New Thiourea-Based Ionic Liquid as an Electrolyte Additive to Improve Cell Safety and Enhance Electrochemical Performance in Lithium-Ion Batteries

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ABSTRACT: Our society is critically dependent on lithium-ion batteries (LIBs) as a power source for portable electronic gadgets. One of the major problems with these batteries is the degradation of the materials inside them. In addition to the reduced cell life, building-up of these degraded products inside the cells is very detrimental to the safe operation. Herein, we report the synthesis and characterization of a novel thiourea-based room temperature ionic liquid (IL), 3-heptyl-1-(3-(3-heptyl-3-phenylthioureido)-propyl)-1H-imidazole-3-ium hexafluorophosphate. Its electrochemical and thermal properties including transport phenomena have been studied. It is proposed to be used as a nominal additive to commercially used electrolytes, ethylene carbonate and di-methyl carbonate mixtures. The comparative performance characteristics of the LIBs in the presence and the absence of this IL additive have been demonstrated with a traditional lithium nickel cobalt manganese oxide cathode (NMC111), a graphite anode, and an ethylene carbonate and di-methyl carbonate (1:1, v/v) electrolyte. It is further demonstrated that use of this electrolyte additive in batteries helps to address some of the major concerns of the conventional electrolytes such as safety issues and cycling performance as well as coulombic efficiency with enhanced discharge capacities.

1. INTRODUCTION

Lithium-ion batteries (LIBs) are key enablers of modern day technologies not only because of their high energy densities (approx. 240 Wh kg⁻¹)²,³ and high operating voltage (approx. 3.6 V) but also their less self-discharge capacities and long cycle life, and most importantly their environment-friendly character. Their performance is particularly important for ultraportable electronic gadgets like mobile phones, tablets, laptops, smart watches, and many other such applications. Two additional high potential areas of applications include electrical energy storage at different capacity levels spanning from home to grid-levels and power sources for electric vehicles.⁴,⁵ Several research has been carried out on advanced electrode materials, separators, and electrolytes for LIBs.⁶,⁷ However, long cycling performance and safety are the major concerns for these types of batteries and they require immediate attention.⁸–¹⁰ Kalhoff et al.¹¹ summarized state-of-the-art and perspectives of safer electrolytes for LIBs. The cathode and anode materials, which have been used in lithium ion batteries, are generally not stable toward conventional electrolytes, for example, cyclic carbonates,¹² because of their low redox potential limits. To improve the performances of LIBs, the most economic and effective method is to use electrolyte additives.¹³ Haregewoin et al.¹⁴ and Zhang¹⁵ carefully articulated the recent progress and prospects of electrolyte additives for LIBs. The primary role of these additives is to build a protective coating on the electrode surfaces, which is commonly known as the solid electrolyte interface (SEI), which retains even high ionic conductivity for a better performance. These electrolyte additives may be engineered to enhance different functionalities, which in turn can improve battery performances such as (i) SEI improvers,⁶–¹⁰ (ii) cathode-protective agents,¹⁰,²¹ (iii) LiPF₆ salt stabilizers,²²,²³ (iv) safety-enhancing additives,²⁴,²⁵ and (v) Li deposition improvers.²⁶,²⁷ Typically, these types of additives are used less than 5% either by weight or by volume. In essence, they are supposed to significantly improve the cycle life and cyclability of LIBs even when administered in nominal quantity.

Room-temperature ionic liquids (RTILs) belong to a class of ionic liquids (ILs), which can be specifically engineered to enhance key performance metrics like high thermal stability, adjustable viscosities, a large electrochemical window, high decomposition temperature, good electrochemical and chem-
ical stability, nonflammability,$^{28−31}$ etc. The tuning of physicochemical properties can be achieved by permutation and combination of suitable pairs of cations and anions.$^{32}$ The RTILs are the most popular green solvents compared to volatile organic solvents.$^{33,34}$ Because of their uniqueness, attempts are being made to use ILs as potential electrolytes for many electrochemical devices like LIBs,$^{35−37}$ fuel cells,$^{38,39}$ and solar batteries.$^{40}$

This article elucidates the development of a monocationic thiourea-based RTIL additive to be used in conjunction with the commercially most popular electrolyte, the ethylene carbonate and di-methyl carbonate (EC + DMC) mixture along with 1 M lithium hexafluorophosphate (LiPF$_6$), and its adaptability in LIBs was studied. To establish that these improvements are realizable in real-life applications, the performance improvements are demonstrated in the present study using a full-cell configuration rather than a half-cell configuration, because the former is closer to real-life applications. By using a nominal amount of RTIL additive, we have achieved a better performance and better cell safety. Use of such a nominal additive will help in restricting the cost escalation at the first phase of commercial introduction of this new technology, therefore, making it attractive for quick industrial adaptation.

