Supplementary Material (ESI) for PCCP
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Supplementary Information
Ionic Liquids and Solids with Paramagnetic Anions

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Experimental methods

Fourier-transform Infrared Spectroscopy.

Ambient room temperature (294 ± 1 K) fourier-transform infrared (FT-IR) absorption spectra were recorded using a Thermo Nicolet/Nexus 670 FT-IR spectrometer.

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Results

Fourier-transform Infrared Spectroscopy.

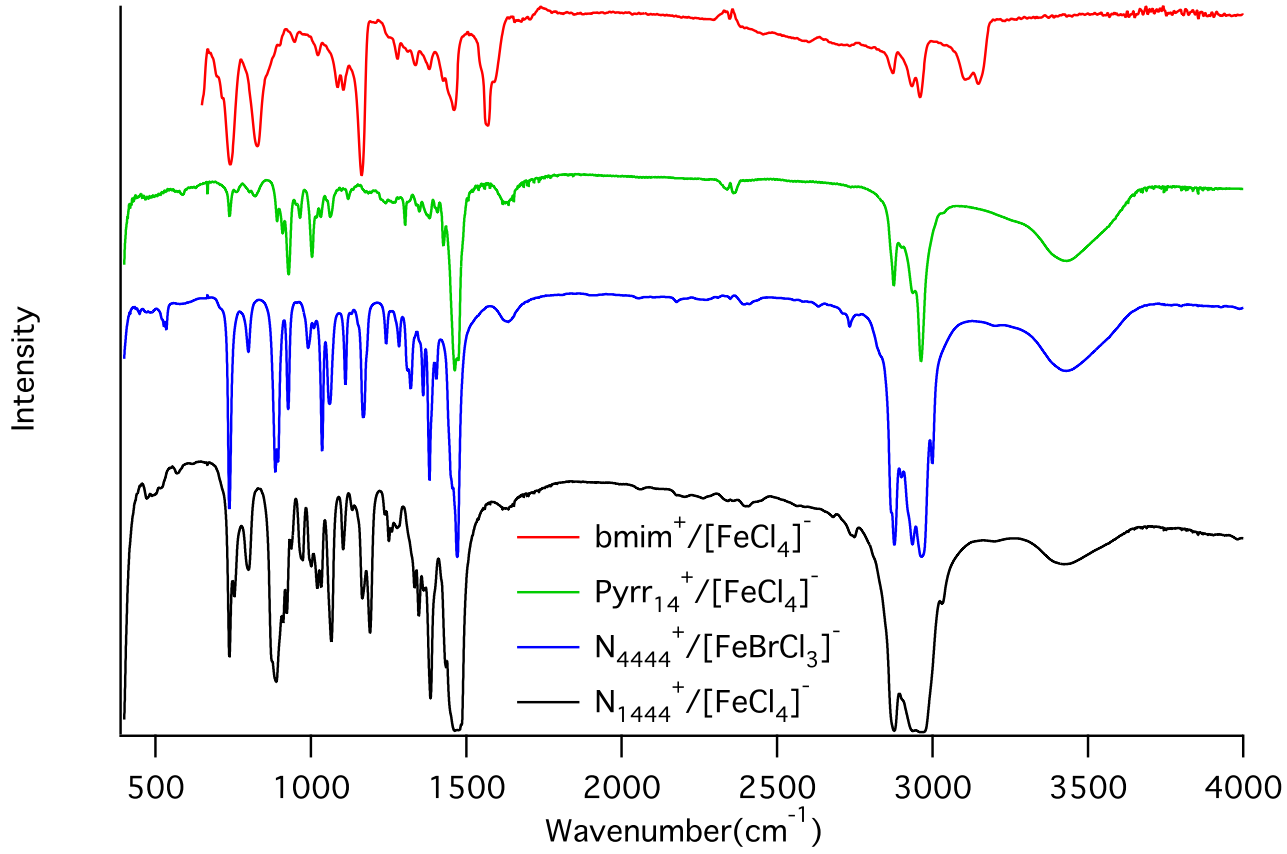

Figure 1: Infrared spectra of $bmim^+/[FeCl_4]^-$, $Pyrr_{14}^+/[FeCl_4]^-$, $N_{4444}^+/[FeBrCl_3]^-$ and $N_{1444}^+/[FeCl_4]^-$.

