*Article*

# Ionic Liquids as Working Fluids for Heat Storage Applications: Decomposition Behavior of N-Butyl-N-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate

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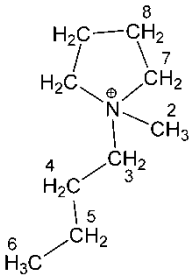
## *Supplementary Material*

**Table S1.** Assignment of $^{1}H$ and $^{13}C$ NMR signals of the [BmPyrr] cation according to the numbering reported in Scheme S1. Signal multiplicity and relative integral values are reported in brackets [a].

| Assignment | $^{1}H$ δ (ppm) | $^{13}C$ δ (ppm) |
|---|---|---|
| 2 | 2.99 (s, 3) | 47.7 (1) |
| 3 | 3.31 (m, 2) | 63.8 (1) |
| 4 | 1.71 (m, 2) | 21.2 (1) |
| 5 | 1.37 (m, 2) | 19.4 (1) |
| 6 | 0.96 (t, 3) | 12.9 (1) |
| 7 | 3.46 (m, 4) | 63.9 (2) |
| 8 | 2.14 (m, 4) | 25.2 (2) |

[a] Abbreviations: s = singlet, t = triplet, m = multiplet.




[BmPyrr]

**Scheme S1.** Numbering of the hydrogen atoms of [BmPyrr] used in the $^{1}H$ signal assignment reported in Table S1.

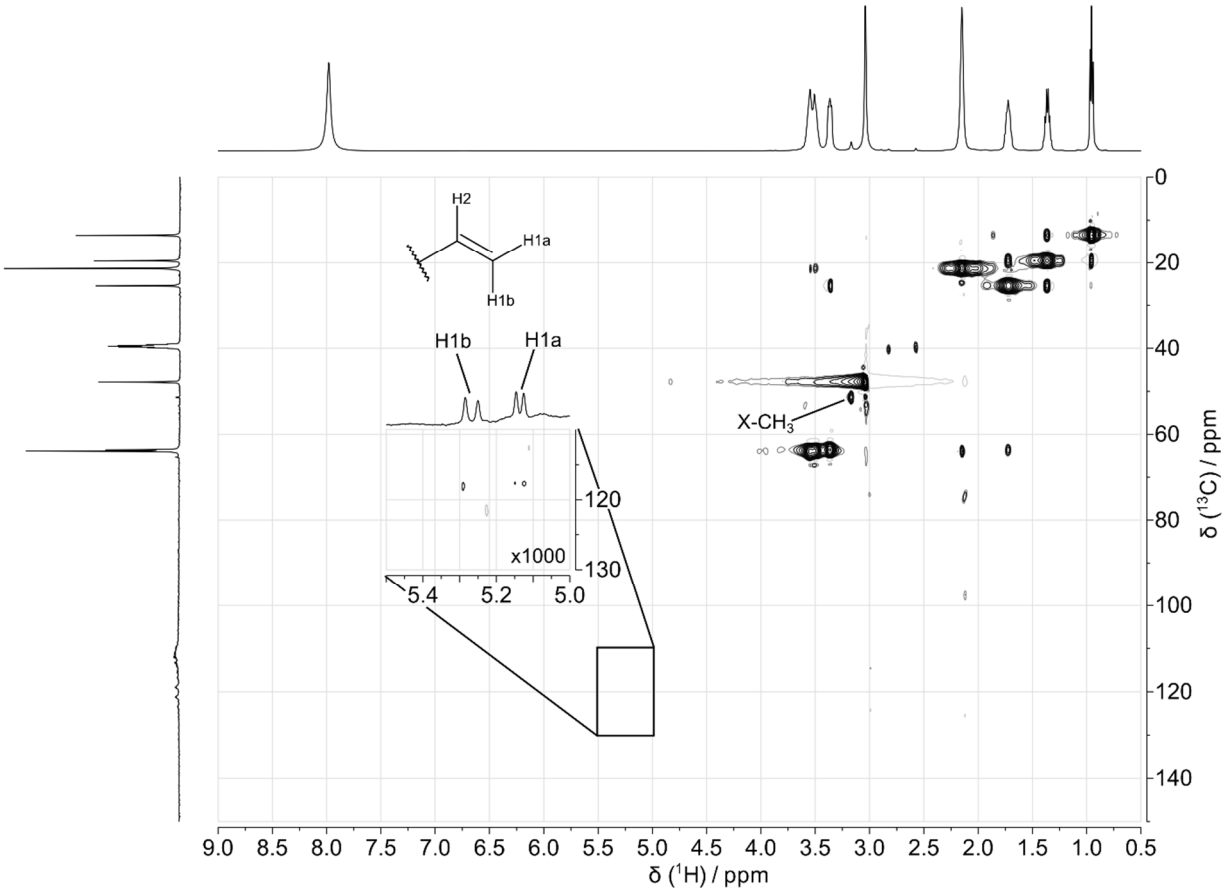



**Figure S1.** $^{1}H$-$^{13}C$ HSQC spectrum of blank_168h.

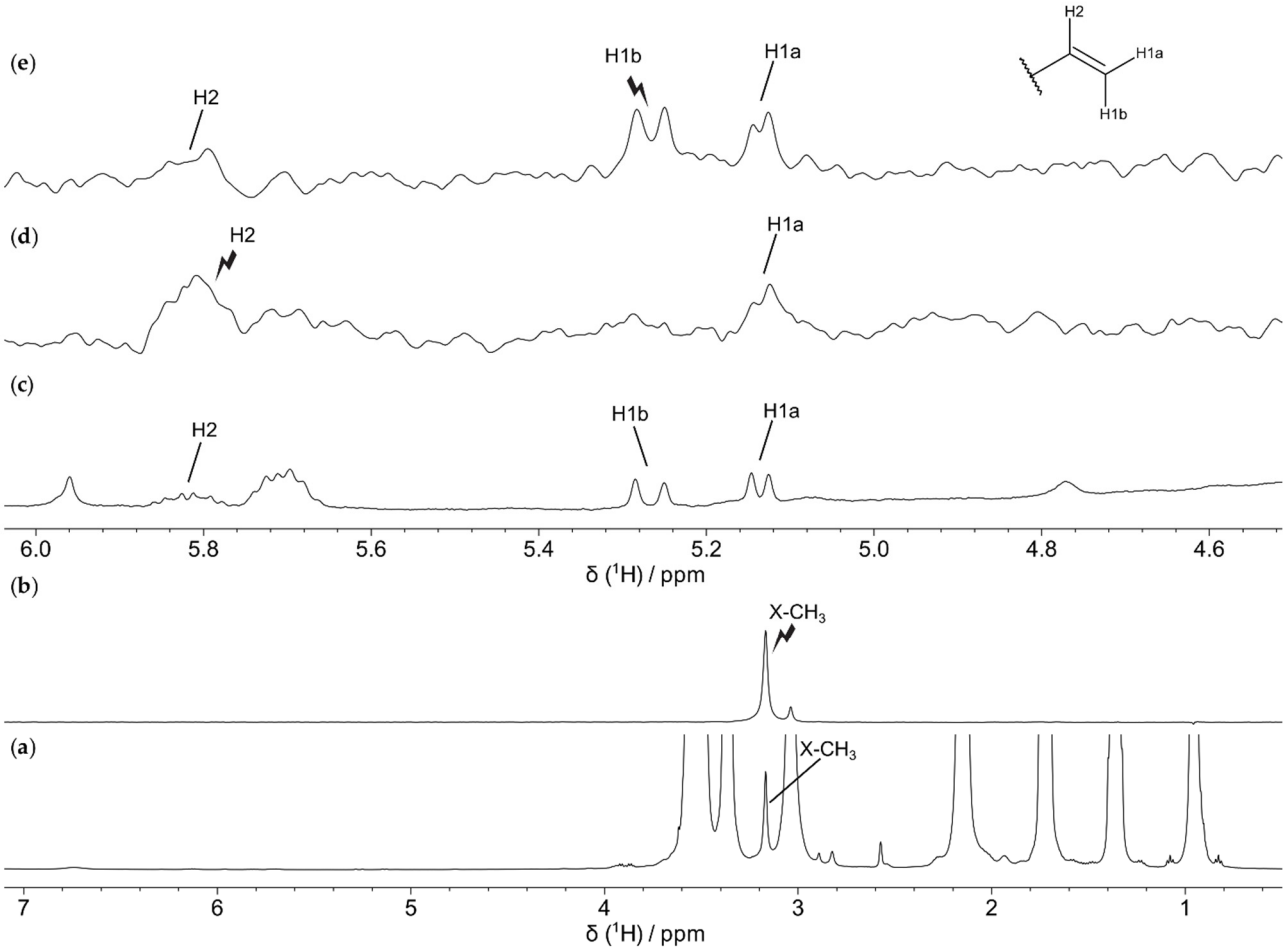



**Figure S2.** Comparison of $^{1}H$ spectrum of blank_168h (**a**) with 1D selective $^{1}H$ TOCSY obtained by irradiating the methyl protons of X-$CH_3$ at 3.17 ppm (**b**). Comparison of the $^{1}H$ spectral region ranging between about 4.5 and 6.0 ppm of blank_168h (**c**) with 1D selective $^{1}H$ TOCSY spectra obtained by irradiating H2 nucleus at 5.81 ppm (**d**) and H1b nucleus at 5.14 ppm (**e**) carried by the terminal vinyl group pictured in the inset.

