

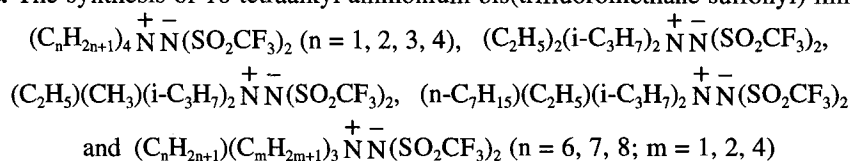
Synthesis and Properties of Ambient Temperature Molten Salts Based on the Quaternary Ammonium Ion

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Abstract. The synthesis of 16 tetraalkyl ammonium bis(trifluoromethane sulfonyl) imide salts,



are reported in this paper. Trends in properties of these salts are discussed. The symmetrical tetraalkyl ammonium salts with the bis(trifluoromethyl sulfonyl) imide anion exhibited a lower melting point than that of corresponding ammonium halides. The salts with low symmetry ammonium cations were found to be of generally lower melting point, and many were stable liquids at room temperature. Several of these did not crystallize during cooling below room temperature and exhibited glass transition temperatures in the region of $-60\text{ }^\circ\text{C} \sim -80\text{ }^\circ\text{C}$. A comparison of properties between the ammonium imide salts and corresponding trifluoromethane sulfonates is also presented.

1. Introduction

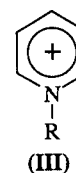
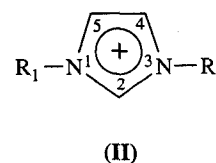
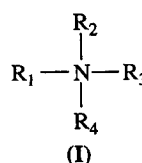
Molten salts have long been the subject of fundamental research as well as productive tools in electrochemistry, fused-salt chemistry, and organic reactivity manipulation [1, 2]. More recently, molten salts, especially those that are liquid at room temperature, have received attention as potentially useful electrolytes in high energy density batteries, photoelectrochemical solar cells, electroplating, capacitors and so on [3-11]. References 3-11 focus on the electrical properties of the molten salts, including conductivity and electrochemical stability, as well as the relation between these properties and the salt structure or composition.

Most ambient temperature molten salts reported to date involve a substituted nitrogen-containing cation, such as the tetraalkyl ammonium [2,4-6] (I), imidazolium [8-11] (II), pyridinium [1] (III) or triazolium [3] cations.

In some cases, the organic salts were mixed with inorganic salts, such as aluminium chloride, to obtain am-

bient-temperature molten salt mixtures. Bonhote et al. [11] reported a series of liquid salts based on the 1,3 dialkyl imidazolium cation.

A fundamental problem [4] associated with molten salts containing the pyridinium cation is the known reduction of the pyridinium cation, which foreshortens the electrochemical window of stability (i.e. the electrochemical potential range within which the salt is stable with respect to electrochemical reactions). The alkylimidazolium salts have a more favourable electrochemical window since the imidazolium cation is not as easily reduced. However, few alkylimidazolium salts are commercially available and the preparation of 1,3 dialkyl imidazolium salts is a multistep process. There are also concerns about



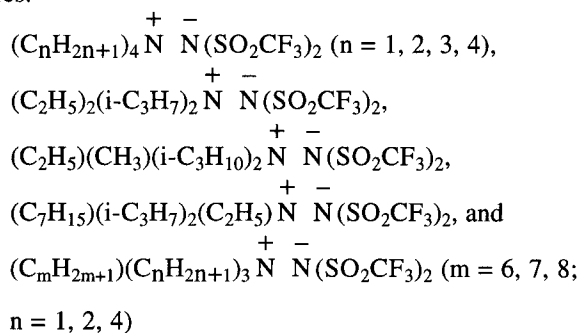
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degradation of these salts by reaction at position 2 of the imidazolium ring.

It has been reported in the literature [11] that some salts composed of the dialkyl imidazolium cation and a perfluorinated anion have low melting points (<-30 °C to ambient temperature). The bis(trifluoromethane sulfonyl) imide anion is found to be particularly effective in lowering the melting point of salts. The perfluorinated sulfonyl groups also produce strong delocalisation of the negative charge, weakening the mostly electrostatic bond with the cation and lowering the viscosity.

