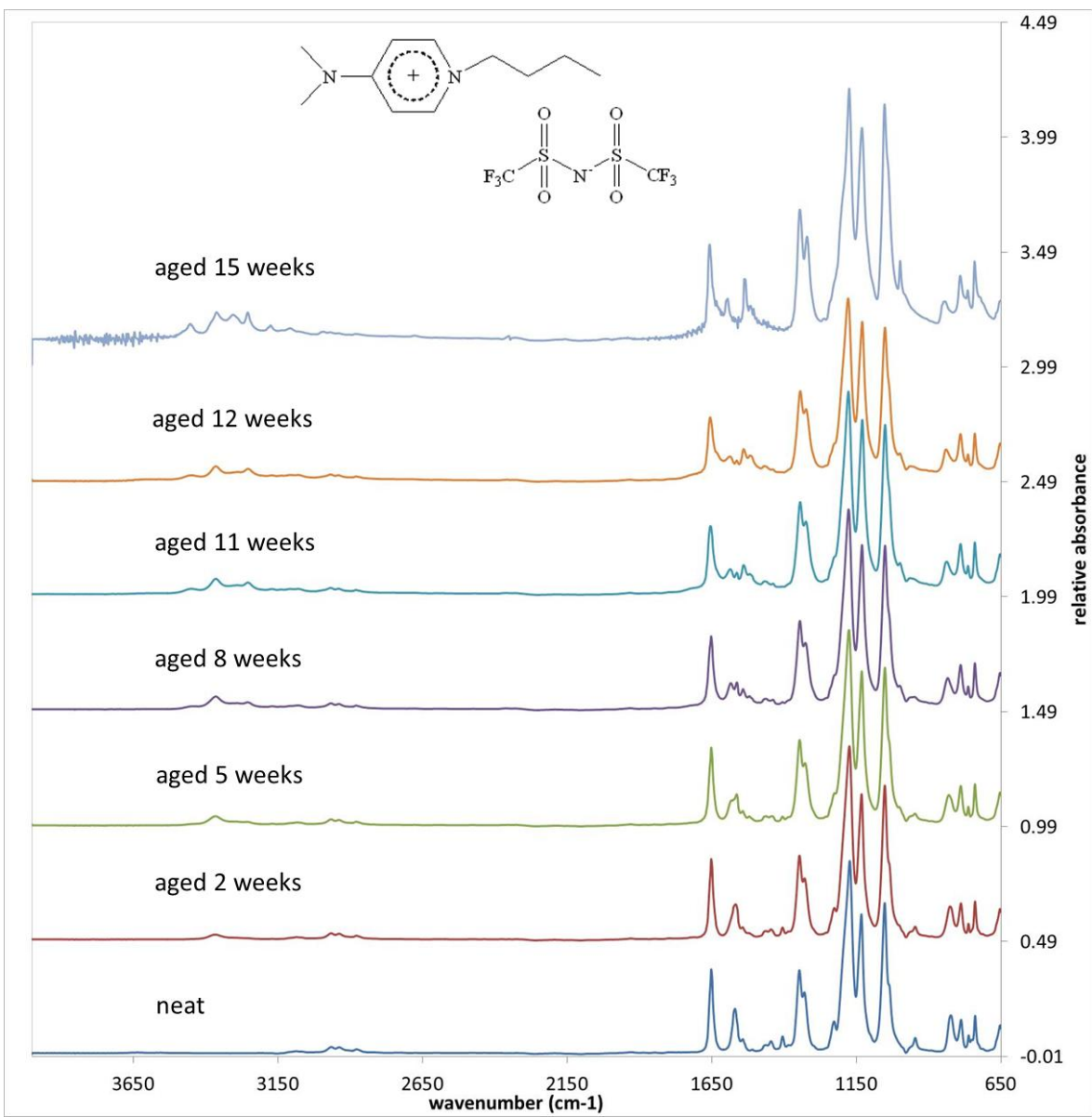


Figure 7: FT-IR spectra of [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N] before and during 15 weeks aging at 200°C.

