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PAPER

Columnar thermotropic mesophases formed by dimeric liquid-crystalline ionic liquids exhibiting large mesophase ranges[†]

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A series of 16 symmetric, dimeric, dicationic liquid-crystalline ionic liquids with mesogenic 3,4,5-tris(alkyloxy)benzyl moieties tethered to two bridged imidazolium cations were designed and synthesised. As a comparison, 12 monocationic imidazolium liquid crystals with the same mesogens were also prepared. The mesomorphic properties of these ionic liquids were characterised in terms of polarised optical microscopy (POM) and differential scanning calorimetry (DSC), while thermal stabilities were obtained by thermogravimetric analysis (TGA). All compounds having chloride (Cl⁻) and tetrafluoroborate (BF₄⁻) anions exhibit hexagonal columnar (Col_h) liquid crystal mesophases, with the dimeric materials showing mesophases over an extended temperature range. The effect of the linking chain, alkyl substituents, and anion type on the thermal properties of these dimers was examined and showed a significant influence. For example, Col_h mesophases were only observed for ionic liquids having Cl⁻ and BF₄⁻ anions, whereas systems with the bis(trifluoromethylsulfonyl)imide (Tf₂N⁻) anion melted directly to an isotropic liquid. A shorter spacer paired with longer alkoxy chains tends to give rise to broad-temperature-range Col_h ionic liquid crystal phases.

Introduction

Materials showing columnar liquid crystal mesophases are of interest as they offer properties such as improved charge transportation,^{1–5} anisotropic ion transportation,^{6–14} and photonic^{15,16} functions. They are also potential components for organic electronic and optoelectronic devices.^{17–19} From this point of view, development of columnar liquid crystals having a large phase width is of some significance. Typical discotic liquid-crystalline molecules have a π -electron-rich aromatic core attached to flexible alkyl chains and columnar phases are formed *via* stacking of the disc-like moieties. A large number of such systems are known and include those with cores based on triphenylenes, porphyrins, phthalocyanines, coronenes, and other aromatic molecules.^{17–23}

The first report of liquid-crystalline ionic liquids based on imidazolium salts is that of Bowlas *et al.*²⁴ who described chloride and tetrahalometallate salts of both imidazolium and pyridinium cations; this work was later followed up by more comprehensive studies by the Belfast group.^{25–27} However, liquid-crystalline ionic liquids of other types pre-date all of this work, and while it is not intended here to give a comprehensive overview, attention is drawn (Fig. 1) to reports of liquid crystallinity at T < 100 °C in viologens in 1987,²⁸ hexacatenar pyrilium salts in 1988.²⁹ Furthermore, 1995 also saw the publication of work describing sub-100 °C mesophases in *N*-alkylpyridinium dodecylsulfates³⁰ as well as tetracatenar complexes of silver(1).³¹

More recently, organic ionic species such as imidazolium and ammonium ionic liquids have been used to design functional liquid-crystalline ion conductors.^{6–14,32,33} Many of these ionic moieties self-assemble into hexagonal columnar liquid crystal mesophases.³⁴ One of the goals of molecular electronics is to develop ion-conductive materials and there can be advantages when this ion conductivity is anisotropic. Liquidcrystalline ionic liquids are very promising candidates for the design of anisotropic, ion-conductive materials because they have an anisotropic structural organisation and contain ions as charge carriers. The incorporation of ionic functionality is also often found to give the liquid crystals a relatively wide mesophase temperature range.

More recently, incorporation of imidazolium cations at the end of alkylene chains bound to a triphenylene derivative resulted in stabilisation of a columnar phase and the mesophase was maintained over a wide temperature range from 4 to 117 °C.³⁵ A series of fan-shaped molecules, 1-methyl-3-[3,4,5-tris(alkyloxy)benzyl]imidazolium salts containing anions such as tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), trifluoromethylsulfonate ($CF_3SO_3^-$), and bis(trifluoromethylsulfonyl)imide (Tf_2N^-), exhibited hexagonal columnar phases with a maximum mesophase range of 160 °C.^{6,34}

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Fig. 1 Non-imidazolium liquid-crystalline ionic liquids reported in or prior to 1995.^{28–31}

On the other hand, compounds with a symmetric molecular structure are well known to have a relatively high thermal stability. The thermal stabilities of the so-called 'gemini'[‡] dicationic ionic liquids are found to be greater than those of most traditional monocationic ionic liquids,³⁶ and as such they have been used as solvents for high-temperature organic reactions³⁷ and gas chromatographic stationary phases.^{38,39}