Gordon and Subba Rao [2] found that the melting point of thirteen long chain tetraalkyl ammonium salts, such as $(C_7H_{15})_2(C_3H_7)_2NBr$ and $(C_{10}H_{21})(C_8H_{17})(CH_3)_2NClO_4$, were below room temperature. Their results suggest that the reduction of the cation symmetry is therefore also a potential method of lowering the melting point of a salt. In this case, however, the size of the cations involved generally resulted in low ionic conductivity and high viscosity.

It appears therefore, that there are two approaches possible to lowering the melting point of these organic salts: the use of perfluorinated anions with highly delocalized charge and/or low symmetry N-substitution of the quaternary ammonium cation. In this work a series of quaternary ammonium bis(trifluoromethane sulfonyl) imide salts were synthesised having either a symmetrically substituted cation (to investigate the effect of the fluorinated anion), or a low symmetry cation containing one relatively long alkyl group with the remainder short to lower the symmetry of the structure. Thus, sixteen novel ammonium imide salts, with the following structures:



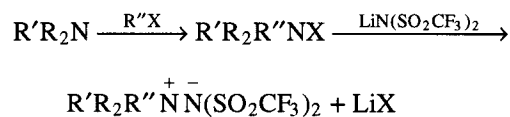
have been synthesised and their thermal and conduction properties examined.

A series of low symmetry tetraalkylammonium salts based on the triflate anion $(CF_3SO_3^-)$ were also prepared

for comparison, the triflate anion being smaller and hence likely to be more mobile, which may lead to higher conductivity.

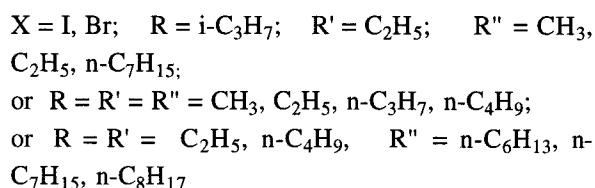
2. Experimental Details

The majority of the salts were prepared by reaction scheme I, using the tetraalkyl ammonium halide as the source of the cation:

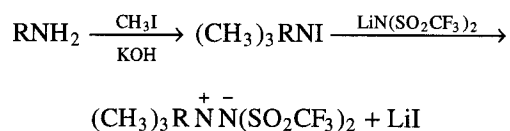


Scheme I

where



In the preparation of the three ammonium imide salts involving the trimethyl ammonium moiety, another synthesis method of the intermediate substituted ammonium iodide [14] was used (scheme II) in order to avoid the use of trimethyl amine (b.p. = 2.9 °C).



Scheme II

where $R = n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}$

Further details of the synthesis and characterization of the compounds are presented in the appendix.

A Perkin-Elmer Differential Scanning Calorimeter Model 7 was used to obtain the thermal properties at scanning rate 10.0 °C per minute. Two standard samples, p-nitrotoluene (m.p. 51.6 °C) and acetic acid (m.p. 16.6 °C), were used for the calibration of temperature in the DSC measurement in the temperature range from -20 °C to 150 °C. Glass transition temperatures were measured at the onset of the transition. Conductivity was measured at 25 °C using a Wayne Kerr Conductance Bridge. Cells were calibrated before and after the measurements using 0.01 demal KCl solutions.

Table 1. Properties of Quaternary Ammonium Imide Salts.