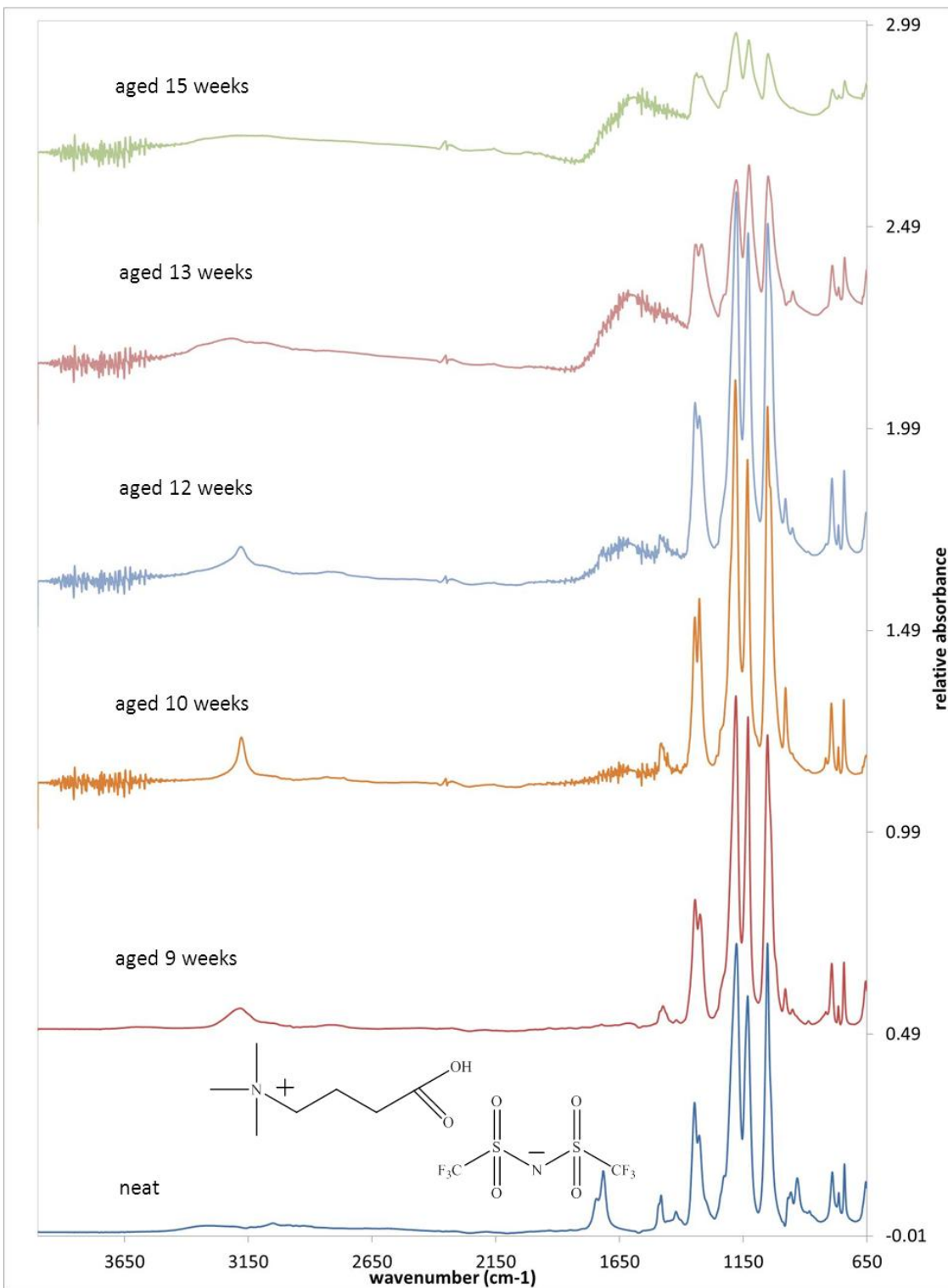


Figure 8: FT-IR spectra of  $[N_{1114}CO_2][Tf_2N]$  before and during aging at  $200^\circ C$ .