2. RESULTS AND DISCUSSION

2.1. Physicochemical Properties. Ionic conductivity of an electrolyte plays a critical role in LIBs. It is well established that the internal resistance of an electrochemical system is significantly affected by the electrical resistivity of an electrolyte solution. Hence, the room-temperature ionic conductivity is measured for the conventional organic carbonate electrolyte mixture and the said mixture in the presence of 5 mM of IL. As expected, the ionic conductivity of the conventional organic electrolyte mixed with the IL is found to be marginally less (11.91 mS cm$^{-1}$) than that of the conventional organic electrolyte (12.2 mS cm$^{-1}$), which is in the range of the ionic conductivity values of the reported electrolytes for LIBs.$^{36,41,42}$ It is worth mentioning here that this nominal decrease in ionic conductivity after addition of the IL to the conventional electrolyte increases the electrode resistance by forming a stable SEI layer leading to the improvement in the performance of LIBs, which has also been confirmed by electrochemical impedance spectroscopy (EIS) (Figure 7).

Furthermore, the viscosity of an electrolyte plays a vital role because it might appreciably alter the transport properties. A pure IL generally shows higher viscosity than commonly used organic electrolytes because of strong interionic interaction.$^{29}$ The viscosity of the electrolyte decreases monotonically (Figure 1) as the temperature is increased.

In order to investigate the effect of the RTIL additive on the electrochemical stability window of the electrolyte [1 M LiPF$_6$ + (EC + DMC), 1:1], cyclic voltammograms (CVs) have been recorded at 300 K with a scanning rate of 1 mV s$^{-1}$ as depicted in Figure 2. The steep increment in current for both reduction and oxidation represents the redox potential limits of the electrolyte containing the RTIL additive. It has been found that the electrolyte in the presence of IL possesses a wider electrochemical window ranging from −0.101 to +6.679 V versus E° (Li/Li$^+$) compared to the base electrolyte’s window (from −0.002 to +6.600 V versus E° (Li/Li$^+$)), which is one of the advantageous properties of the IL to be used as an electrolyte in LIBs.$^{33−45}$ It has also been observed that within this range, the electrolyte acts as an ideally polarizable solvent.$^{46}$ One interesting point is observed when the scan is reversed, that is oxidative decomposition is noticed at −0.75 V versus Li/Li$^+$. This may be the reason for the formation of a protective SEI layer over the electrodes. Thus, this IL can be used as a practical electrolyte additive for the next generation high-voltage LIBs.$^{47}$

Safety has always been remaining one of the main concerns for the development of LIBs. Nonflammability, which is an inherent property of IL-based electrolytes also plays an important role in the safety of LIBs. Comparative flammability tests for the conventional electrolyte, the conventional electrolyte with IL, and pure IL have been performed and the results are presented below (Figure 3). It is observed that conventional electrolyte LiPF$_6$ (1 M) + EC + DMC (1:1) immediately catches fire because of its low flash point; however, the electrolyte with 5 mM IL slowly catches fire after 10 s whereas the pure IL does not catch fire at all. Thus, it clearly suggests that the electrolyte with the IL additive improves the thermal stability as compared to the conventional

![Figure 1. Variation of viscosities of equimolar mixture of EC + DMC containing 1 M LiPF$_6$ + IL.](image1)

![Figure 2. CVs of LiPF$_6$ (1 M) + EC + DMC (1:1) (black) and LiPF$_6$ (1 M) + EC + DMC (1:1) + 5 mM IL (red) at the Pt working electrode. Redox potentials shown here are versus the Li/Li$^+$ reference electrode.](image2)

![Figure 3. Comparative flammability test for the conventional electrolyte (left), the conventional electrolyte with IL (middle), and the pure IL (right).](image3)
organic electrolyte and thereby helps to enhance the safety of LIBs.

