Effect of counter-ion on the thermotropic liquid crystal behaviour of bis(alkyl)-tris(imidazolium salt) compounds

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Recently, new thermotropic ionic liquid crystals (LCs) with a hexyl-linked tris(imidazolium bromide) core and two terminal alkyl chains were synthesised and characterised. To explore the effect of different counter-ions on the LC behaviour of this system, derivatives with BF$_4^-$ and Tf$_2$N$^-$ counter-ions were prepared and analysed. Five of the BF$_4^-$ derivatives were found to exhibit thermotropic LC behaviour. The 12-, 14- and 16-carbon tail BF$_4^-$ compounds form SmA phases. The 18- and 20-carbon tail homologues form what appears to be a smectic phase but are weakly mesogenic and harder to characterise. Only two of the Tf$_2$N$^-$ derivatives exhibited mesogenic behaviour. The 18-carbon tail Tf$_2$N$^-$ compound forms an as-yet unidentified, highly periodic smectic phase with positional order while the 20-carbon tail homologue forms a periodic SmA phase. The Tf$_2$N$^-$ mesogens have much lower clearing points even though their LC phases have more order than the Br$^-$ and BF$_4^-$ mesogens. X-ray diffraction showed that these mesogens have different amounts of tail interdigitation between the smectic layers depending on the counter-ion present. Atomistic molecular dynamics simulations indicated that counter-ion size plays an important role in defining the density of the ionic region, which in turn affects the amount of interdigitation in the smectic phases.

Keywords: tris(imidazolium) salts; counter-ions; thermotropic ionic liquid crystals; smectic A phase; higher order smectic phase

1. Introduction

Ionic liquid crystals (ILCs) are a relatively new but highly valued class of LCs that combine the inherent characteristics of conventional uncharged LCs (e.g. self-order and flow) with many of the salt-based properties of room-temperature ionic liquids (RTILs) (e.g. very low vapour pressure, ionic and electrical conductivity, high CO$_2$ uptake vs. other light gases).[1] The latter properties also give ILCs the potential to act as designer solvents for catalysts, enzymes and reactions in much the same fashion that RTILs can.[2] Such desirable properties have driven the study of ILCs and have led to advances in related fields of soft materials, electronics and reactive chemistry. Directed largely by the same self-assembly mechanics of uncharged thermotropic LCs, thermotropic ionic liquid crystal (TILC) phases are largely the product of the size of the mesogen and the immiscibility of regions within their molecular architectures. For example, a rigid aromatic section within a TILC will tend to separate from a softer n-alkyl section. Similarly, a polar and hydrophilic unit will avoid interacting with a hydrophobic section in the same molecule because of their very dissimilar natures. Ionic units often appear in polar sections or assemble into a purely ionophilic section to counteract the hydrophobic architecture.

Imidazolium-based ILCs, in particular, have recently been of great interest in the LC materials community because of the modularity and property control afforded by the use of the imidazolium ring as a cationic construction unit.[1,3] In order to investigate the effect of multiple, linearly chained oligo(imidazolium) units on TILC behaviour, our research group recently synthesised and characterised a series of symmetric polyion compounds containing a hexyl-bridged tris(imidazolium bromide) central core and two peripheral n-alkyl tails containing an even number of carbons (series I) (Figure 1).[4] This initial paper on tris(imidazolium salt) core-based TILCs focused on understanding how the relative lengths of the ionophilic core and the symmetrical n-alkyl hydrophobic tails affected thermotropic LC characteristics. It was found that only when the length of the n-alkyl tails was approximately equal to or longer than the overall length of the hexyl-bridged tris(imidazolium) ionic core did thermotropic LC properties begin to appear. Specifically, only the homologues with 16-, 18- and 20-carbon tails (1h, 1i and 1j) formed smectic A (SmA) phases and a more ordered, as-yet unidentified smectic (SmX) phase, whereas homologues with shorter tails did not show any LC behaviour. Powder X-ray diffraction (PXRD) determined that the spacing of the SmA layers was similar or slightly less...
than the calculated extended length of the corresponding mesogen, confirming that the length of the mesogen dictated the assembly of the layers and the phase.[4]

However, the relative length of the alkyl tails to the ionic core is not the only factor that can affect an ILC’s mesogenic capabilities: the organic salt’s counter-ion or ion is another important variable. The nature of the counter-ion can also greatly alter the characteristics and capabilities of an ILC system, and many common, small-chain anions have been studied for their influences on mesogenic organisation. For example, a series of pyrazolium salts with six different anions was characterised, and the resulting trends were compared.[5] Geometry-wise, spherical and quasi-spherical anions like halides and SbF$_6^-$ are found to have more favourable solid-state packing and therefore higher melting points. Conversely, lower melting trends were found with anions that pack less favourably, such as boron tetrafluoride (BF$_4^-$). The Kouwer group recently published a room-temperature ILC paper in which a switch from BF$_4^-$ to the bis(trifluoromethylsulfonyl)imide anion (Tf$_2$N$^-$) resulted in a 100°C decrease in the mesogen’s clearing point.[6] In 2011, Meyer’s group studied a series of imidazolium salts based on the same 1,3-didodecylimidazolium cation but paired with seven different anions in order to analyse the influence of the anion on crystalline packing, thermal behaviour and the conformation of the cation.[7] Of the seven anions studied, only iodide ($I^-$) was capable of forming a mesophase (SmA). Ionic 1,3,4-oxadiazole molecules with a single ionic unit produced similar trends with broad smectic ranges for halides and BF$_4^-$, as well as perchlorate and dodecylsulfate counter-ions.[8] The perchlorate-based TILCs behaved similarly to the BF$_4^-$ analogues, most likely due to the anion’s tetrahedral shape. With the largest of the anions studied, the dodecylsulfate-containing mesogens had the lowest isotropic points, all else remaining the same in these molecules. Consequently, we thought that the nature of the free counter-ion (i.e. anion) in our new tris(imidazolium salt) core-based TILCs may also play a significant role in determining their LC properties.

Herein, we present two series of linear, symmetrical bis(alkyl)-tris(imidazolium)-core compounds with either BF$_4^-$ or Tf$_2$N$^-$ as the mobile counter-ions (i.e. free anions) in order to study the effect of the counter-ion on thermotropic mesogenicity in this new tricationic ILC platform (Figure 2). Unfortunately, compound 1a (the methyl-tail Br$^-$ compound) could not be purified [4]; therefore, no BF$_4^-$ (2a) or Tf$_2$N$^-$ (3a) analogues of it were synthesised and characterised for this current study. Using a combination of variable-temperature polarised light microscopy (PLM), differential scanning calorimetry (DSC) and either PXRD or small-angle X-ray scattering (SAXS), it was found that the BF$_4^-$ series offers five thermotropic LC mesogens (the 12-,
14-, 16-, 18- and 20-carbon tail homologues), allowing for a larger range of LC homologues than the original Br$^{-}$ series. The 12-, 14- and 16-carbon tail BF$_4^-$ compounds were found to form SmA phases. The 18- and 20-carbon tail homologues form what appears to be an as-yet unidentified smectic phase (Sm$^{\prime}$) according to SALS analysis. However, these two compounds are more weakly mesogenic, making their LC behaviour much harder to characterise by PLM and DSC. The BF$_4^-$ mesogens were observed to generally have higher clearing points than the original Br$^{-}$-containing mesogens. In contrast, only two of the Tf$_2$N$^-$ derivatives (the 18- and 20-carbon tail homologues) exhibit thermotropic LC behaviour. The 18-carbon tail Tf$_2$N$^-$ compound forms highly periodic, an as-yet unidentified smectic phase with some positional order within the layers (Sm$^{\prime}$) (possibly an SmB or soft crystal SmE phase), whereas the 20-carbon tail homologue forms a highly periodic SmA phase. Interestingly, unlike the Br$^{-}$ and BF$_4^-$ mesogens, the two Tf$_2$N$^-$ mesogens have much lower (i.e. sub-100°C) clearing points, even though their LC phases generally have more order than those of the Br$^{-}$ and BF$_4^-$ compounds. Analysis of the PXRD and/or SALS data for the smectic phases of the three sets of mesogenic derivatives suggested that they have very different amounts of tail interdigitation between the layers. Computational simulations of three of these mesogens with the same cationic backbone and tails but different anions revealed that the organisation within the formed smectic layers is greatly affected by the counter-ions present.

2. Experimental details

2.1 Materials

All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Compounds used that do not have a detailed experimental synthesis listed below for them are commercially available from Sigma-Aldrich. All reactions were performed under argon unless otherwise noted. Anhydrous N,N-dimethylformamide (DMF) was prepared by bubbling Ar gas through DMF that was cannulated from a fresh bottle, and anhydrous tetrahydrofuran was collected from an anhydrous alumina-packed solvent delivery system.