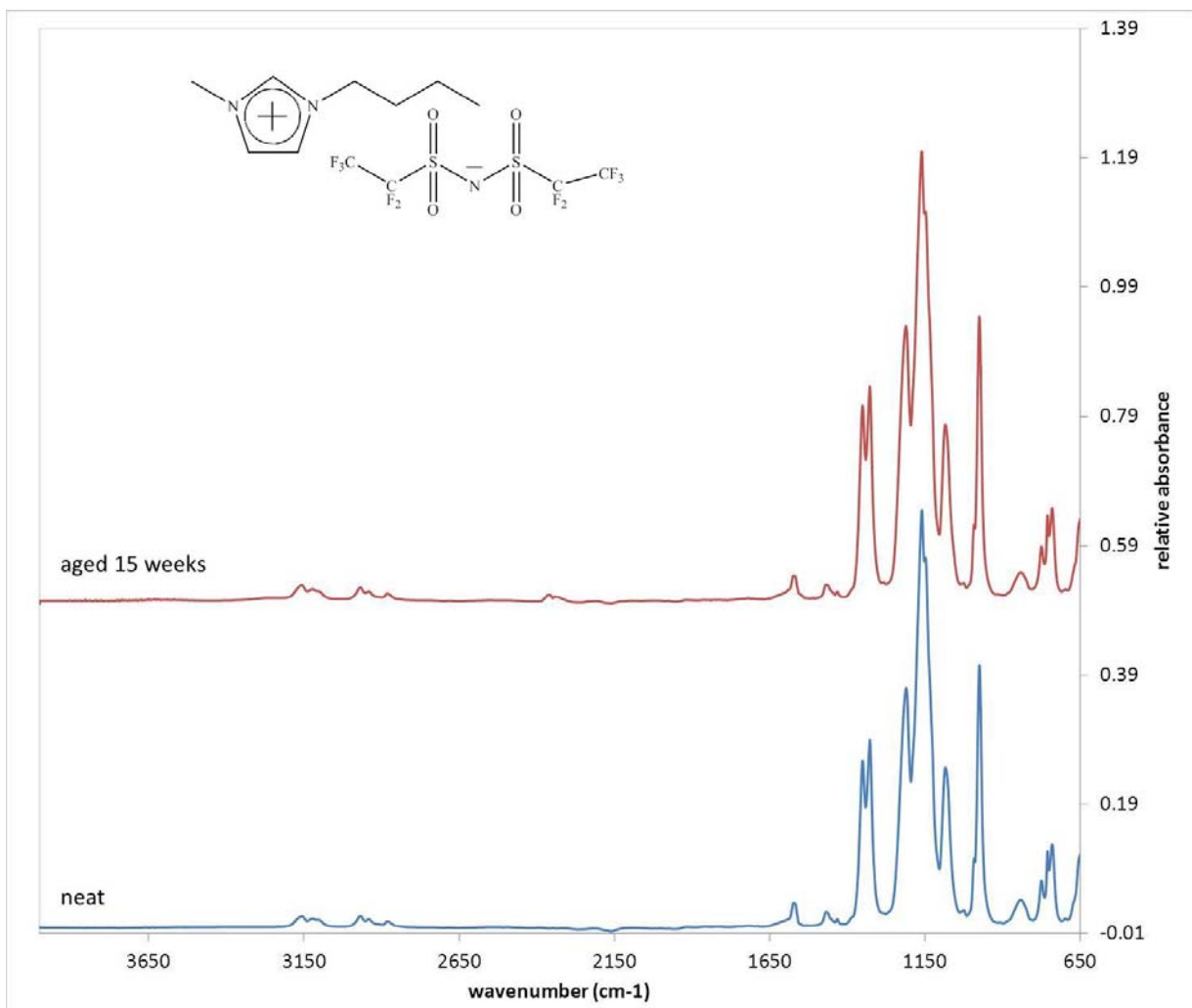


Figure 9: FT-IR spectra of [C<sub>4</sub>mim][BETI] before and after 15 weeks aging at 200°C.