Both symmetric and unsymmetric liquid crystal dimers composed of two mesogenic groups (identical or different, respectively) linked *via* a flexible or rigid spacer have been reported extensively^{35,40–48} and their physical properties are significantly different from those of conventional low-molarmass materials.^{44,49–52} For example, there are very pronounced odd-even effects that depend upon the parity of the flexible spacer and, more recently, they have been suggested as materials with significant flexoelectric response.⁵³

In ionic systems, the imidazolium cation provides a highly tunable and modular platform for the design and synthesis of dimeric cationic liquid crystals which offers excellent structure control.⁵⁴ Wishing to introduce ionic moiety into symmetrical molecular structures, the design strategy employed here is to modify dimeric imidazolium ionic liquids to prepare broadtemperature-range ionic liquid crystal materials that exhibit fluid ordered states of a columnar nature, maintaining high ionic conductivities and room-temperature mesophases.

So far, the liquid crystal behaviour of the dimeric imidazolium dicationic ionic liquids has been scarcely reported. Indeed, there is rather little literature on flexibly linked, ionic, dimeric liquid crystals. Initial studies reported examination of the behaviour of entirely aliphatic diammonium salts^{55,56} and it was only very recently that Bara *et al.*^{54b} took as a template the flexibly linked bis(imidazolium) salts reported by Anderson *et al.*³⁶ and simply (and elegantly) extended the terminal chains to arrive at materials (Fig. 2) showing smectic A phases, while in addition also using oligo(ethylene oxides) as spacers, related to studies reported by Dreja *et al.*⁵⁷ Curiously, in some of these reports aspects of the mesomorphism are interpreted in terms of possible smectic C phase formation, although it is not at all clear that such a phase has ever truly been seen in ion-separated ionic liquid crystals.

$$C_nH_{2n+1}$$
, N , R^1 , N , R^1 , N , C_nH_{2n+1} , $n = 10, 12, 14$
2 X⁻, Z_n , $X = Br, BF_4$

 $\mathsf{R}^1 = -(\mathsf{CH}_2)_m - or -(\mathsf{CH}_2\mathsf{CH}_2\mathsf{O})_p\mathsf{CH}_2\mathsf{CH}_2 -$

Fig. 2 General structure of dimeric imidazolium amphiphiles synthesized by Bara *et al.*^{54b}

[‡] The term dimeric is preferred here both because the term 'gemini' properly refers to surfactant systems and also because the dimeric nature of these materials is much more akin to the flexibly linked structures found in the study of thermotropic liquid crystals. None-theless, it is recognised that the early examples of such thermotropic behaviour originated in derivatives of gemini surfactants.



 $R^2 = -(CH_2)m^-$ m = 6, 8, 9, 10, 12Fig. 3 Structure of triphenylene-imidazole-based ionic dimers reported by Kumar and Gupta.⁵⁸

A similar idea was then reported by Kumar and Gupta⁵⁸ who used the same methylene-bridged bis(imidazolium) core while attaching triphenylene terminal groups (Fig. 3) to give materials with Col_h phases.

In contributing to the study of such dimeric materials, this work reports the synthesis and thermal properties of a series of ionic liquid crystal dimers, which have been designed to probe the relationship between molecular structure and mesophase behaviour. Structural variables encompassed the spacer length (number of repeat units), the anion (Cl⁻, BF₄⁻ and Tf₂N⁻), and terminal chain length (octyl and dodecyl). For comparison, 12 monocationic imidazolium liquid crystals with the same mesogenic groups and anions (Cl⁻, BF₄⁻, and Tf₂N⁻) were also prepared.

Results and discussion

Synthesis of the ionic liquid crystals

The new salts were prepared as follows. Following the procedure of Kumar and Gupta,⁵⁸ *N*-methylimidazole was reacted with the relevant α, ω -dibromoalkylene in the presence of sodium hydride to give the dimeric bis(imidazole) **1**-*m*; yields ranged from *ca.* 60% for **1**-4 to $\geq 95\%$ for **1**-6 and **1**-8. The dimeric imidazoles were then further reacted with two molar equivalents of a 3,4,5-trialkoxybenzyl chloride to give the doubly quaternised dichloride, **2**-*n*,*m* (*m* represents the number of carbon atoms in the bridging methylene chain, while *n* represents the number of carbon atoms in the terminal chains). Metathesis of the anion with AgBF₄ or LiTf₂N then led to related salts **3**-*n*,*m* and **4**-*n*,*m*.