Acronym	STRUCTURE	YIELD	M.P.	T _g	σ/10 ⁻⁴ S cm ⁻¹
		/ %	/ °C	/ °C	(25°C)
N ₁₁₁₁	(CH ₃) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	89	133	-	-
N ₂₂₂₂	(C ₂ H ₅) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	93	109	-	-
N ₃₃₃₃	(n-C ₃ H ₇) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	98	105	-	-
N ₄₄₄₄	(n-C ₄ H ₉) ₄ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	97	96	-	-
N _{223'3'}	(CH ₃ CH ₂) ₂ (i-C ₃ H ₇) ₂ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	92	148	-	-
N _{123'3'}	(CH ₃)(CH ₃ CH ₂)(i-C ₃ H ₇) ₂ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	93	140	-	-
N ₆₁₁₁	(n-C ₆ H ₁₃)(CH ₃) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	65	-	-74	4.3
N ₇₁₁₁	(n-C ₇ H ₁₅)(CH ₃) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	74	-	-73	4.0
N ₈₁₁₁	(n-C ₈ H ₁₇)(CH ₃) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	65	-	-73	3.5
N ₆₂₂₂	(n-C ₆ H ₁₃)(C ₂ H ₅) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	97	20	-81	6.7
N ₇₂₂₂	(n-C ₇ H ₁₅)(C ₂ H ₅) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	96	-	-79	5.1
N ₈₂₂₂	(n-C ₈ H ₁₇)(C ₂ H ₅) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	97	-	-74	3.3
N ₆₄₄₄	(n-C ₆ H ₁₃)(n-C ₄ H ₉) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	94	26	-68	1.6
N ₇₄₄₄	(n-C ₇ H ₁₅)(n-C ₄ H ₉) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	94	-	-67	1.6
N ₈₄₄₄	(n-C ₈ H ₁₇)(n-C ₄ H ₉) ₃ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	97	-	-63	1.3
N _{723'3'}	(n-C ₇ H ₁₅)(C ₂ H ₅)(i-C ₃ H ₇) ₂ N ⁺ N ⁻ (SO ₂ CF ₃) ₂	90	-	-82	3.1

3. Results and Discussion

The synthesis yields and properties of the ammonium imide salts are shown in Table 1. The first four ammonium imide salts in Table 1, i.e. (CH₃)₄N⁺N⁻(SO₂CF₃)₂ (denoted N₁₁₁₁, where the subscript numbers indicate the number of carbon atoms in the alkyl groups of the ammonium cation), N₂₂₂₂, N₃₃₃₃, and N₄₄₄₄, were synthesised only by the second reaction in scheme (I). Thus the corresponding commercially available tetraalkyl ammonium halide was reacted with the lithium imide salt, LiN(SO₂CF₃)₂. The other two solid imide salts, N_{223'3'} and N_{123'3'}, were prepared by the two steps of scheme (I). The delocalisation of the charge on the imide anion results in a relatively hydrophobic quaternary ammonium salt. Therefore, the quaternary ammonium imide salt separates readily from the aqueous solution in scheme I, whereas the reactants and other products are water soluble. This allows the second reaction in scheme I to readily go to-

wards completion and results in high yields. It also allows purification of the product through washing to remove the water-soluble impurities. As shown in Table 1, most of the solid ammonium imide salts were synthesised with yield higher than 90%, except for N₁₁₁₁, which, having the shortest alkyl group in the cation, is less hydrophobic than the others.

Table 1 also shows the synthesis yield of the ten ammonium imide salts having non-symmetric ammonium cations. These were all liquid at room temperature. In these latter salts, the second reaction in schemes (I) and (II) proceeds smoothly at room temperature and the resultant product forms an organic liquid phase, thereby separating from the aqueous system during the reaction. As a result, the yields of N₆₂₂₂, N₇₂₂₂, N₈₂₂₂, N₆₄₄₄, N₇₄₄₄, N₈₄₄₄ and N₆₂₂₂, as shown in Table 1, are very satisfactory (90-97%). The yields of N₆₁₁₁, N₇₁₁₁ and N₈₁₁₁ were lower than the others in Table 1, since the three

trimethyl alkyl ammonium imides are less hydrophobic and therefore more product was lost in the purification procedures (washing with distilled water).