Raman spectroscopy

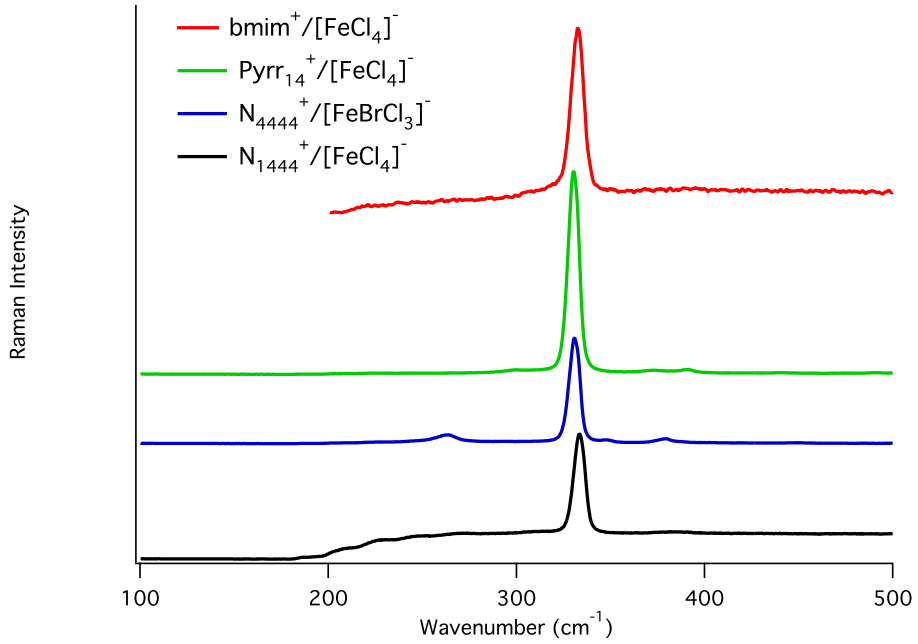

Figure 2: Raman spectra of $bmim^+/[FeCl_4]^-$, $Pyrr_{14}^+/[FeCl_4]^-$, $N_{4444}^+/[FeBrCl_3]^-$ and $N_{1444}^+/[FeCl_4]^-$.

$bmim^+/[FeCl_4]^-$	4.689
$Pyrr_{14}^+/[FeCl_4]^-$	4.157
$N_{4444}^+/[FeBrCl_3]^-$	3.976
$N_{1444}^+/[FeCl_4]^-$	4.253

Table 1: FWHM for Raman lineshapes in cm^{-1}.