The 1-(3,4,5-trialkoxybenzyl)-3-methylimidazolium chlorides, 5-*n*, were prepared by quaternisation of *N*-methylimidazole while the corresponding tetrafluoroborates, 6-*n*, and triflamides, 7-*n*, were obtained by metathesis of the chloride using AgBF₄ and LiTf₂N, respectively. The compounds were characterised by their ¹H and ¹³C NMR spectra and by elemental analysis. The absence of halide impurities in the purified BF₄ and Tf₂N salts was confirmed by addition of AgNO₃ to methanol washes of the products, which resulted in no observable silver halide precipitates. In total, some twenty-eight compounds were prepared. The chloride salts were further analysed by Karl-Fischer titration, which showed a small degree of hydration, consistent with the results of elemental analysis (Table S1, ESI†).

General properties of the imidazolium-based ionic liquids

The large number and variety of both symmetric dicationic dimeric ionic liquids and unsymmetric monocationic ionic liquids in this study permitted the evaluation of both cationic structure and anionic effects. Some homologues of 5-*n*, 6-*n* and 7-*n* have been prepared previously (n = 8 and 12)^{6,34} but new homologues (n = 10 and 14) were prepared here to provide a more systematic comparison with the new materials.

Polarised optical microscopy was first used to determine the liquid crystal phase behaviour, but it proved difficult to obtain good optical textures as most compounds decomposed on or before clearing. As such, cooling textures were found only for certain BF_4^- salts that were found to be thermally stable. Thus, investigation of dimeric tetrafluoroborates, 3-*n*,*m* was first undertaken and the thermal data are found in Table 1.

All of these salts melted from the crystal phase into a columnar hexagonal phase, which could be identified by its characteristic optical texture, an example of which is shown in Fig. 4. These textures were obtained on slow cooling from the isotropic liquid in which all homologues appeared stable for the duration of the experiment and as studied by TGA. The one exception was 3-12,4, which decomposed/cleared at 255.7 °C and for which no texture could be seen on cooling.

For the chloride salts, textures could not be found on cooling as all derivatives underwent decomposition and clearing simultaneously; it is not clear which one drives the other. Therefore the nature of the mesophase that was formed was determined in two different ways. First, a small portion of the sample was dissolved in either toluene or dimethyl sulfoxide (DMSO) and a couple of drops were placed on a microscope slide on the hot plate, whose temperature was held at 90 °C. The solvent was allowed to evaporate over a prolonged period and the texture was observed. An example is given as Fig. 5, which shows characteristic features of the Col_h phase. The phase identity was further confirmed in several contact experiments, where samples of the BF₄ and Cl salts were allowed to come into contact within their mutual mesophase ranges but well below the decomposition temperature of the chloride. Under all conditions, each of these contact preparations showed the two samples to be continuously miscible, thus identifying the mesophase as Col_h.

Examination of the tetrafluoroborate salts of the trialkoxybenzylimidazolium cation (6-n) revealed that all homologues