2.2 General synthesis procedure for symmetric tris (imidazolium tetrafluoroborate) (series 2) and tris (imidazolium bis(trifluoromethanesulfonylimide) salts (series 3) with long n-alkyl tails

Compounds 1b–j by anion exchange of the Br$^{-}$ anions using sodium tetrafluoroborate (NaBF$_4$) or lithium bis(trifluoromethanesulfonylimide) (LiTf$_2$N), respectively. The tris(imidazolium bromide) compounds 1b–j (Figure 2) were synthesised as detailed in our prior publication, and their characterisation and purity data were consistent with those published.[4] The best purification procedure for each homologue of 1 was dependent upon the length of the peripheral n-alkyl tails on the product as detailed in our prior publication.[4] Spectroscopic and purity analyses data for 1b–j were consistent with those reported for these compounds.[4] The shortest tailed of the bromide ionic organic compounds, 1a, could not be sufficiently purified to proceed, and as a result, neither BF$_4^-$ or Tf$_2$N$^-$ homologues (2a and 3a) were synthesised or characterised. To prepare compounds 2b–j and 3b–j, the Br$^{-}$ counter-ions on 1b–j were exchanged with slightly over three equivalents of NaBF$_4$ or LiTf$_2$N, respectively, in deionised (DI) water overnight. The best purification procedure for each homologue of 2 and 3 prepared (as detailed below) was dependent upon the length of the peripheral n-alkyl tails on the product and the resulting counter-ion present.

2.2.1 Synthesis of 1’-(1’-butyl-3’-hexylimidazolium)-3-(1’-butyl-3’-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2b)

Compound 1b (182 mg, 138 mmol) was dissolved into DI water (20 mL), and NaBF$_4$ (46.2 mg, 0.421 mmol) was added to this solution. The reaction mixture was stirred at ambient temperature overnight before being concentrated via rotator evaporation. The resulting white residue was dissolved in dry acetone (20 mL) and filtered. The acetone was concentrated via rotatory evaporation to give a clear fluid as the desired product 2b. Yield = 50 mg (27%). $^1$H NMR (300 MHz, $d_6$-DMSO) δ = 9.19 (s, 3 H), 7.79 (s, 6 H), 4.15 (s, 12 H), 1.78 (s, 12 H), 1.27 (s, 13 H), 0.90 (t, J = 7.0 Hz, 6 H). $^{13}$C NMR (75 MHz, $d_6$-DMSO) δ = 136.35, 122.91, 49.12, 31.74, 29.54, 25.39, 19.25, 13.73. HRMS: calculated as [M-BF$_4$]$^+$ = 657.4239; found = 756.4227.

2.2.2 Synthesis of 1’-(1’-hexyl-3’-hexylimidazolium)-3-(1’-hexyl-3’-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2c)

This compound was produced by mixing 1c (204 mg, 0.262 mmol) with NaBF$_4$ (87.5 mg, 0.797 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2c was worked up and checked for purity using the same procedure.
described for 2b above. The product was a clear fluid. Yield = 209 mg (99.9%). $^1$H NMR (300 MHz, d$_6$-DMSO) $\delta$ = 9.19 (s, 3 H), 7.79 (s, 6 H), 4.15 (s, 12 H), 1.78 (s, 12 H), 1.27 (s, 13 H), 0.90 (t, $J$ = 7.0 Hz, 6 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) $\delta$ = 136.36, 122.89, 49.32, 49.20, 30.95, 29.70, 29.57, 29.51, 25.59, 25.36, 22.33, 14.27. HRMS: calculated as [M-B$_2$F$_8$]$^{2+}$ = 341.2726; found = 341.2743.

2.2.3 Synthesis of 1-(1'-octyl-3'-hexylimidazolium)-3-(1'-octyl-3'-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2d)

This compound was produced by mixing 1d (100 mg, 0.120 mmol) with NaBF$_4$ (40.0 mg, 0.365 mmol) in a manner similar to that employed in the synthesis of 2b. The reaction mixture was extracted with CH$_2$Cl$_2$ (4 x 20 mL), and the organic layer dried over anhydrous magnesium sulphate before concentration via rotatory evaporation to produce the desired product 2d as a white solid. Yield = 76.7 (74.8%). $^1$H NMR (300 MHz, d$_6$-DMSO) $\delta$ = 9.16 (s, 1 H), 7.80 (d, $J$ = 6.1 Hz, 2 H), 4.15 (s, 4 H), 1.79 (s, 4 H), 1.24 (s, 10 H), 0.85 (d, $J$ = 7.0 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) $\delta$ = 136.32, 122.95, 122.88, 49.32, 49.20, 31.68, 29.75, 29.61, 29.55, 29.22, 29.02, 28.78, 25.94, 25.43, 22.54, 14.42. HRMS: calculated as [M-B$_2$F$_8$]$^{2+}$ = 341.2726; found = 341.2743.

2.2.4 Synthesis of 1-(1'-decyl-3'-hexylimidazolium)-3-(1'-decyl-3'-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2e)

This compound was produced by mixing 1e (127 mg, 0.142 mmol) with NaBF$_4$ (0.046 mg, 0.426 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2e was purified using the same work-up procedure described for the purification of 2d. The final product was a white solid. Yield = 53.6 mg (41.3%). $^1$H NMR (300 MHz, d$_6$-DMSO) $\delta$ = 9.14 (d, $J$ = 7.1 Hz, 1 H), 7.79 (dd, $J$ = 5.3, 1.5 Hz, 2 H), 4.27–4.07 (m, 4 H), 1.95–1.60 (m, 4 H), 1.24 (s, 12 H), 0.86 (t, $J$ = 6.6 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) $\delta$ = 136.32, 122.94, 122.87, 49.32, 49.20, 31.73, 29.75, 29.60, 29.55, 29.33, 29.27, 29.11, 28.78, 25.94, 25.42, 22.55, 14.42. [M-B$_2$F$_8$]$^{2+}$ = 657.4239; found = 756.4227. [M-B$_2$F$_8$]$^{2+}$ = 369.3040; found = 369.3047.

2.2.5 Synthesis of 1-(1'-dodecyl-3'-hexylimidazolium)-3-(1'-dodecyl-3'-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2f)

This compound was produced by mixing 1f (100 mg, 0.106 mmol) with sodium tetrafluoroborate (36.3 mg, 0.330 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2f was purified using the same work-up procedure described for the purification of 2d. The final product was a white solid. Yield = 86.5 mg (84.7%). $^1$H NMR (300 MHz, d$_6$-DMSO) $\delta$ = 9.14 (d, $J$ = 5.8 Hz, 1 H), 7.79 (dd, $J$ = 4.7, 3.2 Hz, 2 H), 4.15 (t, $J$ = 7.2 Hz, 4 H), 1.88–1.66 (m, 4 H), 1.24 (s, 15 H), 0.85 (t, $J$ = 6.7 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) $\delta$ = 136.31, 122.92, 122.86, 49.23, 49.19, 31.75, 29.58, 29.53, 29.47, 29.38, 29.28, 29.17, 28.79, 25.95, 25.39, 22.55, 14.41. HRMS: calculated as [M-B$_2$F$_8$]$^{2+}$ = 397.3353; found = 397.3356.

2.2.6 Synthesis of 1-(1'-tetradecyl-3'-hexylimidazolium)-3-(1'-tetradecyl-3'-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2g)

This compound was produced by mixing 1g (200 mg, 0.199 mmol) with sodium tetrafluoroborate (65 mg, 0.592 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2g was purified using the same work-up procedure described for the purification of 2d. The product was a white solid. Yield = 179 mg (87.8%). $^1$H NMR (300 MHz, d$_6$-DMSO) $\delta$ = 9.15 (d, $J$ = 5.4 Hz, 1 H), 7.79 (ddd, $J$ = 5.4, 3.6, 1.8 Hz, 2 H), 4.15 (t, $J$ = 7.2 Hz, 4 H), 1.85–1.72 (m, 4 H), 1.34–1.18 (m, 18 H), 0.86 (t, $J$ = 6.7 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) $\delta$ = 136.32, 122.93, 122.87, 49.32, 49.20, 31.75, 29.51, 29.47, 29.39, 29.28, 29.17, 28.80, 25.96, 25.42, 22.55, 14.42. HRMS: calculated as [M-B$_2$F$_8$]$^{2+}$ = 426.3666; found = 426.3671.

2.2.7 Synthesis of 1-(1'-hexadecyl-3'-hexylimidazolium)-3-(1'-hexadecyl-3'-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2h)

This compound was produced by mixing 1h (100 mg, 0.094 mmol) with sodium tetrafluoroborate (31.5 mg, 0.287 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2h was purified using the same work-up procedure described for the purification of 2d. The product was a white solid. Yield = 82.1 mg (80.5%). $^1$H NMR (300 MHz, d$_6$-DMSO) $\delta$ = 9.15 (d, $J$ = 5.3 Hz, 1 H), 7.79 (ddd, $J$ = 5.6, 3.7, 1.8 Hz, 2 H), 4.15 (t, $J$ = 7.1 Hz, 4 H), 1.86–1.69 (m, 4 H), 1.24 (s, 20 H), 0.95–0.73 (m, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) $\delta$ = 136.31, 122.93, 122.87, 49.32, 49.19, 31.75, 29.51, 29.47, 29.40, 29.29, 29.17, 28.81, 25.96, 25.41, 22.55, 14.42. HRMS: calculated as [M-B$_2$F$_8$]$^{2+}$ = 453.3980; found = 453.3987.
2.2.8 Synthesis of 1-(1’-octadecyl-3’-hexylimidazolium)-3-(1’-octadecyl-3’-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2d)

This compound was produced by mixing 1i (100 mg, 0.090 mmol) with sodium tetrafluoroborate (30.0 mg, 0.273 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2i was purified using the same work-up procedure described for the purification of 2d. The product was a white solid. Yield = 91.1 mg (89.4%). 1H NMR (300 MHz, d6-DMSO) δ = 9.15 (d, J = 5.3 Hz, 1 H), 7.79 (ddd, J = 5.5, 3.7, 1.8 Hz, 2 H), 4.15 (t, J = 7.3 Hz, 4 H), 1.94–1.69 (m, 4 H), 1.35–1.10 (m, 23 H), 0.86 (t, J = 6.7 Hz, 2 H). 13C NMR (75 MHz, d6-DMSO) δ = 136.36, 122.88, 49.31, 49.17, 31.7529.58, 29.50, 29.40, 29.30, 29.16, 28.81, 25.97, 25.38, 22.55, 14.42. HRMS: calculated as [M-B2F8]2+ = 480.9311; found = 480.9304.