-Supplemental Information for-

## Aging effects on the properties of imidazolium, quaternary ammonium, pyridinium and pyrrolidinium-based ionic liquids used in fuel and energy production

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This supplement information section presents the subtraction data for the FT-IR spectra found within the main body of the journal article. The subtraction data is presented to give the reader a representative idea of the spectra of the aged sample minus the “background” of the neat sample. Samples were collected according to specifications within the main section and processed using the OMNIC software. The subtraction spectra for [C<sub>4</sub>mim][Tf<sub>2</sub>N], [C<sub>4</sub>mmim][Tf<sub>2</sub>N], [N<sub>4111</sub>][Tf<sub>2</sub>N], and [C<sub>4</sub>mim][BETI] are nearly identical, with the exception of the strong peak at 1060 cm<sup>-1</sup> for [C<sub>4</sub>mim][BETI]. The chemical structure changes in [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N] are apparent after 2 weeks and continue to increase in absorption intensity throughout the aging process. While the chemical changes in [N<sub>1114</sub>CO<sub>2</sub>][Tf<sub>2</sub>N] are more dramatic leading directly to decomposition. This is supported by the evidence presented in the main body of the journal article.

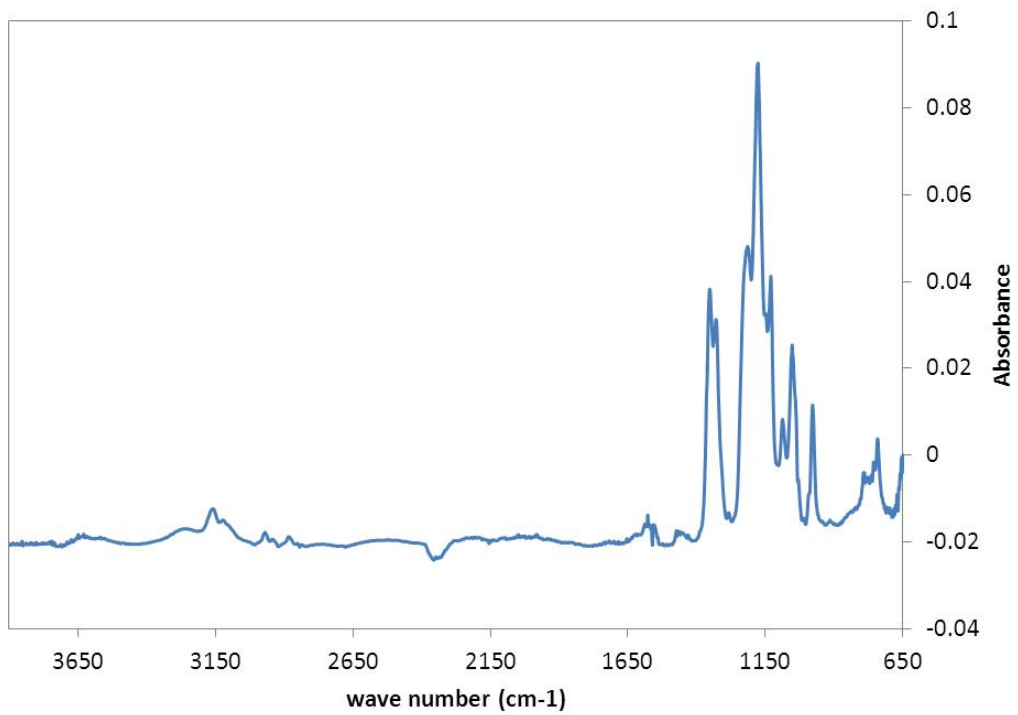


Figure 1: FT-IR subtraction spectra of [C<sub>4</sub>mim][Tf<sub>2</sub>N] after 15 weeks aging at 200°C.