The melting points of the six solid imide salts are shown in Table 1. The melting points of the four tetraalkyl ammonium imide salts in Table 1 are notably quite low, as compared to their corresponding tetraalkyl ammonium halides (around 150-300 °C [12]). It appears, therefore, that introduction of the large, charge delocalised $^{-}\text{N}(\text{SO}_2\text{CF}_3)_2$ anion has a strong effect in lowering the melting point of the salts. For these symmetrical salts, the melting points increase with decreasing length of the alkyl groups in the cation; as also found in the corresponding tetraalkyl ammonium halides. The hypothesis involved in introducing the diisopropyl groups to the ammonium cation was to produce the corresponding imide salt with increased branching. This has the effect of lowering both boiling point and melting point for many organic compounds [13]. However, the results in Table 1 show that the two imide salts having diisopropyl substituents in the ammonium ion, $\text{N}_{223'3'}$ and $\text{N}_{123'3'}$, have higher melting points than their corresponding straight-chain alkyl analogs. This result indicates that the factors affecting melting point are quite complicated in this series of tetraalkyl ammonium imide salts. This was also observed in Bonhote et al.'s work [11], in which they found that it was difficult to correlate the melting point of the imidazolium imide salts with their chemical structures.

The remainder of the ammonium imide salts listed in Table 1 are present in the liquid state at room temperature. The DSC thermograms indicate that only a glass transition is observed in the temperature range from -120 °C

to 20 °C. The glass transition temperatures, T_g , were generally in the range -70 °C to -80 °C as shown in Table 1. N_{6444} , and N_{6222} displayed DSC melting transitions around 20 °C to 25 °C; however, they showed no tendency to crystallise when cooled to slightly under their melting point. For example, N_{6222} was stored at -4 °C for 7 days and remained in its liquid state. This phenomenon indicates that these two imide salts are quite stable in their supercooled state.

Comparing the results in Table 1 as a function of the ammonium ion structure, it can be seen that symmetry of molecular structure plays an important role in their thermal behaviour. Taking N_{6222} as an example, this salt has a melting point of 20 °C and a glass transition at -80.7 °C, while N_{3333} , which has the same molecular weight as N_{6222} but is more symmetrical, has a much higher melting point (105 °C).

The increase in molecular weight of the cation in the case of the symmetric tetraalkyl ammonium salts leads to a decreasing melting point, as one would expect with a greater shielding of the ionic interactions. For the lower symmetry cations based on trimethyl substituted salts, there is little effect of the length of the fourth substituent on T_g or conductivity. This probably reflects the fact that interactions are dominated by the methyl substituents. When these methyl groups are replaced by ethyl or propyl substituents, the length of the fourth group becomes more important. For example, T_g increases and conductivity decreases from N_{6222} to N_{8222} and N_{6444} to N_{8444} . In addition, there appears to be a maximum in conductivity and mobility (as reflected in T_g) at N_{6222} ; thus there seems to be a competition between size of the cation and

Table 2. Synthesis Yield and Properties of Quaternary Ammonium Triflate Salts.

STRUCTURE	YIELD / %	M.P. or T_g / °C	$\sigma/S\text{ cm}^{-1}$ (25°C)
$(\text{C}_7\text{H}_{15})(\text{C}_4\text{H}_9)_3\text{N}^+\text{O}^-\text{SO}_2\text{CF}_3$	89	$T_g = -55$	-
$(\text{C}_7\text{H}_{15})(\text{C}_2\text{H}_5)_3\text{N}^+\text{O}^-\text{SO}_2\text{CF}_3$	57	M.P. = 54	-
$(\text{C}_7\text{H}_{15})(\text{CH}_3)_3\text{N}^+\text{O}^-\text{SO}_2\text{CF}_3$	48	M.P. = 140	-
$(\text{C}_6\text{H}_{13})(\text{C}_4\text{H}_9)_3\text{N}^+\text{O}^-\text{SO}_2\text{CF}_3$	88	M.P. = 72	-
$(\text{C}_8\text{H}_{17})(\text{C}_4\text{H}_9)_3\text{N}^+\text{O}^-\text{SO}_2\text{CF}_3$	97	$T_g = -57$	1.7×10^{-5}

strength of ionic interactions in determining ion mobility.