2.2.9 Synthesis of 1-(1’-eicosyl-3’-hexylimidazolium)-3-(1’-eicosyl-3’-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (2j)

This compound was produced by mixing 1j (100 mg, 0.085 mmol) with sodium tetrafluoroborate (28.6 mg, 0.260 mmol) in a manner similar to that employed in the synthesis of 2b. The resulting product 2j was purified using the same work-up procedure described for the purification of 2d. The product was a white solid. Yield = 87.7 mg (86.2%) 1H NMR (300 MHz, d6-DMSO) δ = 9.16 (d, J = 4.9 Hz, 1 H), 7.79 (td, J = 4.2, 1.8 Hz, 2 H), 4.15 (t, J = 7.1 Hz, 4 H), 1.79 (d, J = 6.9 Hz, 4 H), 1.23 (s, 25 H), 0.91–0.81 (m, 2 H). 13C NMR (75 MHz, d6-DMSO) δ = 136.32, 122.93, 122.87, 49.31, 49.19, 31.75, 29.78, 29.60, 29.48, 29.41, 29.30, 29.16, 28.82, 25.97, 25.42, 14.42. HRMS: calculated as [M-B2F8]2+ = 509.4608; found = 509.4501.

2.2.10 Synthesis of 1-(1’-butyl-3’-hexylimidazolium)-3-(1’-butyl-3’-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonylimide) (3b)

Compound 1b (100 mg, 0.138 mmol) was dissolved into DI water, and LiTf2N (121 mg, 0.422 mmol) was added to this solution and stirred at ambient temperature overnight. The reaction mixture was extracted with CH2Cl2 (4 × 20 mL), and the organic layer dried over anhydrous magnesium sulphate before concentration via rotatory evaporation to produce a yellow liquid. A small sample was dissolved in DI water with silver nitrate and showed no reaction. Yield = 180 mg (98.1%). 1H NMR (300 MHz, d6-DMSO) δ = 9.16 (d, J = 8.4 Hz, 1 H), 7.79 (dt, J = 8.5, 2.1 Hz, 2 H), 4.15 (dd, J = 13.2, 6.1 Hz, 4 H), 1.87–1.63 (m, 4 H), 1.35–1.19 (m, 4 H), 0.90 (t, J = 7.3 Hz, 2 H). 13C NMR (75 MHz, d6-DMSO) δ = 136.33, 122.93, 122.86, 119.93 (q, J = 321.9 Hz), 49.21, 49.06, 31.74, 29.56, 25.43, 19.23, 13.69. HRMS: calculated as [M-(Tf2N)2]2+ = 381.6669; found = 381.6668.

2.2.11 Synthesis of 1-(1’-hexyl-3’-hexylimidazolium)-3-(1’-hexyl-3’-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonylimide) (3c)

This compound was produced by mixing 1c (100 mg, 0.128 mmol) with LiTf2N (112 mg, 0.390 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a yellow liquid. Yield = 165 mg (93.3%). 1H NMR (300 MHz, d6-DMSO) δ = 9.16 (d, J = 8.4 Hz, 1 H), 7.79 (dt, J = 8.5, 2.1 Hz, 2 H), 4.15 (dd, J = 13.2, 6.1 Hz, 4 H), 1.87–1.63 (m, 4 H), 1.35–1.19 (m, 4 H), 0.90 (t, J = 7.3 Hz, 2 H). 13C NMR (75 MHz, d6-DMSO) δ = 136.33, 122.94, 122.87, 119.92 (q, J = 321.8 Hz, 1 C), 49.32, 49.21, 30.94, 29.70, 29.54, 25.28, 25.43, 22.31, 14.24. HRMS: calculated as [M-(Tf2N)2]2+ = 409.6982; found = 409.6988.

2.2.12 Synthesis of 1-(1’-octyl-3’-hexylimidazolium)-3-(1’-octyl-3’-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonylimide) (3d)

This compound was produced by mixing 1d (100 mg, 0.120 mmol) with LiTf2N (105 mg, 0.366 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a yellow liquid. Yield = 154 mg (89.3%) 1H NMR (300 MHz, d6-DMSO) δ = 9.16 (d, J = 6.7 Hz, 3 H), 7.79 (dt, J = 7.5, 1.7 Hz, 6 H), 4.15 (dd, J = 9.3, 4.8 Hz, 12 H), 1.96–1.64 (m, 12 H), 1.25 (s, 28 H), 0.85 (t, J = 6.7 Hz, 6 H). 13C NMR (75 MHz, DMSO) δ = 136.33, 122.94, 122.86, 119.93 (q, J = 322.0 Hz), 49.32, 49.20, 31.58, 29.73, 29.54, 28.92, 28.73, 25.94, 25.43, 22.49, 14.38. HRMS: calculated as [M-(Tf2N)2]2+ = 437.7295; found = 437.7296.

2.2.13 Synthesis of 1-(1’-decyl-3’-hexylimidazolium)-3-(1’-decyl-3’-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonylimide) (3e)

This compound was produced by mixing 1e (100 mg, 0.112 mmol) with LiTf2N (98.1 mg, 0.342 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a white solid. Yield = 69.5 mg (41.5%). 1H NMR (300 MHz, d6-DMSO) δ = 9.16 (d, J = 8.4 Hz, 1 H), 7.79 (dt, J = 8.5, 2.1 Hz, 2 H), 4.15 (dd, J = 13.2, 6.1 Hz, 4 H),
2.2.14 Synthesis of 1-(1'-dodecyl-3'-hexylimidazolium)-3-(1''-dodecyl-3''-hexylimidazolium)-imidaza
dium tri(bis(trifluoromethanesulfonyl)imide) (3f)
This compound was produced by mixing 1f (92.4 mg, 0.320 mmol) with LiTf$_2$N (92.4 mg, 0.312 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a white solid. Yield = 63.1 mg (38.6%). $^1$H NMR (300 MHz, d$_6$-DMSO) δ = 9.17 (s, 1 H), 7.80 (d, J = 6.6 Hz, 2 H), 4.15 (t, J = 7.0 Hz, 4 H), 1.78 (s, 4 H), 1.24 (s, 15 H), 0.84 (d, J = 7.0 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) δ = 136.32, 122.93, 122.87, 119.93 (q, J = 321.9 Hz), 49.32, 49.20, 31.74, 29.54, 29.45, 29.37, 29.26, 29.15, 28.78, 25.94, 25.43, 22.54, 14.38. HRMS: calculated as [M-(Tf$_2$N)$_2$]$_2^{2+}$ = 493.7921; found = 493.7928.

2.2.15 Synthesis of 1-(1'-tetradecyl-3'-hexylimidazolium)-3-(1''-tetradecyl-3''-hexylimidazolium)-imidaza
dium tri(bis(trifluoromethanesulfonyl)imide) (3g)
This compound was produced by mixing 1g (100 mg, 0.100 mmol) with LiTf$_2$N (87.2 mg, 0.304 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a white solid. Yield = 63.1 mg (45.6%). $^1$H NMR (300 MHz, d$_6$-DMSO) δ = 9.16 (d, J = 8.4 Hz, 1 H), 7.79 (dt, J = 8.5, 2.1 Hz, 2 H), 4.15 (dd, J = 13.2, 6.1 Hz, 4 H), 1.87–1.63 (m, 4 H), 1.35–1.19 (m, 4 H), 0.90 (t, J = 7.3 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) δ = 136.32, 122.93, 122.86, 119.93 (q, J = 321.9 Hz), 49.32, 49.20, 31.75, 29.55, 29.51, 29.46, 29.16, 24.95, 25.43, 22.55, 14.39. HRMS: calculated as [M-(Tf$_2$N)$_2$]$_2^{2+}$ = 521.8234; found = 521.8236.