Thermal stability is very much needed for battery safety. To check the thermal stability, thermogravimetric analysis (TGA) of (LiPF₆ + EC + DMC), (LiPF₆ + EC + DMC + IL), and the pure IL has been performed and the results are shown in Figure 4. One-stage decomposition behavior is observed for the mixed electrolyte during this test. The decomposition temperature is increased and % weight loss is less when the IL is used as the additive.

To ensure the stability at low temperature, the IL is kept at −20 °C in a fridge for 6 h. It remains liquid at that temperature. DSC measurement has been carried out (Figure S1) to find out the melting/glass transition temperature. No peak is observed but at approx. −22 °C, a phase change occurred that is the glass transition temperature of this RTIL is approx. −22 °C.

2.2. Density Functional Theory Calculations. Density functional theory (DFT) calculations have been performed using the Gaussian 09 package in order to gain better theoretical insights into the electrochemical behavior of the electrolyte used in LIBs. These calculations are performed at the RB3LYP level using the 6-311 + G(d) basis set. Molecular properties such as ionization potential and electronegativity can be calculated in a semi-quantitative manner correlating the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. The optimized structure of electrolytes is summarized in Table 1. To obtain the HOMO and LUMO energy values in eV units, the Hartree constant of 27.21 for unit conversion is used.

| Electrolyte | Frontier Orbital | Frontier Orbital |
|-------------|-----------------|-----------------|
| Energy (eV) | HOMO            | Energy (eV)     |
|-------------|-----------------|-----------------|
| EC          | -8.4666         | 0.2772          |
| DMC         | -8.1823         | 0.0666          |
| IL          | -7.7548         | -4.8545         |

In Figure 4, TGA curves of LiPF₆ + EC + DMC (black; conventional electrolyte), LiPF₆ + EC + DMC + IL (red; conventional electrolyte with the nominal IL mixture proposed in this study), and the pure IL (blue; the IL designed and synthesized in this study).

The cyclability of the cells with- and without-IL additive is investigated further and the results are displayed in Figure 6a. During the first few cycles, the discharge capacity of the cell without the additive is slightly higher than the cell with the IL additive. However, after around 50 cycles, the trend in capacity fading for the two types of cells is changed and the cell with the IL additive shows a better capacity than the cell without the IL additive. This is indicative of the fact that the addition of the IL additive significantly improves the safety of the cell for a long run. Furthermore, the feasibility of the RTIL electrolyte additive can be evaluated by EIS of the cells. These measurements have been performed after the 1st and 100th cycles over a frequency range from 0.1 Hz to 100 kHz measured at the corresponding applied current conditions as this can be helpful in revealing the important traits of lithiation and delithiation capacity behaviours of the cells.

In Figure 5a, we compare the capacity of the cells with and without the IL additive in the first cycle. We see a marginal drop (from 155 to 145 mA h g⁻¹, when operated at 0.3 mA current) in capacity for the cell with the IL additive compared to the cell without it. The obtained columbic efficiency of the first charge–discharge cycle for the electrolyte without and with IL is ~76 and ~80%, respectively. In the first cycle, the marginal drop in capacity for the electrolyte with IL additive is not a cause of concern because this drop happens at the expenses of stable SEI formation, which is very crucial for the better stability of the cell for a long run.

In Figure 5b, we probe the changes in kinematic/rate performances by probing the cell (with the IL additive) at different applied currents ranging from 1.2 to 3 mA. The corresponding observed capacities range from 139 to 119 mA h g⁻¹. These results show the expected trend that is a higher capacity at a low current rate and a lower capacity at a high current loading. There is a nominal drop in the capacity when the loading current is changed from 1.2 to 3.0 mA, which is a good sign of cell performance.

Furthermore, the feasibility of the RTIL electrolyte additive can be evaluated by EIS of the cells. These measurements have been performed after the 1st and 100th cycles over a frequency range from 0.1 Hz to 100 kHz measured at the corresponding applied current conditions as this can be helpful in revealing the important traits of lithiation and delithiation capacity behaviours of the cells.
Figure 5. (a) First charge−discharge cycling performance of the cell for the electrolyte without and with IL at a current rate of 0.3 mA. (b) Rate performance of the cell for the electrolyte with the IL at different current rates of 1.2, 2.1, and 3.0 mA.