**Table S2.** Correlations between $^{1}H$ and $^{13}C$ nuclei of the degradation products, as detected from the $^{1}H$-$^{13}C$ HSQC spectrum. Signal multiplicity and integration are reported in brackets [a].

| **$^{1}H$ δ (ppm)** | **$^{13}C$ δ (ppm)** |
|---|---|
| 3.17 (s) | 51.3 |
| 5.14 (d) | 118.3 |
| 5.27 (d) | |
| 5.81 (m) | - |

[a] Abbreviations: s = singlet, d = doublet, m = multiplet.

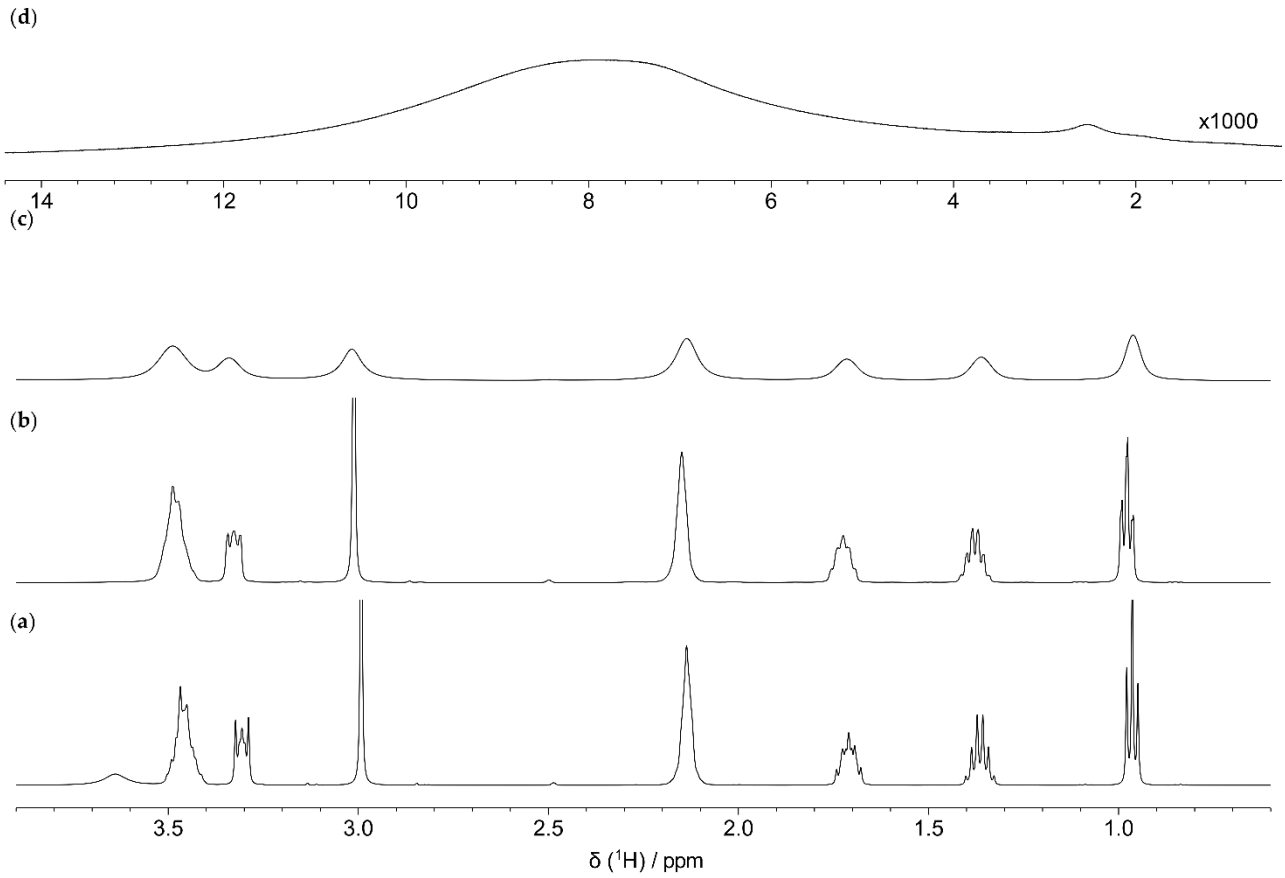



**Figure S3.** $^{1}$H HRMAS NMR spectra of blank_0h (**a**), steel _4h (**b**), steel_24h (**c**) and steel_168h (**d**).