2.2.16 Synthesis of 1-(1'-hexadecyl-3'-hexylimidazolium)-3-(1''-hexadecyl-3''-hexylimidazolium)-imidaza
dium tri(bis(trifluoromethanesulfonyl)imide) (3h)
This compound was produced by mixing 1h (100 mg, 0.094 mmol) with LiTf$_2$N (80.0 mg, 0.287 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a white solid. Yield = 63.1 mg (45.6%). $^1$H NMR (300 MHz, d$_6$-DMSO) δ = 9.15 (d, J = 5.2 Hz, 1 H), 7.79 (dd, J = 5.3, 3.7 Hz, 2 H), 4.15 (t, J = 7.2 Hz, 4 H), 2.00–1.59 (m, 4 H), 1.23 (s, 20 H), 0.85 (t, J = 6.7 Hz, 2 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) δ = 136.32, 122.94, 122.86, 119.92 (q, J = 321.8 Hz), 49.32, 49.20, 31.75, 29.55, 29.50, 29.46, 29.16, 28.79, 25.95, 25.44, 22.55, 14.40. HRMS: calculated as [M-(Tf$_2$N)$_2$]$_2^{2+}$ = 549.8547; found = 549.8554.

2.2.17 Synthesis of 1-(1'-octadecyl-3'-hexylimidazolium)-3-(1''-octadecyl-3''-hexylimidazolium)-imidaza
dium tri(bis(trifluoromethanesulfonyl)imide) (3i)
This compound was produced by mixing 1i (200 mg, 0.179 mmol) with LiTf$_2$N (152 mg, 0.549 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a white solid. Yield = 269.0 mg (87.4%). $^1$H NMR (300 MHz, DMSO) δ = 9.16 (d, J = 5.2 Hz, 1 H), 7.79 (ddd, J = 5.9, 3.9, 1.8 Hz, 2 H), 4.15 (t, J = 7.1 Hz, 4 H), 1.79 (d, J = 6.9 Hz, 4 H), 1.23 (s, 23 H), 0.92–0.78 (m, 2 H). $^{13}$C NMR (75 MHz, DMSO) δ = 136.32, 122.94, 122.87, 119.93 (q, J = 322.0 Hz) 49.32, 49.20, 31.75, 29.77, 29.49, 29.46, 29.39, 28.28 29.16, 28.80, 25.96, 25.44, 22.55, 14.41. HRMS: calculated as [M-(Tf$_2$N)$_2$]$_2^{2+}$ = 557.8860; found = 557.8868.

2.2.18 Synthesis of 1-(1'-eicosyl-3'-hexylimidazolium)-3-(1''-eicosyl-3''-hexylimidazolium)-imidaza
dium tri(bis(trifluoromethanesulfonyl)imide) (3j)
This compound was produced by mixing 1j (200 mg, 0.171 mmol) with LiTf$_2$N (149 mg, 0.521 mmol) in a manner similar to that employed in the synthesis and purification of 3b. The product was a white solid. Yield = 277.2 mg (91.6%). $^1$H NMR (300 MHz, d$_6$-DMSO) δ = 9.16 (d, J = 4.6 Hz, 3 H), 7.79 (ddd, J = 5.6, 3.7, 1.8 Hz, 6 H), 4.15 (t, J = 7.2 Hz, 12 H), 1.90–1.61 (m, 12 H), 1.23 (s, 76 H), 0.91–0.78 (m, 6 H). $^{13}$C NMR (75 MHz, d$_6$-DMSO) δ = 136.32, 122.94, 122.87, 119.93 (q, J = 322.0 Hz), 49.32, 49.20, 31.75, 29.55, 29.48, 29.40, 29.29, 29.16, 28.80, 25.96, 25.44, 22.55, 14.41. HRMS: calculated as [M-(Tf$_2$N)$_2$]$_2^{2+}$ = 605.9173; found = 605.9180.

2.3 Confirmation of final compound purity
Elemental analysis (Galbraith Laboratories, Knoxville, TN, USA) was attempted on 2b-j and 3b-j, but the results were inconclusive because these imidazolium salt compounds did not completely compound during analysis. This behaviour has been observed for the tris(imidazolium bromide) compounds 1b-j in our prior publication.[3] Consequently, in addition to HRMS data, copies of the ‘clean’ $^1$H and $^{13}$C NMR spectra of 2b-j and 3b-j are included in the Supplementary Information to...
help verify their purity. To confirm anion purity (after preparation from the bromide salts 1b–j), aqueous solutions of 2b–j and 3b–j were contacted with silver nitrate. The absence of observable silver bromide precipitate formation confirmed the absence of residual bromide in these compounds. Additionally, energy-dispersive spectroscopy (EDS) was performed on representative samples of 2b–j and 3b–j to quantify the elemental ratio of F to residual Br. The tested samples showed negligible bromide by EDS. EDS was performed using a JEOL JSM-6480 scanning electron microscope (JEOL, Tokyo, Japan) with an elemental detection lower limit of carbon.

2.4 PLM analysis

PLM studies were performed using a Leica DMRXP polarising light microscope (Leica, Solms, Germany) equipped with a Linkam LTS 350 thermal stage, a Linkam CI 94 temperature controller (Linkam, Surrey, UK) and a Q-Imaging MicroPublisher 3.3 RTV digital camera (Q-Imaging, Surrey, UK). Linkam Linksys32 software was used to automate temperature profiles and for image capture. PLM specimens were prepared by pressing samples between a glass microscope slide and cover slip. The prepared specimens were placed on the variable-temperature stage and heated past the compounds’ isotropic temperatures. After annealing, the samples were then lowered to room temperature at a decreased rate to allow complete cooling. The samples were heated at a rate of 5°C/min with digital PLM image capture at every 1.25°C and continuous reading of the observed light intensity.

2.5 PXRD and SAXS analyses

PXRD profiles were obtained using an Inel CPS 120 powder X-ray diffraction system (Inel, Artenay, France) equipped with a Cu Kα tube source and a custom-built, temperature-programmable, rotating sample pan heater system. All PXRD spectra were calibrated against a silver behenate diffraction standard (d100 = 58 Å). Spectra were collected with the samples in the X-ray beam for about 15–30 min. PXRD profiles of the thermotropic LC samples were obtained by initially annealing and then slowly heating the samples to the desired LC temperature range, before finally collecting the PXRD data after 5 min to allow the system to adjust properly.

SAXS profiles were collected at Colorado State University using a Rigaku SMax 3000 High Brilliance three-hole SAXS system (Rigaku, Tokyo, Japan) outfitted with a MicroMax-007HF rotating anode (Rigaku; Cu Kα), a Confocal Max-Flux Optic (Rigaku), a Gabriel multi-wire area detector (Rigaku) and a Linkam thermal stage. Exposure times for samples were typically 1200 s.

2.6 DSC analysis

DSC measurements were performed using a Mettler Toledo DSC823° (Mettler Toledo, Columbus, OH, USA) and a Julabo FT100 Intracoooler (Julabo, Allentown, PA, USA). Specimens were weighed to between 3 and 5 mg in the aluminium sample pans before being placed on the heating stage. After being heated to 170°C or 270°C (for the BF$_4^-$ compounds) or 100°C (for the Tf$_2$N$^-$ compounds) at 10°C/min to initially anneal the samples, each specimen was cooled to 25°C at 10°C/min before beginning a DSC run. The observed DSC profiles were taken by heating the samples at 5°C/min to a maximum temperature of 170°C or 270°C (for the BF$_4^-$ analogues) or 100°C (for the Tf$_2$N$^-$ analogues), and then cooled at the same rate back to 25°C.

2.7 MD simulations

The MD simulations were performed in the Bedrov group at the University of Utah using an in-house-developed MD simulation package and the APPLE&P force field. The latter incorporates induced many-body polarisation interactions and has been extensively validated against experimental data for variety of ILs and polymers. For the MD simulations, C$_{20}$–IM–C$_6$–IM–C$_6$–IM–C$_{20}$ chains (where IM = an imidazolium unit; C$_n$ = linear alkyl spacers or tails with a total of $n$ carbon atoms) were selected as the cationic backbone section. This cationic section was then paired separately with Br$, BF_4^-$, and Tf$_2$N$^-$ anions for the MD simulations (i.e. to correspond to compounds 1j, 2j and 3j, respectively). Initially, all the chains were set up in a stretched conformation (i.e. C–C–C–C dihedrals in the trans orientation) oriented along z-axis of the simulation cell and with the corresponding counter-ions initially paired with the IM groups. These initial chains were arranged into two layers, with the layers being oriented perpendicular to z-axis. Over a short simulation of roughly 10 ps, the initial configurations were shrunk to the dimensions $52$ Å $\times 52$ Å $\times 105$ Å, which roughly gives a volume necessary to yield the expected density for the systems. During this equilibration, the system maintained the layered structure and the overall perpendicular orientation of the chains to the formed layers. Following the initial shrinking, simulations were switched to the NPT ensemble where the x-y and z dimensions were equilibrated independently to allow the corresponding
components of the stress tensor \((P_{xx} + P_{yy})/2\) and \(P_{zz}\) to have an average value of 1 atm. After initial equilibration in the NPT ensemble, production runs were conducted over 30 ns to sample the molecular structure of the formed smectic phases.