Figure 6. (a) Cyclic discharge performances of the cell in the electrolyte without (black) and with the IL (red); (b) Cyclic coulombic efficiency performances of the cell containing the electrolyte without (black) and with the IL (red).

Figure 7. (a) AC impedance response of the cell for the electrolyte without and with the IL additive. The measurements were conducted after the 1st cycle (inset) and 100th cycle of the cell. (b) Equivalent circuit of a lithium ion battery. (c) The corresponding resistance values are represented in the bar chart for the fitted equivalent circuit.
open circuit potentials with a perturbation amplitude of 10 mV.

Figure 7a shows the results of impedance studies in the form of a Nyquist plot. The inset shows the results after the 1st cycle. It is to be noted that the overall impedance of the cell with the IL and without the IL for the 1st cycle is more or less the same but for the 100th cycle, the cell with the IL offers overall less impedance. This implies that the addition of the IL is beneficial for the overall electrochemical stability in general and for long-term cycling performance, in particular. However, from the viewpoint of the scientific understanding of this improvement, it is imperative to ascribe this to a specific transformation and establish causality. In order to obtain this specific insight, the impedance results are fitted to the closest equivalent electric circuit for the lithium ion battery under study, which is shown in Figure 7b. This equivalent circuit comprises of the resistance of the SEI ($R_s$), electrode ($R_e$), and the capacitance of the surface film, and enables the ion ($Li^+$) transport through the liquid (electrolyte) media ($R_{liq}$), and the electrical double layer is denoted by CPE$_1$ and CPE$_2$, respectively. Because we are using the IL in a nominal amount ($5 \text{ mM}$), its addition is not likely to appreciably change the electrolyte resistance $R_{liq}$ and this is supported by Figure 7c. This parameter is a strong function of transport number, thereby of diffusivity and temperature. What is really remarkable is that after 100 cycles, the electrolyte resistance for the cell with the IL becomes significantly lower than that for the cell without the IL. This is a clear indication of lower electrolyte degradation because of IL addition. We also notice a similar improvement for SEI resistance, this may be because of the formation of a stable SEI over the electrode with the IL additive. Perhaps, the most remarkable point is the electrode resistance, which hardly changes with the cycle number for the cell with the IL additive. Therefore, it can be reasonably guessed that even an insignificant use is extremely beneficial for the overall electrochemical stability of the cell.

2.4. Morphology Study. During charging–discharging, a passivation layer, which is known as the SEI forms because of the decomposition of the electrolyte inside the battery. The formation of a SEI, in general, improves the performance by allowing $Li^+$ ion transportation but blocks electrons, which is the cause of further electrolyte degradation. The evidence for SEI formation is supported by the microstructural and surface chemistry changes of the electrodes when they are exposed to the electrolyte mixture. SEM imaging has been performed on the graphite anode and the NMC cathode of the full cells. The morphological changes are observed under fresh conditions as well as after completion of 10 cycles of charging–discharging. The SEM morphographs of the graphite anode and the NMC cathode before cycling are shown in Figure 8a,d, respectively. Without the IL additive, the graphite anode can be observed as the nonuniform surface films (Figure 8b) while a homogeneous and smooth morphology can be seen in Figure 8c with the IL additive.

Most interesting observation is made for the NMC cathode. The NMC cathode with the IL additive shows a smoother morphology than the fresh NMC cathode as well as without the IL additive as shown in Figure 8d–f, implying the formation of a protective layer over the cathode also. These results though are not completely unexpected if we take into account the energy level (HOMO–LUMO) of the electrolyte and additive (Table 1), where it was evident that a comparatively smaller electrochemical window of the IL likely causes the degradation on both the electrodes, thus making a truly sacrificial electrolyte additive.