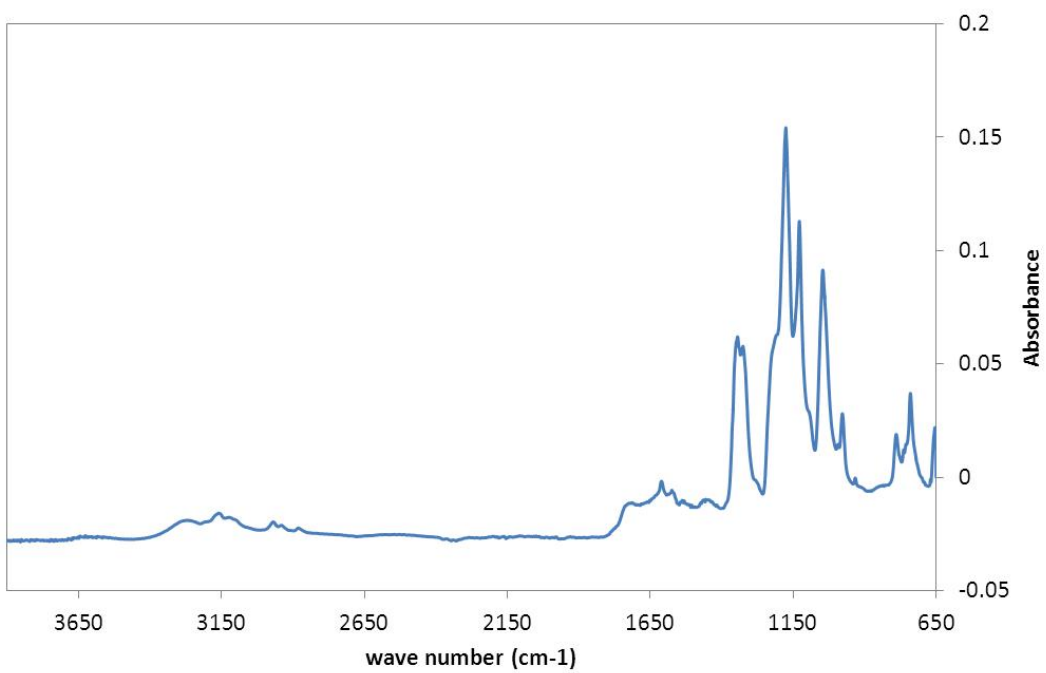


Figure 2: FT-IR subtraction spectra of [C<sub>4</sub>mmim][Tf<sub>2</sub>N] after 15 weeks aging at 200°C.

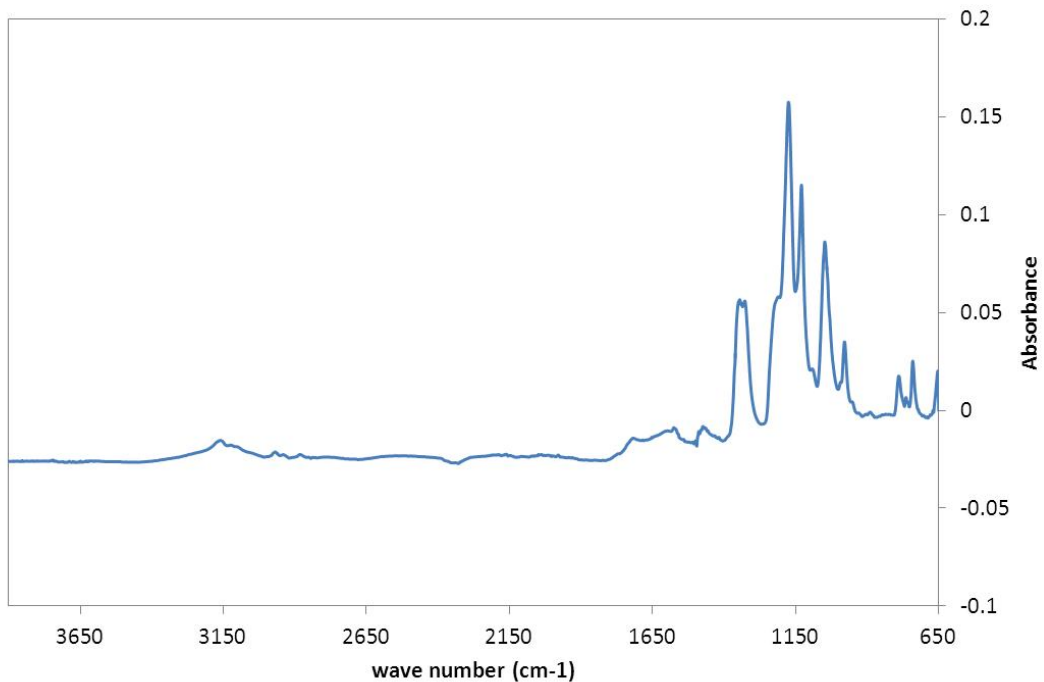


Figure 3: FT-IR subtraction spectra of [N<sub>4111</sub>][Tf<sub>2</sub>N] after 15 weeks aging at 200°C.