Compound	Transition	$T/^{\circ}\mathrm{C}^{a}$	$\Delta H/kJ mol^{-1}$
2 -8,4	Cr–Col _h	46.0	26.20
• • • •	Col _h –I	241.4	1.82
2-8,6	Cr_1 - Cr_2	62.3	21.93
	Cr_2-Col_h	81.4 226.7	20.11
2-8.8	$Co_h - 1$	-20.6	3.36
2-0,0	$Cr_1 - Cr_2$ $Cr_2 - Col_1$	-20.0	43 56
	Colu-I	183.9	1.58
2 -12,4	$Cr_1 - Cr_2$	49.3	59.18
, .	Cr ₂ -Col _h	72.3	104.56
	Col _h –I	212.9	2.94
2- 12,6	Cr_1 – Cr_2	35.9	27.22
	Cr2-Colh	100.5	69.05
	Col _h –I	220.8	2.14
2 -12,8	Cr–Col _h	36.7	60.99
	Col _h –I	215.8	2.93
3-8,4	Cr–Col _h	34.4	12.58
	Col _h –I	237.5	2.43
3 -8,6	Cr–Col _h	41.4	14.64
	Col _h –I	185.0	2.85
3-8,8	Cr–Col _h	98.2	37.99
	Col _h –I	135.3	2.28
3-12,4	Cr–Col _h	4.0	18.89
	Col _h –I	255.7	1.68
3-12,6	Cr–Col _h	5.9	7.88
	Col _h –I	246.2	3.90
3-12,8	Cr_1 - Cr_2	36.2	17.01
	Cr_2-Col_h	51.0	12.11
4.0.4	Col _h -I	213.2	3.88
4-8,4	Cr-I Cr-I	42.5	64.52
4-8,8	Cr-I Cr-I	<-40.0	116.02
4-12,4	CI-I Cr. Cr.	32.0	67.04
4-12-0	$Cr_1 - Cr_2$	20.0	14.16
5-8	Cr ₂ -r	40.0 52.2	38.94
5-0	Colu-L	185.7	0.95
5-10	Cr-Col	64.1	58.89
5 10	Colu-I	198 7	1 18
5-12	Cr–Col	70.1	89.43
0.12	Colu-I	187.5	0.81
5-14	Cr–Col	80.6	121.96
	Col _b –I	163.1	0.98
6- 8 ^b	g-Col _b	-35.1	
	Col _h –Ï	132.7	0.96
6- 10	Cr–Col _h	46.9	40.39
	Col _h –I	172.7	0.75
6 -12	Cr–Col _h	61.3	55.61
	Col _h –I	184.8	0.81
6- 14	Cr ₁ –Cr ₂	52.6	
	Cr ₂ –Cr ₃	58.2	
	Cr ₃ –Cr ₄	71.6	67.44
	Col _h –I	178.3	0.96
7-8	Cr–I	9.0	37.90
7-10	Cr ₁ –Cr ₂	-13.4	19.74
	Cr ₂ –I	19.3	21.74
7-12	Cr–I	39.7	72.25
7-14	Cr-I	51.0	80.79
^{<i>a</i>} Temperatures	are DSC onset val	ues. b g = glass	transition.

Thermal data for symmetric dimeric and unsymmetric ionic

showed a Col_h phase as determined unequivocally by their optical textures, which could be obtained on cooling from the isotropic liquid owing to their thermal stability. These salts mostly melted around 50–60 °C with the exception of **6**-8 where it was not possible to observe a melting point as the salt was already liquid crystalline at room temperature, although low-temperature DSC measurements did show what appeared to be a glass transition at -35 °C. The corresponding chloride



Fig. 4 Optical texture of 3-8,8 at 136.6 °C on cooling.



Fig. 5 Optical texture of 2-8,4 obtained after prolonged evaporation of a DMSO solution at 90 $^\circ$ C.

salts, **5**-*n*, had been reported previously^{6,34} but there was no mention of any mesomorphic properties. In common with chlorides **2**-*n*,*m*, these materials were also unstable thermally and so no textures could be obtained on cooling from the isotropic state. Thus, the mesophase was once more identified in contact preparations with known materials described above and a Col_h phase was found in each case.

Finally here, it is noted that none of the triflamide salts (4-n,m nor 7-n) was mesomorphic, attributed to the destabilising effect of the large anion (large excluded volume), which is also evident in the rather low melting points, all of which are below 60 °C. Dependence of liquid crystal properties on anion size for ionic liquids is a well-described phenomenon.^{34,59,60}

In considering the thermal stability of these materials, the chlorides and tetrafluoroborates follow the general trends recorded elsewhere both in simple 1-butyl-3-methylimid-azolium (bmim) ionic liquids and in non-mesomorphic,^{36,61} dimeric materials akin to those reported here. In all of the other studies, triflimides are found to be even more stable, but given the low melting points of the materials described here, no comparisons are possible.

Given the thermal instability of these salts, only limited structure/property relationships can be extracted. Fig. 6 shows the clearing points of the tetrafluoroborates 3-n,m as a function of both spacer and terminal chain length, and these are plotted against the limits of stability of the corresponding

Table 1

liquids



Fig. 6 Plot of clearing point *vs.* compound—BF₄ salts (3-*n*,*m*) in lighter shading and Cl (2-*n*,*m*) salts in darker shading. 'Clearing points' for the Cl salts are in fact the highest temperature at which a phase is seen and it is not possible reliably to know if clearing drives decomposition or *vice versa*. Note that the ordinate starts at 120 °C, which is above the melting point of all the samples in the plot.

chlorides, 2-n,m. With both an octyloxy and a dodecyloxy terminal chain, compounds 3-n.m show a monotonic decrease in mesophase stability as the length of the spacer chain increases. This is most pronounced for 3-8,m where the clearing point drops from ca 237.5 °C for m = 4 to 135.3 °C for m = 8—about 50 °C for each pair of methylene groups. For the series 3-12.m, the effect is less dramatic. The linear correlation across all three homologues is not evident owing to the decomposition of 3-12,4 at 255.7 °C, but extrapolating a line from 3-12,6 and 3-12,8 would imply a clearing point of 282 °C to give a gradient of 34 °C per two methylene groups. That the clearing point decreases with an increase in the length of the methylene spacer is entirely consistent with the behaviour in more conventional flexibly linked dimeric liquid crystals and is understood in relation to the gradual decoupling of the two ends as the chain length increases.