The MD simulations were conducted at 350 K, a temperature at which the selected cation is expected to show smectic phases with all three anions investigated. Covalent bond lengths were constrained using the velocity-Verlet form of the SHAKE algorithm.\(^9\) The Ewald summation method was used for treatment of long-range electrostatic forces. A cut-off of 10 Å was used for all van der Waals interactions as well as the real part of electrostatic interactions in the Ewald summation. A multiple-time-step reversible reference system propagator algorithm\(^{10-12}\) was employed. A time step of 0.5 fs was used for bonding, bending, dihedral and out-of-plane deformation motions, while a 1.5-fs time step was used for non-bonded interactions within a cut-off radius of 6.0 Å. Finally, the non-bonded interactions in the range between 6.0 and 10.0 Å and the reciprocal portion of the electrostatic interactions were updated every 3 fs.

3. Results and discussion

3.1 Synthesis of the compounds

To study the effect of the counter-ions on the compounds’ potential for thermotropic LC behaviour, the \(\text{Br}^-\) anions on compounds 1b–j were exchanged for \(\text{BF}_4^-\) or \(\text{TF}_2\text{N}^-\) to generate compounds 2b–j and 3a–j, respectively. To do this, each homologue of 1 was dissolved in DI water with slightly more than three equivalents of either \(\text{NaBF}_4\) or \(\text{LiTF}_2\text{N}\) added (see Figure 2). As with the previous ionic compounds 1a–j, purification was the most challenging step in the synthesis of these new organic salts. Most of the anion-exchanged compounds were cleaned easily with organic-aqueous washes. However, the butyl- and hexyl-tailed \(\text{BF}_4^-\) compounds were more soluble in the aqueous layer than either chloroform or dichloromethane. For these compounds, the water was evaporated and the residue dissolved in dry acetone and filtered to remove the elemental salts. To verify the completion of the exchange from bromide, samples of the \(\text{BF}_4^-\) and \(\text{TF}_2\text{N}^-\) compounds were exposed to \(\text{AgNO}_3\) in water. Complete removal/exchange of the bromide ions was confirmed when the silver nitrate contacted solutions of the new salt compounds did not exhibit any transfluence or opacity (i.e. no \(\text{AgBr}\) precipitate formation). Further confirmation of the anion purity of the mesogens was provided by EDS, which showed either negligible bromide within the samples or that the amount of residual bromide was within ±0.4% of the expected value of the clean compound (i.e. in the typically accepted range to be considered ‘pure’ by elemental analysis) (see the Supplemental Information for example EDS profiles obtained).

3.2 Characterisation of thermotropic LC behaviour

Once confirmed for structure and purity, each of the pure compounds 2b–j and 3b–j was analysed for thermotropic LC behaviour using a variable-temperature PLM, DSC and variable-temperature PXRD or SAXS. PLM was used to quickly screen for the presence of any thermotropic LC behaviour in the compounds and to qualitatively determine the type of phases formed. Where possible, DSC analysis was used to more precisely map out the number of LC phases formed upon heating and cooling, as well as their phase transition temperatures. Unfortunately, in many cases, the LC-to-isotropic transition points were too broad and subtle to be reasonably measured via DSC. In these instances, the transition points are taken from observation via PLM, when the texture began to vanish. Finally, PXRD or SAXS was used to help quantitatively identify the structures of thermotropic LC phases observed, in combination with PLM optical texture analysis. Based on the results of these studies, Table 1 summarises the thermotropic LC phase behaviour of the nine tris(imidazolium \(\text{BF}_4^-\)) homologues prepared, and Table 2 summarises the thermotropic LC phase behaviour of the nine tris

| Compound | MW (g/mol) | Liquid crystal behaviour (phase transition temperatures in °C) |
|----------|-----------|-------------------------------------------------------------|
| 2b (n = 3) | 744.18 | Isotropic fluid → Iso |
| 2c (n = 5) | 800.29 | Isotropic fluid |
| 2d (n = 7) | 856.40 | Cr → 56 → Iso |
| 2e (n = 9) | 912.50 | Cr → 65 → Iso |
| 2f (m = 11) | 968.61 | (Anneal) SmA → 67 → Iso Iso → 46 → SmA |
| 2g (m = 13) | 1024.70 | (Anneal) SmA → 118 → Iso Iso → 116 → SmA |
| 2h (m = 15) | 1080.80 | (Anneal) Cr → 46 → SmA → 184 → Iso Iso → 183 → SmA → 36 → Cr |
| 2i (m = 17) | 1137.00 | (Anneal) Cr → 48 → Sm′ → 237 → Iso Iso → 237 → Sm′ → 35 → Cr |
| 2j (m = 19) | 1193.00 | (Anneal) Cr → 70 → Sm′ → (> approx. 250) → Iso Iso → (approx. >250) → Sm′ → 68 → Cr |
Table 2. Summary of the thermotropic LC behaviour observed for the Tf$_2$N$^-$ compounds 3b–j (homologues that showed mesogenic behaviour are in red). The temperature ranges specified for the phase regions are taken from peak-to-peak analysis of the DSC data or from PLM data when distinct optical texture changes were observed. The label Sm$^*$ for 3i denotes an as-yet unidentified, higher order smectic phase with some positional ordering that is different from the previously reported SmX phase for 1b–j.

| Compound  | MW (g/mol) | Liquid crystal behaviour |
|-----------|------------|-------------------------|
| 3b (m = 3) | 1324.2     | Isotropic fluid         |
| 3c (m = 5) | 1380.3     | Isotropic fluid         |
| 3d (m = 7) | 1436.4     | Isotropic fluid         |
| 3e (m = 9) | 1492.5     | Cr $\rightarrow$ 55 $\rightarrow$ Iso |
| 3f (m = 11) | 1548.6    | Cr $\rightarrow$ 44 $\rightarrow$ Iso |
| 3g (m = 13) | 1604.7    | Cr $\rightarrow$ 49 $\rightarrow$ Iso |
| 3h (m = 15) | 1660.8    | Cr $\rightarrow$ 64 $\rightarrow$ Iso |
| 3i (m = 17) | 1716.9    | (Anneal) Sm$^*$ $\rightarrow$ 68 $\rightarrow$ Iso |
|           |            | Iso $\rightarrow$ 44 $\rightarrow$ Sm$^*$ $\rightarrow$ 28 $\rightarrow$ Cr |
| 3j (m = 19) | 1771.6    | (Anneal) SmA $\rightarrow$ 75 $\rightarrow$ Iso |
|           |            | Iso $\rightarrow$ 44 $\rightarrow$ SmA |

(imidazolium Tf$_2$N$^-$) homologues. Only the BF$_4^-$ homologues with alkyl tails containing $\geq$12 carbon atoms (2f–j) exhibited LC behaviour, whereas only the Tf$_2$N$^-$ homologues with the two longest alkyl tails (3i, 3j) showed LC formation. The following subsections discuss in more detail the assignment of the thermotropic LC phases observed for 2f–j and 3i, 3j with respect to the different characterisation techniques used.

3.2.1 PLM analysis of the BF$_4^-$ and Tf$_2$N$^-$ mesogens

It was observed that the mesogens with BF$_4^-$ and Tf$_2$N$^-$ counter-ions are more viscous than typical non-charged LCs because of intermolecular ionic interactions, which inhibit some molecular motions. PLM texture analysis of LC phases is typically performed in commercial cells; however, most of the BF$_4^-$ materials were too viscous to fill these cells. These samples were prepared for PLM texture analysis by ‘sandwiching’ a small amount of annealed material between glass slides followed by shearing. The filled LC glass sandwich cells were heated above the clearing point of the sample compounds and slowly cooled into the LC phase.

Except for 2j (which showed an oily string texture), all of the BF$_4^-$ and Tf$_2$N$^-$ mesogens showed similar weakly birefringent focal conic domains between crossed polarisers (Figure 3). The extinction brushes of these focal conics for 2f–i, 3i and 3j were along the polariser and analyser, suggesting an SmA or anticlinic smectic C (SmC$_A$) phase.[13] The SmA phase is characterised by a diffuse layered structure with the molecular long axes aligned, on the time average, parallel to the layer normal.[13] The SmC$_A$ phase is characterised by a diffuse layered structure with the molecular long axis tilted with respect to the layer normal.[13] If the molecular tilt is unidirectional, then it is called sycnlinic. If the tilt direction alternates 180°, around the azimuth, from layer to layer, then it is antclinic. The observed optical textures of 2f–i, 3i and 3j are also visually similar to the SmA phases formed by the related TILC bromide salts (1h–j) previously studied; however, they do not show the optical features characteristic of the higher order SmX phase exhibited by 1h–j.[4] It should also be noted that the black optical texture observed for the LC phase of 2g upon heating (Figure 3(a)(ii), top) appears to be a homeotropically aligned smectic phase, where the planes of the phase are aligned