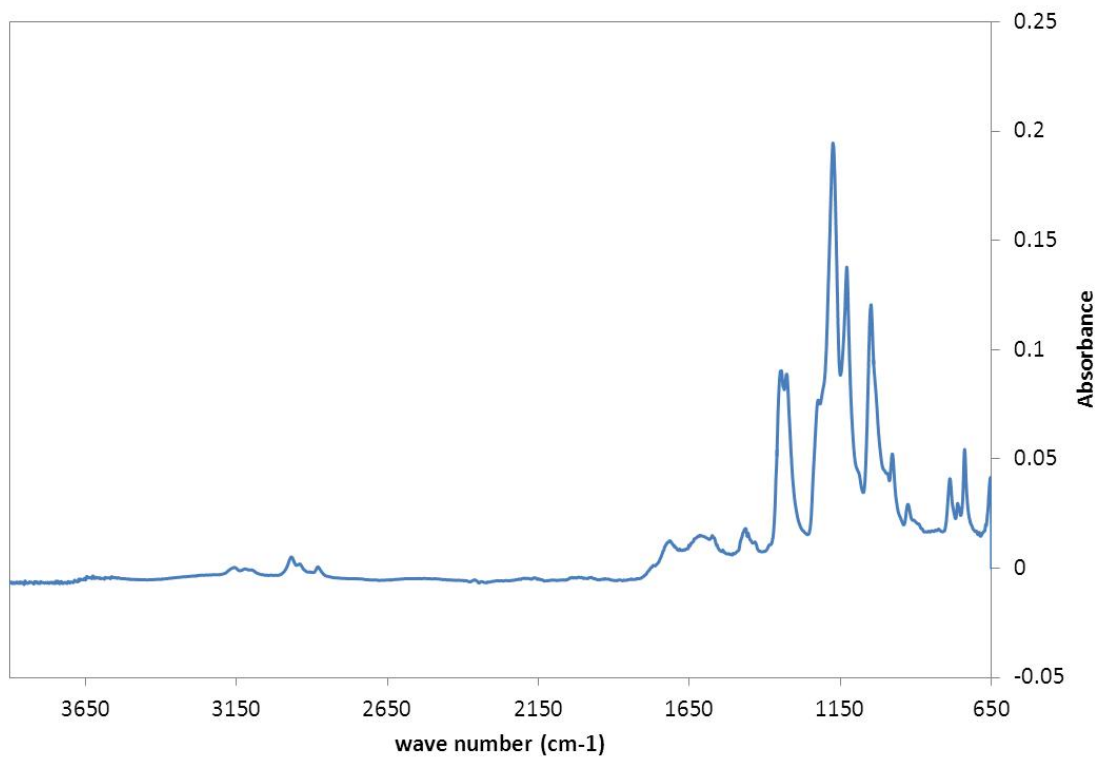


Figure 4: FT-IR subtraction spectra of [C<sub>4</sub>mpyrr][Tf<sub>2</sub>N] after 15 weeks aging at 200°C.