Since the triflate anion, $^{-}\text{OSO}_2\text{CF}_3$, is smaller than the bis(trifluoromethane sulfonyl) imide anion, $^{-}\text{N}(\text{SO}_2\text{CF}_3)_2$, it was hypothesized that the former should have higher mobility. Therefore, in order to obtain a liquid salt with lower viscosity and hence potentially higher conductivity, lithium triflate was used in scheme (II), instead of lithium bis(trifluoromethane sulfonyl) imide, to prepare the quaternary ammonium triflates. The five quaternary ammonium triflates synthesised in this work are shown in Table 2. It was found that

$(\text{C}_6\text{H}_{13})(\text{C}_2\text{H}_5)_3\text{N}^+ \text{OSO}_2\text{CF}_3$,
 $(\text{C}_6\text{H}_{13})(\text{CH}_3\text{N}^+ \text{OSO}_2\text{CF}_3$,
 $(\text{C}_8\text{H}_{17})(\text{C}_2\text{H}_5)_3\text{N}^+ \text{OSO}_2\text{CF}_3$ and
 $(\text{C}_8\text{H}_{17})(\text{CH}_3)_3\text{N}^+ \text{OSO}_2\text{CF}_3$, were water-soluble and could not be separated from the reaction system.

From the results in Table 2, it can be seen that two room temperature liquid salts were obtained in this family and, unexpectedly, their T_g 's were higher than those of the corresponding imide salts with the same ammonium cations. It can also be deduced that the four water-soluble triflates are likely to be solid at room temperature by observing the trends in T_m when the alkyl groups in the cation are changed from (C_4H_9) to (C_2H_5) and (CH_3) . The $(\text{C}_7\text{H}_{15})(\text{C}_4\text{H}_9)_3\text{N}^+ \text{OSO}_2\text{CF}_3$ salt is a liquid, while $(\text{C}_7\text{H}_{15})(\text{C}_2\text{H}_5)_3\text{N}^+ \text{OSO}_2\text{CF}_3$ is solid at room temperature and $(\text{C}_7\text{H}_{13})(\text{CH}_3)_3\text{N}^+ \text{OSO}_2\text{CF}_3$ has an even higher melting point. It appears that stronger ionic interaction between the quaternary ammonium cation and the triflate ion, compared with the imide ion, is the dominant factor in determining T_m and T_g in these systems.

4. Summary and Conclusions

A family of quaternary ammonium imide and triflate salts have been successfully prepared with high yield. Some of these are liquid at and below room temperature. In particular, the low symmetry quaternary ammonium ions produce a low or non-existent melting point. The room temperature liquids were conductive ($\sigma = 1-7 \times 10^{-4}$ S/cm) with the highest conductivities obtained with the hexyl triethyl ammonium salt. The imide salts generally had higher conductivities and lower T_g and T_m than the corresponding triflates.

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6. Appendix

Synthetic and Characterization Details Diethyl diisopropyl ammonium iodide (N_{223'3'I}). 5.30 g (0.041 mol) diisopropyl ethyl amine (Aldrich, all chemicals were used as received except as otherwise specified) was mixed with 12.30 g (0.079 mol) ethyl iodide (M&B, freshly distilled) and 20 g butanone (Aldrich). The mixture was refluxed at 85-90 °C (oil bath) for 5 days. The product was filtered to remove the liquid phase and washed with butanone twice to remove any organic impurities. The final product was dried under vacuum at room temperature for more than 48 hrs and 5.33 g of the product was obtained (yield 45.5 %). Anal. calculated for C₁₀H₂₄NI: C, 42.11; H, 8.48; N,

4.91; I, 44.49. Found: C, 41.68, H, 9.03, N, 4.66, I, 44.43.

Diisopropyl ethyl methyl ammonium iodide ($N_{123'3'}$), *Diisopropyl ethyl n-heptyl ammonium iodide* ($N_{723'3'I}$), *n-Hexyl triethyl ammonium iodide*, *n-Heptyl triethyl ammonium iodide*, *n-Octyl triethyl ammonium iodide*, *n-Hexyl tri-n-butyl ammonium iodide*, *n-Heptyl tri-n-butyl ammonium iodide* and *n-Octyl tri-n-butyl ammonium iodide* were prepared using the same procedure as for $N_{723'3'I}$.