![Figure 3. (colour online) (a) PLM optical textures (mag. = 40X) of the thermotropic LC phases of the BF$_4^-$ compounds 2f, 2g, 2h, 2i and 2j that exhibited mesogenic behaviour: (i) 2f (top: $T = 55°C$ upon heating (homeotropic sample alignment, see Supplemental Information); bottom: $T = 60°C$ upon cooling); (ii) 2g (top: $T = 100°C$ upon heating; bottom: $T = 110°C$ upon cooling); (iii) 2h (top: $T = 151°C$ upon heating; bottom: $T = 179°C$ upon cooling); (iv) 2i (top: $T = 127°C$ upon heating; bottom: $T = 50°C$ upon cooling); and (v) 2j (top: $T = 120°C$ upon heating; bottom: $T = 140°C$ upon cooling). (b) PLM optical textures (mag. = 40X) of the thermotropic LC phases of the Tf$_2$N$^-$ compounds 3i and 3j that exhibited mesogenic behaviour: (i) 3i (top: $T = 50°C$ upon heating; bottom: $T = 35°C$ upon cooling); and (ii) 3j (top: $T = 65°C$ upon heating; bottom: $T = 65°C$ upon cooling).](image-url)
parallel to the polarised light to produce a black optical texture.[13] Pressing on the LC sample caused a discernible flash of light under crossed polarisers as the mesogens are mechanically forced out of parallel alignment with the light path (see the Supplemental Information, Figure S37). (Additional confirmation for a smectic phase for 2g was provided by PXRD (see Section 3.2.3).) Unfortunately, the oily string, mostly dark texture of the LC phase of 2j could not be readily identified by PLM analysis. Pressing on the sample under crossed polarisers did not produce a discernible flash of light to suggest a homeotropically aligned smectic phase (see the Supplemental Information, Figure S38). Consequently, its phase identification had to rely primarily on SAXS characterisation instead (see Section 3.2.3). In summary, initial PLM analysis indicated that the majority of Tf2N+ and BF4− mesogens form smectic phases, and that for all of them, their phase transition temperatures are highly anion-dependent.

### 3.2.2 DSC analysis of the BF4− and Tf2N+ mesogens

The full heating and cooling DSC profiles of the five BF4− and two Tf2N+ homologues that showed LC behaviour by PLM are included in the Supplementary Information (see Figures S39 and S40). Unfortunately, most of the BF4− compounds that showed mesogenic behaviour by PLM yielded DSC profiles that only showed very subtle, hard-to-detect phase transition peaks. For example, the SmA − Iso transitions during heating and the Iso − SmA transitions during cooling for 2h and 2i are very broad, subtle, step transitions. In addition, the corresponding ΔH values for each phase transition could not be easily calculated by DSC (see the Supplementary Information). Consequently, although DSC data were collected for all of the mesogenic homologues, their LC phase behaviour and LC phase assignments were primarily based on PLM analysis in combination with PXRD or SAXS studies.

Although DSC was not particularly useful for characterising the phase behaviour of many of the BF4− and Tf2N+ mesogens, the following general trends could be observed via a combination of PLM and DSC analysis: the clearing points for the two longest BF4− mesogens are above 150°C, while the Tf2N+ mesogens (3i, 3j) show clearing points below 80°C. Thin films of the BF4− mesogens form enantiotropic LC phases (i.e. LC phases exhibited on both heating and cooling). In contrast, the Tf2N+ analogues, while enantiotropic in LC behaviour, show meta-stable LC phases. Unstable crystallisation occurs above the exothermic temperature seen by DSC but if held just above the transition point for an extended time, the observed crystallisation disappears. Upon cooling, the Tf2N+ mesogen 3j transitions from a focal conic texture to an isotropic texture at approximately 60°C without any related endothermic or exothermic event in the compound’s DSC profile. As 3j cools further, spherulite crystal domains appear well above the crystallisation temperature seen by DSC (approx. 44°C).

### 3.2.3 X-ray diffraction analysis of the thermotropic LC phases of the BF4− and Tf2N+ mesogens

To help confirm the structure of the thermotropic LC phases exhibited by the BF4− and Tf2N+ mesogens (as well as to compare the influence of counter-ions on the organisation and orientation on the LC phases), variable-temperature PXRD or SAXS scans were collected. Because of the temperature limit of the heating stage for the PXRD system, PXRD profiles upon heating and cooling from the isotropic melt were only taken of the mesogens that had clearing points lower than 200°C. For those with clearing points higher than 200°C, their LC phases were analysed using a SAXS system equipped with a higher temperature-range programmable sample heater. The PXRD and SAXS profiles of the LC phases of the BF4− mesogens are shown in Figure 4, and the PXRD profiles of the LC phases of the Tf2N+ mesogens are presented in Figure 5.

Smectic LC phases are typically characterised by PLM focal conic optical textures and X-ray diffraction (i.e. PXRD or SAXS) profiles with a d-spacing ratio of 1:1/1:2/1:3, etc., characteristic of periodic layers.[4] As can been seen in Figure 4(ii) and (iii), 2g and 2h both exhibit an LC phase that has only one intense principal diffraction peak (d100). This result, coupled with the PLM optical textures of their LC phases, is consistent with SmA phase formation. Previous work with both the bromide TILC analogues and similar bis(imidazolium salt)-based LC compounds supports this conclusion, with similar focal conic textures and single-peak PXRD profiles.[4]

However, the PXRD profile of the LC phase of 2f (Figure 4(i)) diverges from this pattern, possibly due to the relative shortness of the n-alkyl tails on 2f. While the LC phases of 2g and 2h only show a single, main d100 peak, the LC phase of 2f exhibits additional peaks that index to a periodic lamellar assembly (i.e. d300, d500 and d400 peaks). The presence of these additional periodic peaks suggests that the LC phase of 2f is a smectic phase with increased long-range periodicity. PLM texture and DSC analyses were consistent with a SmA phase, and not a SmX phase with some molecular (i.e. positional) order within the layers, as reported for some of the mesogenic homologues of 1.[4] The increase in long-range order (i.e. more
Figure 4. Variable-temperature PXRD or SAXS profiles of the thermotropic LC phases formed by the BF₄⁻ mesogens 2f, 2g, 2h, 2i and 2j upon heating and cooling: (i) 2f (left: SmA phase, $T = 40^\circ$C upon heating; right: SmA phase, $T = 35^\circ$C upon heating); (ii) 2g (left: SmA phase, $T = 100^\circ$C upon heating; right: SmA phase, $T = 60^\circ$C upon heating); (iii) 2h (left: SmA phase, $T = 52^\circ$C upon heating; right: SmA phase, $T = 70^\circ$C upon cooling); (iv) 2i (left: Sm′ phase, $T = 160^\circ$C upon heating; right: Sm′ phase, $T = 80^\circ$C upon heating); and (v) 2j (left: Sm′ phase, $T = 140^\circ$C upon heating; right: Sm′ phase, $T = 120^\circ$C upon heating).

Note: The low intensity peaks in the $2\theta = 19–25^\circ$ wide-angle region are due to long alkyl chain packing/partial ordering, as confirmed by PXRD analysis of the long alkyl tail starting materials.[4]
periodic order between layers) can be rationalised by 2f having the shortest length of n-alkyl tails and therefore less packing interference from the hydrophobic sections of the mesogen.

Since the clearing points of 2i and 2j are higher than 200°C, their LC phase structures were analysed using a variable-temperature SAXS system at Colorado State University that had a higher temperature sample heater. Figure 4(iv) shows the SAXS profiles of the LC phase of 2i upon heating from the crystalline phase and cooling from the isotropic melt. With only one diffraction peak and no secondary peaks to aid in phase identification, the thermotropic LC phase of 2i can only be assigned as an unidentified smectic phase (Sm′) at this point, without more detail possible from PLM texture analysis.

Similarly, the SAXS profiles for 2j (Figure 4(v)) also only show a single diffraction peak. While the PLM textures and SAXS profile of 2i readily suggest a smectic phase, 2j produced no readily discernible PLM optical texture to aid in characterisation (see prior discussion in Section 3.2.1). The oily string, mostly dark optical textures seen for 2j (Figure 3(a)/(v)) are attributed to defects at the glass–LC interface. As mentioned in the PLM analysis section, a homeotropically aligned smectic phase, where the planes of the phase are aligned parallel to the polarised light, will produce a black optical texture. This can explain the mostly dark texture for the LC phase of 2j even though SAXS supports the presence of an ordered mesophase.[3] However, pressing on the LC sample did not cause a discernible flash of light under crossed polarisers to confirm a homeotropically aligned smectic phase, as in the case of 2g (see the Supplemental Information). Between the single peak seen in SAXS and the mesophasic trends seen with the other BF_4^- homologues, we have tentatively chosen to classify the observed LC phase of 2j as an as-yet unidentified smectic phase (Sm′).