Single crystal diffractometry

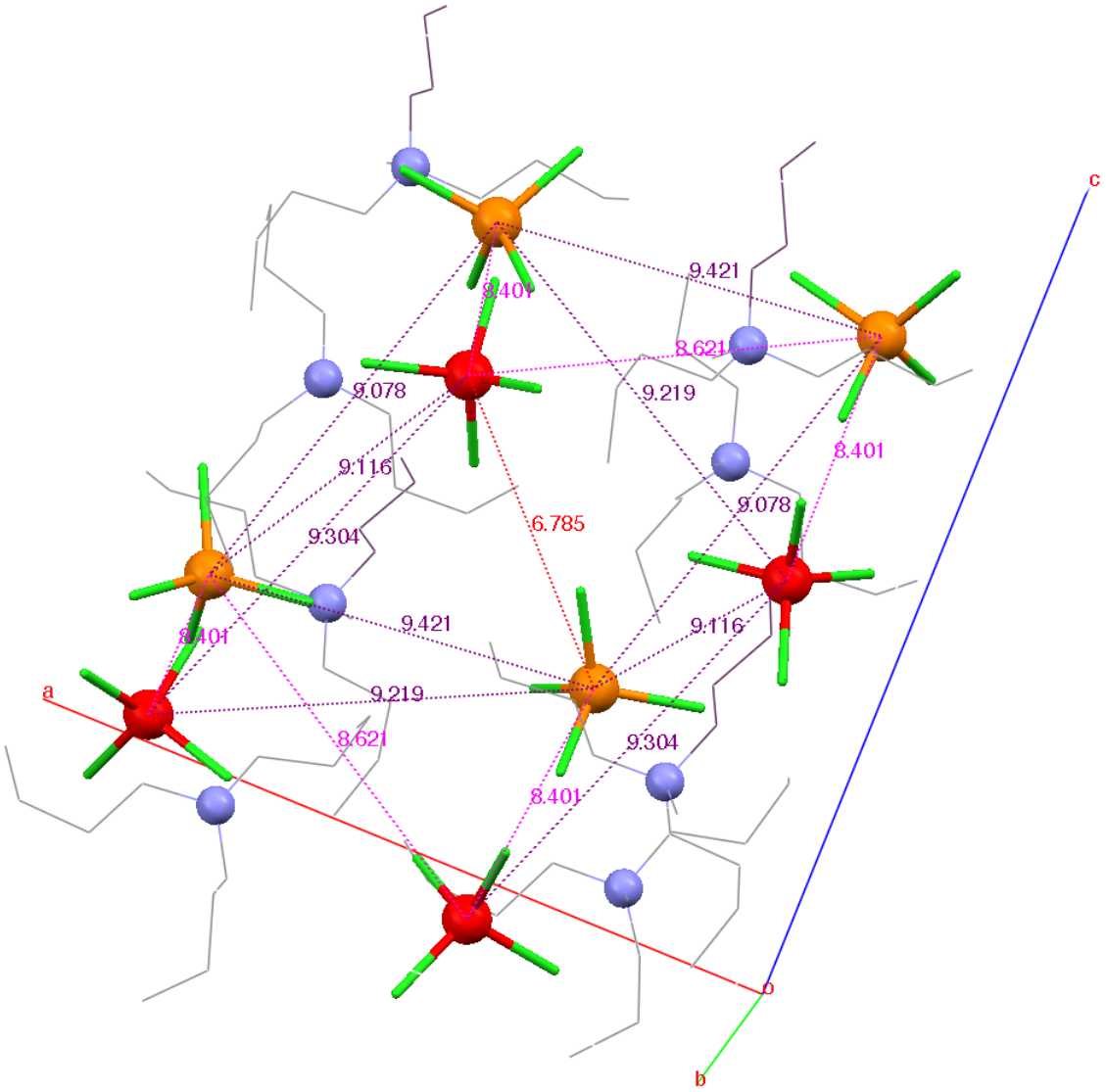

Figure 3: Diagram of the unit cell of $N^{+}_{1444}/[FeCl_4]^{-}$showing the distances between the iron atoms, depicted in red and orange to represent the two inequivalent positions. There is one relatively short separation of 6.785 Å per pair of inequivalent iron atoms. All other distances are greater than 8 Å.

Thermal properties

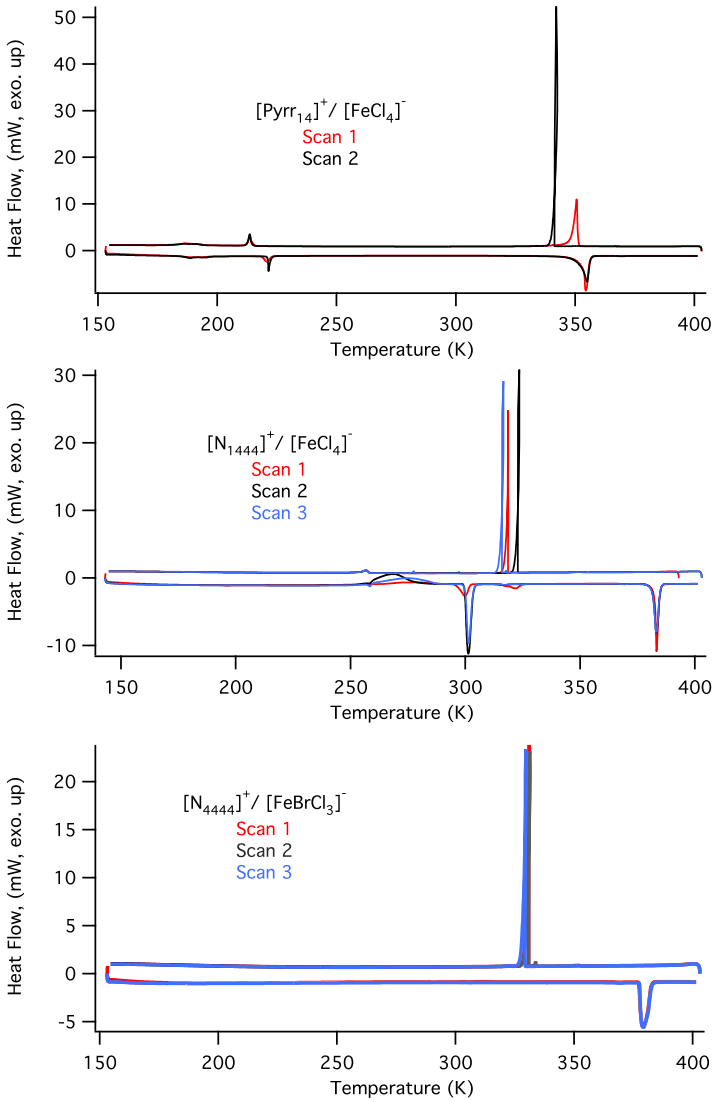

Figure 4: DSC scans of $Pyrr_{14}^{+}/[FeCl_4]^{-}$, $N_{1444}^{+}/[FeCl_4]^{-}$, and $N_{4444}^{+}/[FeBrCl_3]^{-}$. The data in this figure show the repetitive DSC scans measured at Brookhaven National Lab. Upon detailed examination of the data for $N_{4444}^{+}/[FeBrCl_3]^{-}$, the lack of an appreciable heat capacity increase after the transition at 379 K suggested that it was not a melting transition. Consequently, a DSC scan extending to higher temperature was measured at Rutgers and it is shown in Fig. 4 of the paper.