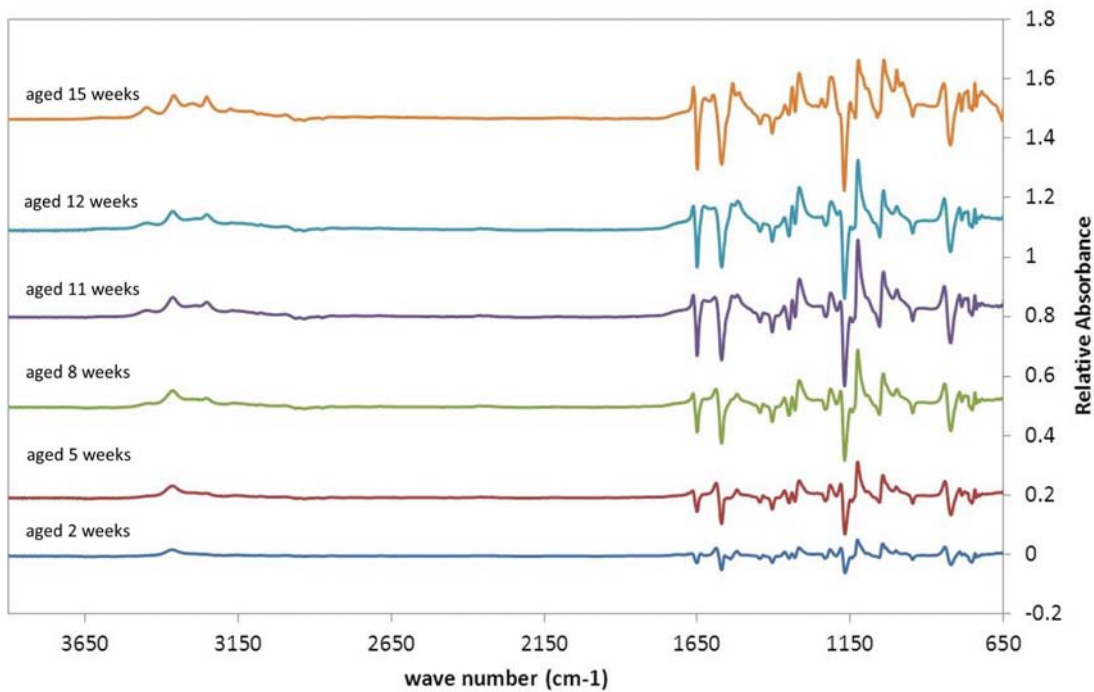


Figure 5: FT-IR subtraction spectra of [C<sub>4</sub>N<sub>11</sub>pyr][Tf<sub>2</sub>N] during 15 weeks aging at 200°C.