As for the TF_2N^- mesogens, 3i and 3j exhibit clearing points well below 100°C, so their LC phases were analysed by the variable-temperature PXRD system at the University of Colorado. As can be seen in Figure 5, the LC phases of 3i and 3j have strongly visible, periodic PXRD peaks between 2θ = 3° and 12° that index to a lamellar (i.e. smectic) assembly. The presence of a significant number of periodic lamellar peaks suggests that not only do these mesogens form smectic phases, but also their mesophases have longer-range order than those of the BF_4^- mesogens. Indeed, the PXRD profiles of these TF_2N^-containing smectic homologues indicate a great deal of long-range layer periodicity.
In addition to these periodic secondary peaks between \(2\theta = 3^\circ\) and \(12^\circ\), the smectic phase of \(3i\) also shows pair of equal-intensity wide-angle peaks located at around \(17^\circ\) during the heating phase (see the red-boxed peaks in Figure 5(i)), suggestive of the highly ordered SmE soft crystal phase.[14] However, the accepted structure of an SmE phase is an orthorhombic ‘herringbone’ arrangement of molecules,[15] which could be hard to visualise considering both the bulk of the \(\text{Tf}_2\text{N}^+\) counter-ions between mesogen neighbours and the narrow width of the calamitic mesogens. Second, the optical texture of the \(3i\) mesophase lacks the subtle striations often found with SmE phases. Alternatively, the additional wide-angle peaks in the smectic phase of \(3i\) might also suggest an SmB phase, which has a degree of hexagonal positional ordering of the mesogens within each layer.[15] However, it was not possible to definitively index these wide-angle peaks to those of a hexatic SmB phase either (typically one narrow and intense peak in the wide-angle region).[14] With this difficulty in identifying which higher ordered smectic subphase is being observed, we chose to call the LC phase of \(3i\) another type of as-yet identified, higher order smectic (Sm\(^{\ast}\)) phase. This Sm\(^{\ast}\) phase is different from the unidentified smectic phase observed previously for \(2i\) and \(2j\) (i.e. Sm\(^{\prime}\)), which has no wide-angle diffraction peaks. Unlike the prior Sm\(^{\prime}\) phase, the new Sm\(^{\ast}\) phase of \(3i\) is a type of a highly periodic smectic phase with some positional ordering. This higher order Sm\(^{\ast}\) phase is also different from the previously reported SmX phase for the bromide analogues [4] and the viologen-based TILCs recently made by Saielli and co-workers.[16] The PLM texture of this higher order smectic phase for \(3i\) lacks the striations seen for the SmX phase.[4] Also, the previously reported SmX phase is often seen between the crystalline phase and the SmA phase in terms of temperature,[4,16] but \(3i\) only exhibits a single smectic phase. PLM analysis of aligned samples of the unidentified Sm\(^{\ast}\) phase of \(3i\) and Sm\(^{\prime}\) phase of \(2i\) and \(2j\) may shed more light on their structures. However, sample alignment will be difficult because the smectic phases of these ionic compounds exhibit very high viscosities as well as difficulty and slowness in forming.

In contrast, the smectic phase observed for \(3j\) appears to be an SmA phase with long-range periodicity, instead of a more-ordered smectic subphase with positional order within the layers. The PXRD profiles upon heating or cooling for this LC phase show some diffraction peaks in the wide-angle region. However, the wide-angle peaks observed for \(3j\) are not in the same region as the tail-packing peaks in the previous \(\text{Br}^-\) and \(\text{BF}_4^-\) mesogens,[4] and they are not defined enough to clearly indicate positional ordering.

Perhaps this system’s ability to positionally order within the layers is inhibited by \(3j\)’s longer tails, allowing \(3j\) to only organise into the simpler SmA phase. The smectic phase of \(3j\) also does not match the SmX phase previously reported for related TILCs [4] for the same reasons mentioned for the LC phase \(3i\) previously. For these reasons, we have chosen to conservatively identify the LC phase of \(3j\) as a highly periodic SmA instead of another type of smectic subphase with positional order within the layers.

In addition to LC phase identification, the PXRD and SAXS data collected for the mesophases also yielded very interesting structural information about molecular organisation within and between the smectic layers. For smectic phases, the principal \(d_{100}\) spacing in PXRD profiles represents the average layer spacing for the system observed.[17] If the observed \(d_{100}\) spacing is approximately the estimated length of the fully extended mesogen, then the molecules are most likely assembled in a layered fashion without tilt and with little or no tail overlap/interdigitation.[4] If the primary \(d_{100}\) spacing is noticeably less than the extended molecule length, then the smectic phase is either an SmA or another type of non-tilted smectic phase with a large amount of interdigitation, or the phase consists of tilted mesogens with respect to the layer planes (i.e. an SmC phase) regardless of the presence of interdigitation. Based on a model developed for the tris(imidazolium bromide) TILCs 1h–j and related bis(imidazolium salt) TILCs that exhibit SmA phases,[4] the observed \(d_{100}\) spacing values of the smectic phases were compared to the calculated extended length of each calamitic \(\text{BF}_4^-\) and \(\text{Tf}_2\text{N}^-\) compound that showed smectic phases. In terms of general trends, the \(\text{BF}_4^-\) mesogens showed moderate interdigitation with \(d_{100}\) values that are about 6 Å shorter than the calculated extended lengths of these compounds.[4] In contrast, the \(d_{100}\) spacings of the smectic phases of the two \(\text{Tf}_2\text{N}^-\) mesogens were on average 17 Å shorter than their calculated extended molecular lengths. With a tilted SmC phase excluded as a possible LC mesophase through PLM texture analysis, these changes in smectic layer dimensions as a function of different free anions need to be rationalised. In order to help understand the basis of these anion-dependent effects, atomistic MD simulations were performed.

### 3.3 Computer simulation of the effect of different anions on mesogenic behaviour

In order to help understand the aforementioned anion-dependent changes in thermotropic LC phase structure, MD simulations of the tricationic \(\text{C}_{20}\text{−IM–C}_6\text{−IM–C}_6\text{−IM–C}_{20}\) unit (where IM = an imidazolium...
ring and \(C_n\), linear alkyl spacers or tails with a total of \(n\) carbon atoms) paired with \(\text{Br}^-, \text{BF}_4^-\) and \(\text{Tf}_2\text{N}^-\) anions (i.e. corresponding to compounds 1j, 2j and 3j, respectively) were simulated in a smectic phase configuration in accordance with protocols and methods used as described in Section 2.

In Figure 6, snapshots of the equilibrated configurations are shown for the systems with different free anions (i.e. representative of the smectic phases of 1j, 2j and 3j). To illustrate the conformations of individual chains, couple representative chains are highlighted in each system. As can be seen in Figure 6, even a coarse examination of these snapshots indicates that anion chemical structure exerts a significant and non-trivial influence on the smectic phase structure. For example, while the presence of \(\text{Br}^-\) or \(\text{Tf}_2\text{N}^-\) anions result in formation of amorphous regions (both ionic core regions and alkyl tails), the \(\text{BF}_4^-\) anion (which has a size somewhere in between of \(\text{Br}^-\) and \(\text{Tf}_2\text{N}^-\)) leads to formation of crystalline alkyl and amorphous ionic regions (Figure 6(c)). Using averaged dimensions of the simulation cell in the directions perpendicular (\(z\) direction) and parallel (\(x–y\) directions) to the nominal smectic layers allows us to determine the equilibrium layer spacing \((D)\) and the lateral density of alkyl chains \((s)\) emerging from the ionic regions. The latter is effectively equivalent to a grafting density of a polymer brush. Table 3 shows the dependence of these characteristics as a function of anion type. The trend in these properties is consistent with the anion size. The \(\text{Br}^-\) anion has the smallest size and the strongest interaction with IM cationic groups in the ionic core, resulting in the densest packing of cationic groups in the ionic region. This, in turn, leads to a high density of \(n\)-alkyl 20-carbon tails emerging from the ionic layer, yielding a decrease in interdigitation of the alkyl ‘brushes’ between the neighbouring layers and, ultimately, the largest interlayer spacing. As anion size increases to a larger \(\text{BF}_4^-\) and even larger \(\text{Tf}_2\text{N}^-\), the packing of cationic groups in the ionic layer decreases, which leads to reduction of \(s\). The reduction in packing density of the alkyl tails allows more interpenetration between alkyl chains from different layers, reducing the spacing between the smectic layers.

To investigate these structural differences more quantitatively, the density profiles of different atoms in the direction perpendicular to the formed layers (i.e. \(z\) direction) were analysed. Figure 7 shows the obtained density profiles for the \(\text{Tf}_2\text{N}^-\)-containing 3j system. In this figure, the density profiles for alkyl carbon atoms were calculated separately for the chains belonging to layers 1 and 2 as well as for atoms representing the ionic groups (i.e. the N atoms in the imidazolium rings and the S atoms in the \(\text{Tf}_2\text{N}^-\) anions). Using these profiles, it was possible to determine the width of the ionic region \((d_i)\), defined as the distance between positions where the density profile of imidazolium nitrogen atoms is equal to half of the maximum, as well as the thickness of the alkyl region \(d_{ji} (=D−d_i)\). Table 3 shows that the systems containing all three anions have quite similar thickness of the ionic regions with the system containing \(\text{BF}_4^-\) anion having the widest. Taking into account that the distribution of imidazolium units in the \(z\) direction is restricted by the hexyl spacers, it is natural to expect only small variations in the thickness of the ionic layer upon...
changing the anion type. Therefore, all the volumetric
changes associated with an increase in anion size are
manifested through changes in the lateral spacing
between the imidazolium groups in the ionic region.
This is particularly apparent for the relatively large
Tf$_2$N$^-$ anion, the presence of which leads to an
$\alpha$-alkyl tail-packing density of roughly 70% that of the system
with Br$^-$ anion. As a result, most of the changes in the
overall spacing of the smectic layers come from the
ability of the alkyl tails to pack and interdigitate in the
interlayer region.