3. CONCLUSION

Here, we report the detailed synthesis and characterization of a novel thiourea-based RTIL, 3-heptyl-1-(3-(3-heptyl-3-phenylthioureido)propyl)-1H-imidazole-3-ium hexafluorophosphate. We investigated both its physical and electrochemical properties. While it can be used for different applications, here we demonstrate its beneficial effects as an electrolyte additive in lithium ion batteries and show that even in nominal quantity, it significantly improves the overall electrochemical stability of the cells. Based on the analyses that is electrochemical impedance of the cell and the SEM study, we have shown that it significantly enhances the stability of the solid–electrolyte interface and also limits the increase in electrode resistance with increasing cycles of use. Therefore, its addition improves the retention of crucial performance metrics even after many cycles. Furthermore, it also adds the antiflammability feature to the cell, thereby addressing one of the most important safety concerns. Using of this type of RTIL in nominal quantity as an electrolyte additive is an attractive way
to improve long cycling performance of LIBs, without any major disruption of LIB fabrication technology and might be commercially exciting.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All solvents (analytical and reagent grade) are obtained from Spectrochem (India) and Sigma-Aldrich (India) and used as received without any further purification. Solvents are dried by using standard literature methods. EC (99%), DMC (99%), and deuterated solvents for NMR are purchased from Sigma-Aldrich (India) and used as received. 1-(3-Aminopropyl)imidazole, phenyl thiocyanate, 2-iodo butane, polyvinylidene fluoride (binding material), and N-methyl-2-pyrrolidone (NMP solvent) are procured from Sigma-Aldrich (India) and used as received. Acetylene black (conducting material) is purchased from MTI Corporation.

1H NMR spectra of the IL are recorded on a Bruker AVANCE 400 NMR spectrometer. The Fourier transform infrared spectra are recorded on a BRUKER ALPHA-T FT-IR spectrometer in the range 400–4000 cm⁻¹. Electrospay ionization mass spectra (ESI-MS) of the IL is recorded on a Bruker microTOF-Q II mass spectrometer. Elemental analysis is carried out using an Elementar vario MICRO cube CHN analyzer. An Anton Par rheometer (MCR 301) is used to measure the viscosity of the compound. A Metler Toledo combined pH and Conductometer (Eutech PC 2700) is used to measure ionic conductivity at room temperature. CVs of the compound are recorded on a CH instruments electrochemical analyzer (model 620D) with a three-electrode system (Pt working electrode, Pt wire as an auxiliary electrode, and an Ag/AgCl reference electrode). Thermogravimetric analysis is performed using a Netzsch STA 449 F5 under an argon atmosphere from room temperature to 450 °C with a heating rate of 10 °C/min. Low-temperature differential scanning calorimetry (DSC) is carried out using a PerkinElmer DSC 8000 under a nitrogen atmosphere from −75 to 80 °C with a cooling/heating rate of 10 °C/min. The flammability tests are carried out using three cotton plugs (1 cm diameter and 0.07 g weight each) soaked with 1 mL of each of the conventional electrolyte, the conventional electrolyte with 5 mM IL as the additive, and the pure IL in three separate watch glasses. Their ignition times are monitored after exposing to a gas lighter’s flame. The coin cells are fabricated in a glove box (M. Braun, Germany) filled with argon with H₂O < 0.5 ppm and O₂ < 0.5 ppm. A Neware BTS-SV10 mA battery tester is used for the charge–discharge and rate capacity measurement of the cells. An AUTOLAB PGSTAT302N (Metrohm) is used to measure EIS of the cells. SEM imaging is performed in FEI Apreo LoVac.

4.2. Synthesis of IL, [(3-Heptyl-1-(3-heptyl-3-fluoroureido)propyl)-1H-imidazole-3-ium] hexafluorophosphate]. 1-(3-Aminopropyl)imidazole (A) (1 g, 7.989 mmol) is dissolved in 20 mL of acetonitrile in a round bottom flask equipped with a magnetic stirrer and a septum under a dry nitrogen atmosphere. Stirring is continued for 10 min. To this solution, an excess of phenyl thiocyanate (B) (1.0519 g, 7.781 mmol), dissolved in 20 mL of acetonitrile, is added dropwise using a syringe as depicted in Scheme 1. The reaction mixture is stirred for 48 h followed by stripping of the solvent in vacuo. The residue (C) is then dried overnight in a high vacuum. The crude material is used in the next step without further purification. Under a nitrogen atmosphere, the reaction residue is redissolved in acetonitrile (25 mL) and treated with 1.789 g (9.726 mmol) of iodohexane (D). The mixture is then heated gently without refluxing and is stirred overnight. The reaction mixture is protected from light by wrapping the flask with aluminum foil. Acetonitrile is removed in vacuo, leaving a sticky residue (E). The residue is suspended in water and the aqueous layer was washed with 30 mL of diethyl ether. A solution of 1.780 g (9.6756 mmol) of KPF₆ was dissolved in 20 mL of water and was added to the previous solution. The mixture is stirred overnight at 60 °C, during this time, the product separates from the water as an oily liquid phase.