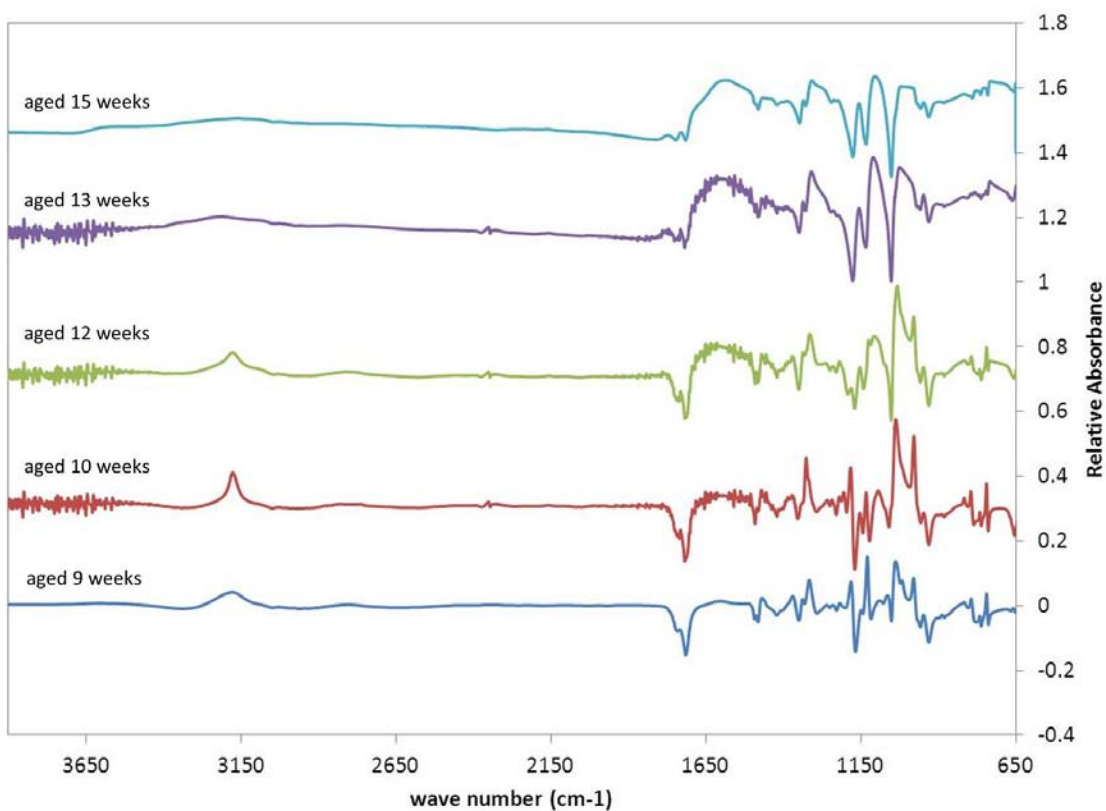


Figure 6: FT-IR subtraction spectra of [N<sub>1114</sub>CO<sub>2</sub>][Tf<sub>2</sub>N] during aging at 200°C.

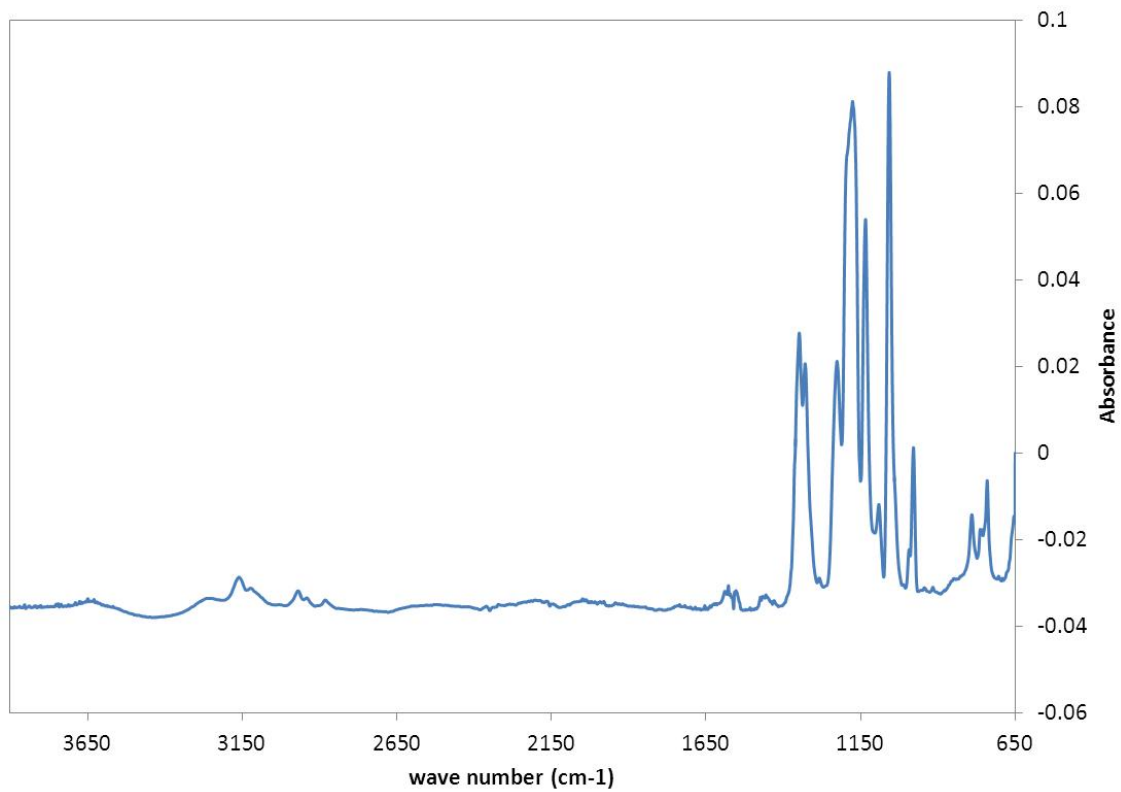


Figure 7: FT-IR subtraction spectra of [C<sub>4</sub>mim][BETI] after 15 weeks aging at 200°C.