SQUID magnetic measurements

Magnetic susceptibility measurements were made on $N^+_{4444}/[FeBrCl_3]^-$, $N^+_{1444}/[FeCl_4]^-$ and $Pyrr^+_{14}/[FeCl_4]^-$. All three compounds display simple paramagnetic behavior in response to an applied field in these temperature ranges.

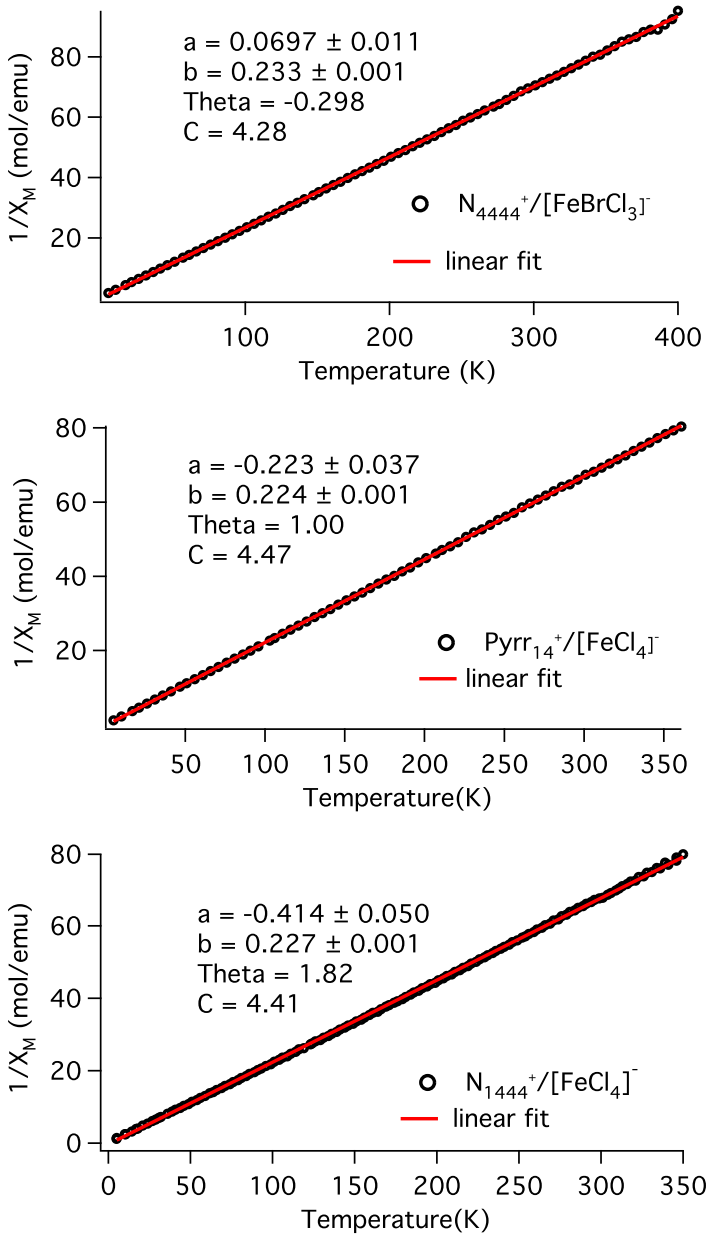

Figure 5: Inverse χ_M of $Pyrr^+_{14}/[FeCl_4]^-$, $N^+_{1444}/[FeCl_4]^-$ and $N^+_{4444}/[FeBrCl_3]^-$.

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Crystallographic Information Files and checkCIF Files

The Crystallographic Information File (.cif file) for $Pyrr_{14}^{+}/[FeCl_4]^{-}$ is named **p14b.cif**; the associated checkCIF file is **P14_checkcif_report.pdf**.

The Crystallographic Information File (.cif file) for $N_{1444}^{+}/[FeCl_4]^{-}$ is named **N1444b.cif**; the associated checkCIF file is **N1444_checkcif_report.pdf**.

These four files are available from the RSC ReSource site at http://rsc.org.