The water is decanted from the product and the product is washed with water 4 times to remove any remaining KPF₆. The final product is dissolved in acetonitrile and toluene is added to it to form an azeotropic mixture to remove water. Furthermore, impurities are removed by dissolving the residue in dichloromethane and washing with distilled water as the compound is hydrophobic. A light yellow-colored oily liquid is obtained (IL). Finally, the trace amount of water is removed by drying the product in a lyophilizer for 48 h. To ensure that the IL is moisture free, Karl Fischer Titration is performed and it is observed that the IL has no water present in it. Yield: 1.72 g (84%).
The synthetic route of the IL is represented in Scheme 1. In order to confirm the purity of the synthesized IL, $^1$H NMR, $^{13}$C NMR, and IR spectroscopy, ESI-mass spectrometry, and elemental analyses have been carried out. NMR analyses are presented on the δ scale and the chemical shift (δ) in ppm is with respect to TMS. $^1$H NMR (400 MHz, DMSO-$d_6$, ppm) δ 0.85 (t, J = 8 Hz, 6H), 1.26 (s, 16H), 1.55 (s, 2H), 1.80 (t, J = 8 Hz, 2H), 2.02 (d, $J = 8$ Hz, 2H), 3.09 (t, $J = 8$ Hz, 2H), 3.49 (s, 2H), 4.17 (t, $J = 8$ Hz, 2H), 4.27 (t, $J = 8$ Hz, 2H), 7.19 (s, 2H), 7.38 (d, $J = 8$ Hz, 1H), 7.47 (t, $J = 8$ Hz, 2H), 7.84 (s, 2H), 9.24, (s, 1H) (Figure S2). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 167.6, 135.8, 135.3, 129.6, 128.6, 126.8, 122.8, 122.2, (PF$_6$)$^+$, 457.34; found, 457.33, calcd for C$_{20}$H$_{31}$N$_4$S ([IL-(PF$_6$)-(heptyl) + H]$^+$), 359.23; found, 359.22 (Figure S5).

and redox potential with respect to Li+/Li. The slurry is coated using black (conducting material), and polyvinylidene anode are the preferable choice for the fabrication of our LIBs. The electrode plate is subsequently dried at 120 °C under vacuum and then circular electrodes of diameter 16 mm with 1 M LiPF$_6$ salt. For fabricating cells with IL additives, all electrolytes containing EC and DMC in a ratio of 1:1 (v/v) are used. NMR analyses are performed in CDCl$_3$. In general, the NMC 111 (composition: 33.33% Ni, 33.33% Mn, and 33.33% Co (LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$)) cathode and the graphite elemental analyses have been carried out. NMR analyses are presented on the δ scale and the chemical shift (δ) in ppm is with respect to TMS. $^1$H NMR (400 MHz, DMSO-$d_6$, ppm) δ 0.85 (t, J = 8 Hz, 6H), 1.26 (s, 16H), 1.55 (s, 2H), 1.80 (t, J = 8 Hz, 2H), 2.02 (d, $J = 8$ Hz, 2H), 3.09 (t, $J = 8$ Hz, 2H), 3.49 (s, 2H), 4.17 (t, $J = 8$ Hz, 2H), 4.27 (t, $J = 8$ Hz, 2H), 7.19 (s, 2H), 7.38 (d, $J = 8$ Hz, 1H), 7.47 (t, $J = 8$ Hz, 2H), 7.84 (s, 2H), 9.24, (s, 1H) (Figure S2). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 167.6, 135.8, 135.3, 129.6, 128.6, 126.8, 122.8, 122.2, (PF$_6$)$^+$, 457.34; found, 457.33, calcd for C$_{20}$H$_{31}$N$_4$S ([IL-(PF$_6$)-(heptyl) + H]$^+$), 359.23; found, 359.22 (Figure S5).

IR (CHCl$_3$, ppm): 167.6, 135.8, 135.3, 129.6, 128.6, 126.8, 122.8, 122.2, (PF$_6$)$^+$, 457.34; found, 457.33, calcd for C$_{20}$H$_{31}$N$_4$S ([IL-(PF$_6$)-(heptyl) + H]$^+$), 359.23; found, 359.22 (Figure S5).

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