Supplementary Information Available

for

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

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Figure S1. ¹H NMR spectrum of 1-(1'-butyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2b**) in DMSO-*d*₆. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S2. ¹³C NMR spectrum of 1-(1'-butyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2b**) in *d*₆-DMSO.

Figure S3. ^1H NMR spectrum of 1-(1'-hexyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2c**) in $\text{DMSO-}d_6$. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S4. ^{13}C NMR spectrum of 1-(1'-hexyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2c**) in d_6 -DMSO.

Figure S5. ^1H NMR spectrum of 1-(1'-octyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2d**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S6. ^{13}C NMR spectrum of 1-(1'-octyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2d**) in d_6 -DMSO.

Figure S7. ¹H NMR spectrum of 1-(1'-decyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2e**) in d₆-DMSO. Note: The water peak in the spectrum is from residual water in the d₆-DMSO NMR solvent.

Figure S8. ¹³C NMR spectrum of 1-(1'-decyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2e**) in *d*₆-DMSO.

Figure S9. ^1H NMR spectrum of 1-(1'-dodecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2f**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S10. ¹³C NMR spectrum of 1-(1'-dodecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2f**) in *d*₆-DMSO.

Figure S11. ¹H NMR spectrum of 1-(1'-tetradecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2g**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S12. ¹³C NMR spectrum of 1-(1'-tetradecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2g**) in *d*₆-DMSO.

Figure S13. ¹H NMR spectrum of 1-(1'-hexadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2h**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S14. ^{13}C NMR spectrum of 1-(1'-hexadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2h**) in d_6 -DMSO.

Figure S15. ¹H NMR spectrum of 1-(1'-octadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2i**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S16. ^{13}C NMR spectrum of 1-(1'-octadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2i**) in d_6 -DMSO.

Figure S17. ¹H NMR spectrum of 1-(1'-eicosyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2j**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S18. ¹³C NMR spectrum of 1-(1'-eicosyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(tetrafluoroborate) (**2j**) in DMSO-*d*₆.

Figure S19. ¹H NMR spectrum of 1-(1'-butyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3b**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S20. ^{13}C NMR spectrum of 1-(1'-butyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3b**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set I are from the carbons on the TF_2N^- counter-ion.

Figure S21. ¹H NMR spectrum of 1-(1'-hexyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3c**) in d₆-DMSO. Note: The water peak in the spectrum is from residual water in the d₆-DMSO NMR solvent.

Figure S22. ^{13}C NMR spectrum of 1-(1'-hexyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3c**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the TF_2N^- counter-ion.

Figure S23. ^1H NMR spectrum of 1-(1'-octyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3d**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S24. ^{13}C NMR spectrum of 1-(1'-octyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3d**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the Tf_2N^- counter-ion.

Figure S25. ^1H NMR spectrum of 1-(1'-decyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3e**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S26. ^{13}C NMR spectrum of 1-(1'-decyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3e**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the Tf_2N^- counter-ion.

Figure S27. ¹H NMR spectrum of 1-(1'-dodecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3f**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S28. ^{13}C NMR spectrum of 1-(1'-dodecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3f**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the Tf_2N^- counter-ion.

Figure S29. ¹H NMR spectrum of 1-(1'-tetradecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3g**) in *d*₆-DMSO. Note: The water peak in the spectrum is from residual water in the *d*₆-DMSO NMR solvent.

Figure S30. ^{13}C NMR spectrum of 1-(1'-tetradecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3g**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the TF_2N^- counter-ion.

Figure S31. ^1H NMR spectrum of 1-(1'-hexadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3h**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S32. ^{13}C NMR spectrum of 1-(1'-hexadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3h**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the Tf_2N^- counter-ion.

Figure S33. ^1H NMR spectrum of 1-(1'-octadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3i**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S34. ¹³C NMR spectrum of 1-(1'-octadecyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3i**) in *d*₆-DMSO. Note: ¹³C NMR peaks grouped as set E are from the carbons on the Tf₂N⁻ counter-ion.

Figure S35. ^1H NMR spectrum of 1-(1'-eicosyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3j**) in d_6 -DMSO. Note: The water peak in the spectrum is from residual water in the d_6 -DMSO NMR solvent.

Figure S36. ^{13}C NMR spectrum of 1-(1'-eicosyl-3'-hexylimidazolium)-3-(1''-butyl-3''-hexylimidazolium)-imidazolium tri(bis(trifluoromethanesulfonyl)imide) (**3j**) in d_6 -DMSO. Note: ^{13}C NMR peaks grouped as set E are from the carbons on the TF_2N^- counter-ion.

Figure S37. PLM 'flash' test for the suspected homeotropically aligned SmA phase of **2g** at 110 °C (left: under crossed polarizers with sample pressed with spatula at top left corner of image; right: without polarizers.) Magnification: 40X.

Figure S38. PLM images for the suspected homeotropically aligned Sm' phase of **2j** at 180 °C (left: under crossed polarizers with sample pressed with spatula at top left corner of image; right: without polarizers.) Magnification: 40X.

Figure S39. DSC profiles for (a) **2f**, (b) **2g**, (c) **2h**, (d) **2i**, and (e) **2j** after initial annealing (temperature ramp rate = 5 °C/min). The red traces are the heating curves, and the blue traces are the cooling curves. Note: The SmA/Sm' $\rightarrow$ Iso transitions during heating and

the Iso $\rightarrow$ SmA/Sm' transitions during cooling for **2h** and **2i** are very broad, subtle, step-transitions. The corresponding ΔH values for each phase transition could not be easily calculated. Their temperature ranges as determined via PLM have been marked to show the mesophase ranges. **2j** is too weakly mesogenic to show a distinctive Sm' $\rightarrow$ Iso or Iso $\rightarrow$ Sm' transition by either PLM or DSC, but these transitions are inferred to be in the $\geq$ ca. 250 °C range.

Figure S40. DSC profiles for **3i** (top) and **3j** (bottom) after initial annealing. (temperature ramp rate = 5 °C/min). The red traces are the heating curves, and the blue traces are the cooling curves.

Figure S41. Example EDS profile for **3i**, showing no detectable peaks for residual bromide.

Figure S42. Example EDS profile for **2g** showing ≤ 0.2 atomic % residual bromide (expected % Br = 0 for pure **2g**). This value is within $\pm 0.4\%$ of the expected element % amount for the clean compound, which is the typically accepted range to be considered “pure” by elemental analysis.