The extension of the alkyl region (‘brush’ height) for
each layer ($h$) can also be calculated using Equation (1):

$$ h = \int_{z_{surf}}^{z_{surf} + \frac{L_z}{2}} z \rho_C(z) dz \int_{z_{surf}}^{z_{surf} + \frac{L_z}{2}} \rho_C(z) dz \quad (1) $$

where $\rho_C(z)$ is the density of carbon atoms in the alkyl
tails and $z_{surf}$ is defined by the interface of the ionic
region (i.e. the location where the corresponding den-
sity profile of the imidazolium nitrogen atoms is equal
to half of its maximum value), while $L_z$ is the simu-
lation cell dimension in the $z$ direction. The direction of
integration is aligned with the extension direction of
alkyl tails. Table 3 shows that the system with the
Tf$_2$N$^-$ anions has the smallest extension of alkyl chains ($h = 13$ Å), while the system with the BF$_4^-$
anions has the largest ($h = 18.9$ Å). This trend is no
longer correlated with anion volume. Another mea-
sure of the arrangement of alkyl tails is the degree of
interdigitation ($I$) of the tails belonging to different
layers (i.e. ‘brush’ interpenetration). This can be esti-
ated as shown in Equation (2):

$$ I = \frac{\int_{z_{surf}}^{z_{surf} + \frac{L_z}{2}} \rho_{C1}(z) \rho_{C2}(z) dz}{\int_{z_{surf}}^{z_{surf} + \frac{L_z}{2}} \rho_{C1}(z) dz \int_{z_{surf}}^{z_{surf} + \frac{L_z}{2}} \rho_{C2}(z) dz} \quad (2) $$

Table 3. Simulation values of the total layer thickness ($D$), density ($s$), thickness of ionic region ($d_i$), thickness of the alkyl
region ($d_a$), extension of alkyl region ($h$) and section length ($I$).

| Anion   | $D$ (Å) | $s$ (chains/nm$^2$) | $d_i$ (Å) | $d_a$ (Å) | $h$ (Å) | $I$ |
|---------|---------|---------------------|-----------|-----------|---------|-----|
| Br$^-$  | 50.2    | 2.96                | 20.2      | 30.0      | 16.3    | 0.15|
| BF$_4^-$| 47.7    | 2.56                | 23.2      | 24.5      | 18.9    | 0.43|
| Tf$_2$N$^-$| 42.8   | 1.74                | 22.8      | 20.0      | 13.0    | 0.31|

Figure 7. (colour online) MD simulations density profiles of several representative atoms in the 3j system along $z$ direction.
Alkyl carbon atom density profiles are shown separately for chains belonging to layers 1 and 2.
where $z_{\text{surf}1}$ and $z_{\text{surf}2}$ are the locations of interfaces of the neighbouring ionic regions (see Figure 6), and $\rho_{C1}(z)$ and $\rho_{C2}(z)$ are the density profiles of carbon atoms in the alkyl tails belonging to layers 1 and 2, respectively. If alkyl tails belonging to different layers have no interdigitation, then $I = 0$. Conversely, if there is a perfect overlap of two layers in the alkyl region (i.e. everywhere in the region there is an equal probability to find carbon atoms belonging to alkyl tails from either layer), then $I = 1.0$. Table 3 shows that the system with $\text{BF}_4^-$ anions (i.e. compound 2j) has the largest degree of alkyl tail interdigitation ($I = 0.43$), while the system containing $\text{Br}^-$ anions (i.e. 1j) has very little overlap between alkyl tails from the neighbouring layers ($I = 0.15$).

Based on the structural analysis conducted above from MD simulations, the following picture of the influence of anion type on the structure of the smectic phases of symmetric hexyl-bridged tris(imidazolium salt) TILCs is emerging and is illustrated in Figure 8. With very small $\text{Br}^-$ anion, the packing of imidazolium groups in the ionic region is very dense, which results in a high packing density of alkyl tails coming out of this region. This tight packing allows only minor overlap between chains belonging to different SmA layers. Despite this tight packing, the alkyl region overall has amorphous structure, although some local orientation correlations between the alkyl chains are observed near the interface with the ionic region. Replacement of the $\text{Br}^-$ anion with the noticeably larger $\text{BF}_4^-$ anion results in lower packing density of the imidazolium groups in the ionic core; hence, the surface density of the alkyl tails is reduced. It appears that the resulting spacing is comparable with the packing of alkyl chains in the crystal phase, and therefore, there is a strong preference of the alkyl region to crystallise. At the same time, the ionic core region appears to preserve amorphous structure in the lateral direction. In this system, we have the largest interdigitation between two adjacent smectic layers. What is also interesting is that the orientations (in the $x$-$y$ plane) of the formed neighbouring crystalline alkyl regions (i.e. separated by ionic regions and sharing the same cationic chains) are not the same and are somewhat different from each other. Taking into account that they are separated by an amorphous ionic region, it is not surprising that the crystal orientation of the alkyl regions can be uncorrelated, and therefore, this material can represent a polycrystalline material in which each layer has its own orientation relative to the $x$-$y$ plane. Finally, introduction of a relatively large $\text{Tf}_2\text{N}^-$ anion results in further separation of the imidazolium groups in the ionic region and leads to the lowest surface density of alkyl tails at the interface. This results in a relatively thin alkyl region (the thickness is comparable to that of the ionic region) in which the alkyl chains have random conformations and orientations and significantly overlap with the chains from the neighbouring smectic layers.

4. Conclusions

Two new series of symmetric hexyl-bridged tris(imidazolium) salts with $n$-alkyl tails between 4 and 20 carbons – one with $\text{BF}_4^-$ anions and the other with $\text{Tf}_2\text{N}^-$ anions – were synthesised and analysed for thermotropic LC behaviour. Out of the nine homologues synthesised in each anion series, five homologues with $\text{BF}_4^-$ anions were found to be mesogenic (2f–h), whereas only two homologues with $\text{Tf}_2\text{N}^-$ were found to be mesogenic (3i and 3j). Variable-temperature PLM, DSC and PXRD or SAXS analyses of these mesogenic compounds confirmed that they generally form smectic mesophases with varied temperature ranges after annealing. The $\text{BF}_4^-$ mesogens 2f–h (i.e. the 12-, 14- and 16-carbon tail homologues) form SmA phases. Compounds 2i

![Figure 8. (colour online) Schematic illustration of the influence of free anion type on the structure of the smectic phases formed by symmetric hexyl-bridged tris(imidazolium) salts with two $n$-alkyl tails. Bromide, boron (in $\text{BF}_4^-$) and sulphur (in $\text{Tf}_2\text{N}^-$) atoms in the different anions are shown as green spheres.](image)
and 2j (i.e. the 18- and 20-carbon tail homologues) are more weakly mesogenic and much harder to characterise, but form what appear to be an as-yet unidentified smectic phase (Sm4) by SAXS analysis. In contrast, the Tf2N− mesogens have much lower clearing points (<100°C) but tend to form smectic phases with more order: 3i (i.e. the 18-carbon tail homologue) forms a highly periodic, as-yet unidentified, higher order smectic phase with some positional order (Smn phase), and 3j (the 20-carbon tail homologue) forms a highly periodic SmA phase. While the d_{100} spacings of the smectic phases of the mesogenic BF4− homologues were generally smaller than the calculated extended length of the respective mesogens (suggesting moderate alkyl tail interdigitation), the mesogenic Tf2N− homologues showed smectic phases with significantly smaller interlayer distances than the mesogen length. Computer simulations of 1i, 2j and 3j (i.e. the same cationic framework and tail lengths but different anions) were performed to better understand the effect of the anion on the mesogenic behaviour and smectic phase organisation. From these simulations, the anion’s effect on the mesogenic behaviour was explained as affecting the density of packing of cationic groups in the ionic core section: The smaller the anion, the more compact the tris(imidazolium) sections of each mesogen align and the tighter the n-alkyl tails pack to allow less interdigitation. Br− has the smallest volume and thus allows the least interdigitation. BF4− is slightly larger and allows more, while the broadest, Tf2N−, creates enough space in between mesogen ‘neighbours’ for their respective tails to considerably interdigitate.

Anions are known to contribute significantly to the physical properties of functional salt compounds such as ILs and ILCs, but the effect of different anions on TILCs containing multiple salt units has rarely been studied in a comparative fashion. n-Alkyl-bridged oligo(imidazolium) TILCs offer the potential benefits of increased imidazolium content and, when paired with different anions, allow for the exploration of this new class of ionic organic compounds and their material properties. Future work with these new TILCs will involve designing polymerisable analogues and evaluating their functional properties such as CO2 gas uptake and ion conductivity.

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Supplemental data

Fully assigned 1H and 13C NMR spectra of compounds 2b–j and 3b–j to provide support for their analytical purity in lieu of elemental analysis data (i.e. the compounds did not properly combust during elemental analysis trials). DSC profiles of compounds 2f–j, 3i, and 3j, which were all observed to be mesogenic by PLM, and PXRD or SAXS. Images of the LC phases of 2g and 2j between crossed polarisers and without crossed polarisers when part of the samples are pressed. Representative EDS spectra of several of the new BF4− and Tf2N−-compounds to verify anion purity after ion-exchange.

Supplemental data for this article can be accessed here.

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