n-Hexyl trimethyl ammonium iodide (N_{611I}). 57.7 g (0.407 mol) methyl iodide (Aldrich) was added dropwise into a methanol solution of 10.0 g (0.099 mol) n-hexyl amine (Aldrich) and 11.1 g (0.20 mol) potassium hydroxide. The mixture was refluxed (oil bath $\sim 65^\circ\text{C}$) for ~ 20 hrs. The potassium iodide produced was removed by filtering the mixture and the solvent was removed by distillation. The iodide was recrystallised with ethyl acetate. 17.7 g of the product was obtained (yield 65.6 %). *n-Heptyl trimethyl ammonium iodide* and *n-octyl trimethyl ammonium iodide* were prepared using the same procedure substituting the appropriate primary amine.

n-Hexyl triethyl ammonium bis(trifluoromethane sulfonyl) imide salt (N_{6222}). 0.048 mol of lithium bis(trifluoromethane sulfonyl) imide salt (3M) was dissolved in 10 g distilled water. 0.046 mol of n-heptyl ethyl diisopropyl ammonium iodide was dissolved in 60 g distilled water. The two aqueous solutions were mixed together and then stirred at room temperature for 3 hrs. The product (organic phase) was separated from the aqueous phase by a separating funnel and was washed with distilled water twice to remove any water-soluble impurities. The final product was dried under vacuum at room temperature for more than 48 hrs and 20.8 g of the product was obtained (yield 95.0 %). $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.25 (q, 6H, $J = 7.3$ Hz), 3.12-3.03 (m, 2H), 1.77-1.61 (m, 2H), 1.39-1.25 (m, 15H), 0.89 (t, 3H, $J = 6.6$ Hz). Anal. calculated for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{S}_2\text{O}_4\text{F}_6$: C, 36.04; H, 6.05; N, 6.00; S, 13.74; O, 13.72; F, 24.44. Found: C, 35.82; H, 6.17; N, 6.00; S, 14.01; O, 13.98; F, 24.16.

In all of the following, the same procedure as above for N_{6222} was used, substituting the appropriate quaternary ammonium iodide starting material:

Diethyl diisopropyl ammonium bis(trifluoromethane sulfonyl) imide salt ($N_{223'3'}$); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.92-3.82 (m, 2H), 3.40 (q, 4H, $J = 7.3$ Hz), 1.61-1.39 (m, 18H). *Diisopropyl methyl ethyl*

ammonium bis(trifluoromethane sulfonyl) imide salt ($N_{123'3'}$); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.92-3.82 (m, 2H), 3.37 (q, 2H, $J = 7.4$ Hz), 2.82 (s, 3H), 1.55-1.33 (m, 15H). *Tetramethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{1111}); $^1\text{H-NMR}$ (DMSO-d_6 , δ/ppm relative to TMS): 3.08 (s). *Tetraethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{2222}); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.25 (q, 2H, $J = 7.3$ Hz), 1.36-1.27 (m, 3H). *Tetra-n-propyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{3333}); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.13-3.08 (m, 2H), 1.37-1.61 (m, 2H), 2.82 (s, 3H), 1.01 (t, 3H, $J = 7.3$ Hz). *Tetra-n-butyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{4444}); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.17-3.11 (m, 2H), 1.62-1.54 (m, 2H), 1.44-1.36 (m, 2H), 0.99 (t, 3H, $J = 7.3$ Hz). *Diisopropyl n-heptyl ethyl ammonium bis(trifluoromethane sulfonyl) imide salt* ($N_{723'3'}$); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.99-3.79 (m, 2H), 3.41 (q, 2H, $J = 7.3$ Hz), 3.22-3.13 (m, 2H), 1.80-1.65 (m, 2H), 1.51-1.39 (m, 15H), 1.36-1.29 (m, 8H), 0.88 (t, 3H, $J = 6.5$ Hz). *n-Heptyl triethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{7222}); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.26 (q, 6H, $J = 7.3$ Hz), 3.21-3.03 (m, 2H), 1.67-1.62 (m, 2H), 1.34-1.27 (m, 17H), 0.88 (t, 3H, $J = 6.4$ Hz). *n-Octyl triethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{8222}); $^1\text{H-NMR}$ (DMSO-d_6 , δ/ppm relative to TMS): 3.29-3.07 (m, 8H), 1.70-1.50 (m, 2H), 1.46-1.21 (m, 10H), 1.18-1.14 (m, 9H), 0.87 (t, 3H, $J = 6.5$ Hz). *n-Hexyl tri-n-butyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{6444}); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.19-3.11 (m, 8H), 1.64-1.50 (m, 8H), 1.46-1.33 (m, 12H), 1.04-0.96 (m, 9H), 0.90 (t, 3H, $J = 6.6$ Hz). *n-Heptyl tri-n-butyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{7444}); $^1\text{H-NMR}$ (CDCl_3 , δ/ppm relative to TMS): 3.17-3.10 (m, 8H), 1.59-1.49 (m, 8H), 1.45-1.29 (m, 14H), 1.02-0.95 (m, 9H), 0.91-0.85 (m, 3H). *n-Octyl tri-n-butyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{8444}); $^1\text{H-NMR}$ (DMSO-d_6 , δ/ppm relative to TMS): 3.21-3.13 (m, 8H), 1.72-1.45 (m, 8H), 1.40-1.18 (m, 16H), 0.97-0.84 (m, 12H). *n-Hexyl trimethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{6111}); $^1\text{H-NMR}$ (DMSO-d_6 , δ/ppm relative to TMS): 3.30-3.21 (m, 2H), 3.03 (s, 9H), 1.74-1.63 (m, 2H), 1.30-1.29 (m, 6H), 0.88 (t, 3H, $J = 6.6$ Hz). *n-Heptyl trimethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{7111}); $^1\text{H-NMR}$ (DMSO-