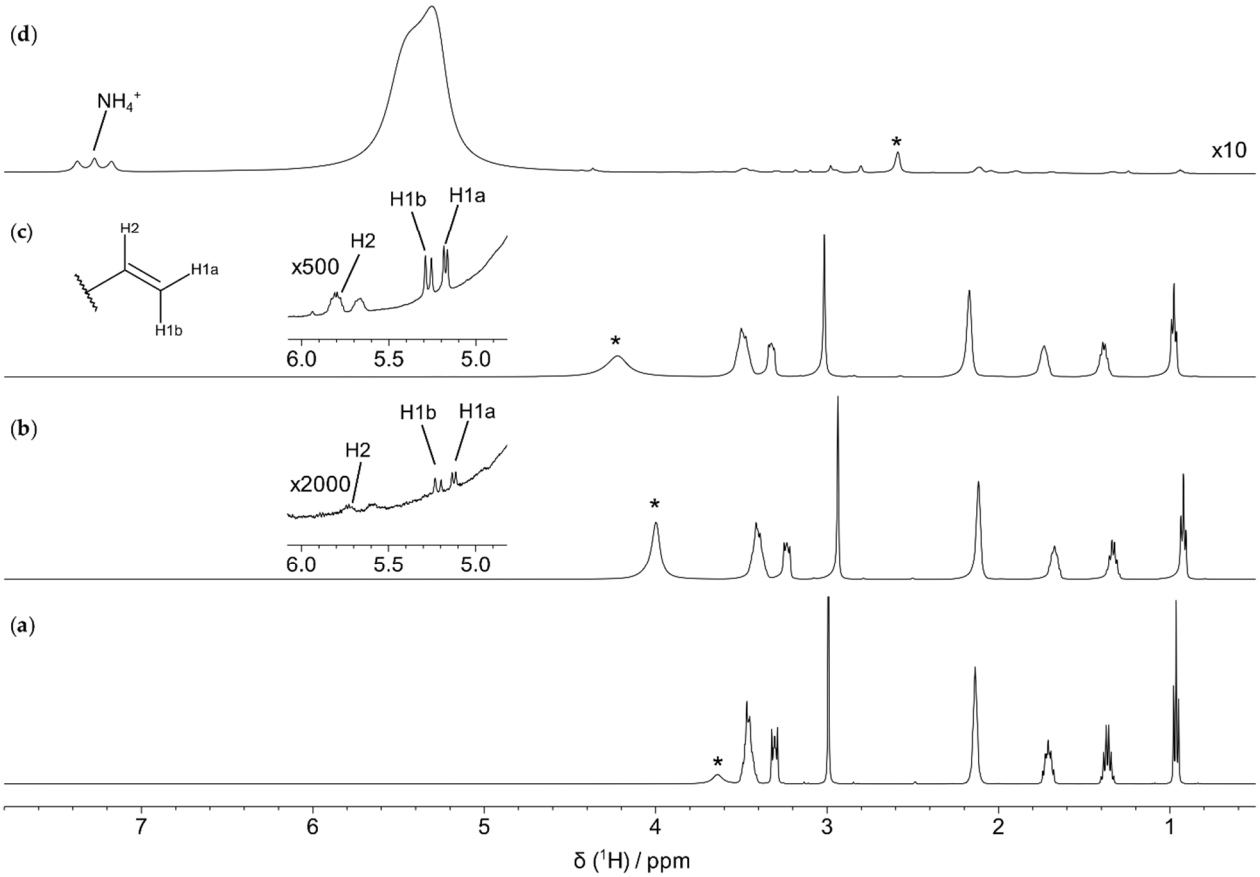



**Figure S4.** $^{1}$H HRMAS NMR spectra of blank_0h (**a**), copper _4h (**b**), copper_24h (**c**) and copper_168h (**d**). Residual water and DMSO are marked with asterisks.

**Table S3.** Assignment of $^{19}$F NMR signals and $^{19}$F-$^{31}$P *J* couplings ($J_{P\text{-}F}$) of the FAP anion of the investigated ionic liquid. The different colors are referred to fluorine atoms in different environments, as reported in the structure of Figure S5. Signal multiplicity and integration are reported in brackets [a].

| Assignment | $^{19}$F δ (ppm) | $J_{P\text{-}F}$ (Hz) |
|---|---|---|
| P-**F** | -87.0 (dm, 2) | 903 (1 bond) |
| P-**F** | -43.7 (dm, 1) | 891 (1 bond) |
| $CF_2$ | -115.6 (dm, 4) | 98 (2 bonds) |
| $CF_2$ | -115.0 (dm, 2) | 83 (2 bonds) |
| $CF_3$ | -81.2 (m, 6) | - |
| $CF_3$ | -79.6 (m, 3) | - |

[a] Abbreviations: s = singlet, d = doublet, t = triplet.

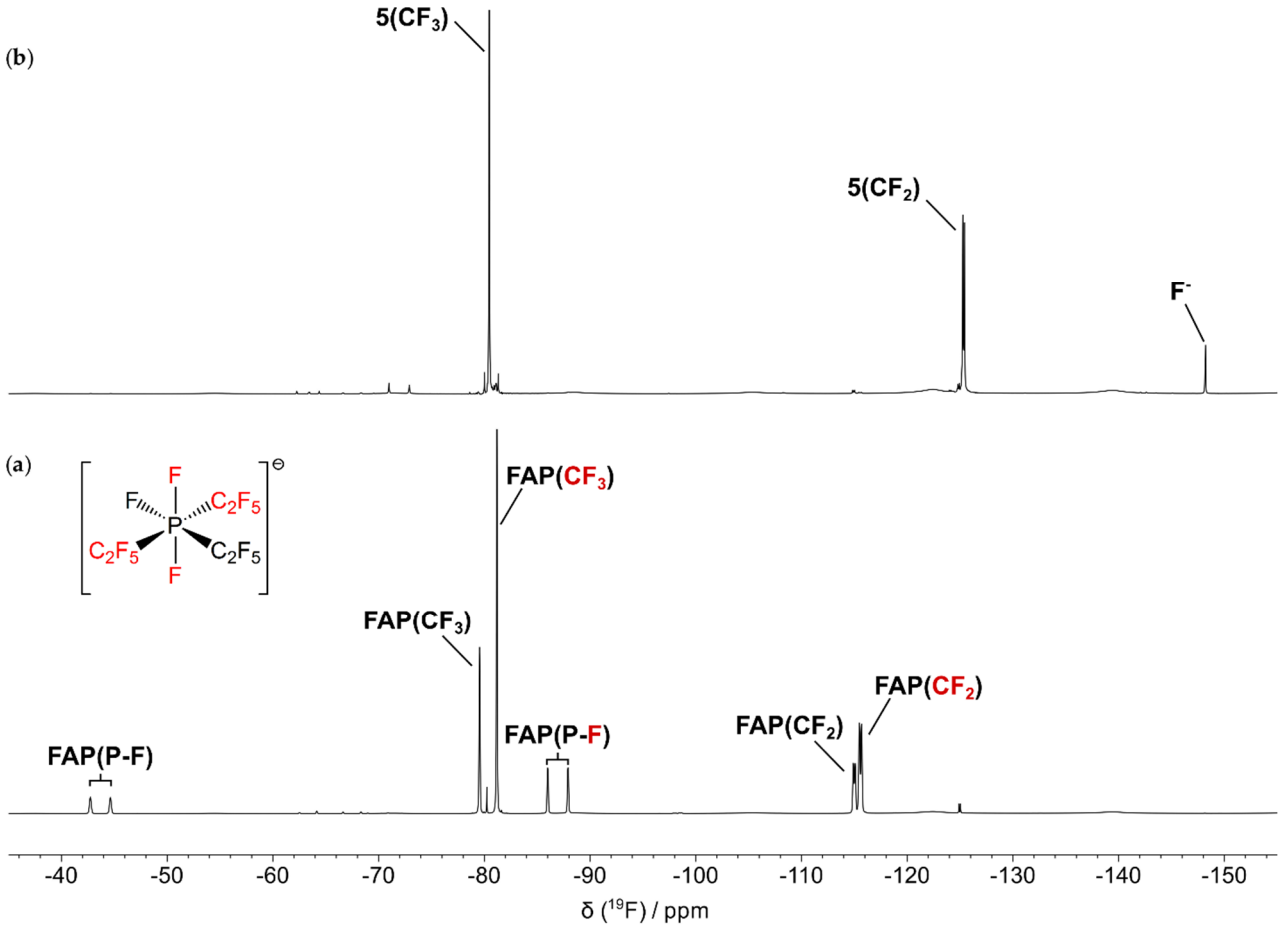



**Figure S5.** $^{19}F$ spectra of blank_0h (**a**) and blank_168h (**b**).