d_6 , δ /ppm relative to TMS): 3.30-3.22 (m, 2H), 3.03 (s, 9H), 1.74-1.63 (m, 2H), 1.29-1.28 (m, 8H), 0.88 (t, 3H, $J = 6.5$ Hz). *n-Octyl trimethyl ammonium bis(trifluoromethane sulfonyl) imide salt* (N_{8111}); $^1\text{H-NMR}$ (DMSO- d_6 , δ /ppm relative to TMS): 3.30-3.21 (m, 2H), 3.03 (s, 9H), 1.68-1.62 (m, 2H), 1.26-1.30 (m, 10H), 0.87 (t, 3H, $J = 6.5$ Hz).

n-Heptyl tri-n-butyl ammonium trifluoromethane sulfonate. The same procedure was used as in N_{6222} ; Lithium trifluoromethane sulfonate (Aldrich) was used instead of the lithium bis(trifluoromethane sulfonyl) imide salt. $^1\text{H-NMR}$ (DMSO- d_6 , δ /ppm relative to TMS): 3.20-3.13 (m, 8H), 1.57-1.40 (m, 8H), 1.36-1.29 (m, 14H), 0.96-0.87 (m, 12H). *n-Heptyl triethyl ammonium trifluoromethane sulfonate*; $^1\text{H-NMR}$ (DMSO- d_6 , δ /ppm

relative to TMS): 3.23 (q, 6H, $J = 7.3$ Hz), 3.14-3.06 (m, 2H), 1.58-1.52 (m, 2H), 1.29-1.12 (m, 17H), 0.87 (t, 3H, $J = 6.4$ Hz). *n-Heptyl trimethyl ammonium trifluoromethane sulfonate*; $^1\text{H-NMR}$ (DMSO- d_6 , δ /ppm relative to TMS): 3.30-3.22 (m, 2H), 3.03 (s, 9H), 1.70-1.62 (m, 2H), 1.29-1.28 (m, 8H), 0.87 (t, 3H, $J = 6.5$ Hz). *n-Hexyl tri-n-butyl ammonium trifluoromethane sulfonate*; $^1\text{H-NMR}$ (DMSO- d_6 , δ /ppm relative to TMS): 3.21-3.13 (m, 8H), 1.57-1.44 (m, 8H), 1.40-1.22 (m, 12H), 0.97-0.85 (m, 12H). *n-Octyl tri-n-butyl ammonium trifluoromethane sulfonate*; $^1\text{H-NMR}$ (DMSO- d_6 , δ /ppm relative to TMS): 3.21-3.13 (m, 8H), 1.71-1.45 (m, 8H), 1.40-1.29 (m, 16H), 0.97-0.84 (m, 12H).

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