Given the lower thermal stability of the chlorides 2-*n*,*m*, a broad and meaningful comparison is not possible, particularly for 2-12,*m* which have all decomposed by 220 °C. However, some comparison of 2-8,*m* and 3-8,*m* is possible as the chlorides decompose above the clearing points of the tetra-fluoroborates. Thus, the columnar phase of the chlorides is in all cases more stable and for m = 6 and 8, the extent is at least 50 °C. This is consistent with the lower steric demands of the chloride anion and is accentuated as the linking chain increases in length, but where this chain is short (m = 4) then the effect is diminished as clearing points are also elevated significantly owing to the small value of *m*.

The other factor of particular note is the effect of the terminal alkoxy chain length. Thus, if the extrapolated clearing point of **3**-12,4 is accepted to be 282 °C, then for m = 4, 6 and 8, the clearing point increases by 45, 61 and 78 °C, respectively as *n* increases from 8 to 12—very significant enhancements.

It is here that comparison with the monosubstituted imidazolium salts becomes of significance, for compounds 6-*n* can be regarded as approximating to the terminal 'half' of flexible dimers 3-*n*,*m*. Thus, in the 'monomers', a combination of the new data recorded here and those reported previously shows that as *n* increases as 8, 10, 12 and 14, the clearing point increases as 132.7, 172.7, 184.8 and 178.3 °C, respectively. Thus, between n = 8 and 12 the clearing point increases by 52.1 °C, which is of a similar magnitude to the values found in 3-*n*,*m*, validating the comparison. Thus, the effect of the terminal chains is not dampened by the flexible spacer.

Other features of the thermal behaviour of these materials are worthy of note. Thus, they show extraordinarily large mesomorphic ranges for materials of this type. The largest absolute range is found for 3-12,4 at 255.7 °C, but this compound decomposes on clearing and so the largest useable range is for 3-12,6, one of 246.2 °C. Kinetically, the range of these materials is further extended as they show a significant propensity to supercool well below their melting points and this is something that could readily be exploited more systematically in mixtures where true eutectics could be formed to give even wider thermodynamic ranges.

Prior to this report, the largest phase range for columnar ionic liquid crystals was observed in a tripodal 4-(trialkoxyphenyl)pyridinium salt with PF_6^- as the anion, which showed a rectangular columnar phase from 24 to 245 °C.¹⁴ Other wide ranges were found in triphenylene derivatives bearing tetradecyl chains with imidazolium termini, which formed widerange cubic mesophases⁶⁰ and the pyrylium salts mentioned earlier where the mesophase extended from ambient temperature to over 200 °C.²⁹

As for the dicationic imidazolium materials reported here, these large-temperature-range ionic liquid crystals undoubtedly represent a promising new family of media with many exciting potential applications, in which a large liquid crystal range and high thermal stability can be exploited.

Moreover, the dimeric dicationic ionic liquids were found to exhibit a slightly higher thermal stability than unsymmetric monocation analogues, and compounds 2-12,4, 3-12,4, 4-12,4, and unsymmetric 5-12, 6-12, 7-12 are used as an example as they have the same terminal chains. The thermal decomposition temperatures determined by TGA for the two series of compounds are collected in Table 2. Symmetric dicationic 2-12,4 showed a decomposition temperature of 244 °C, while the corresponding unsymmetric 5-12 decomposed at 200 °C; The decomposition temperature is 280 °C for 3-12,4 but decreased to 260 °C for 6-12. A similar trend was also found

 Table 2
 Thermal decomposition temperatures for symmetric dimeric and unsymmetric ionic liquids

Compound	$T/^{\circ}\mathbf{C}^{a}$	
2 -12,4	244	
3-12,4	280	
4-12,4	307	
5-12	200	
6- 12	260	
7-12	273	
4 T . T C		

^a Temperatures are TGA onset values.

by the comparison between 4-12,4 and 7-12, the decomposition of the former took place at 307 °C, while 273 °C for the latter. It can be further seen from Table 2 that the triflamide salts are more stable than BF_4 and further Cl salts.

In addition, the dimeric dicationic ionic liquids have generally exhibited wider mesophase ranges than the unsymmetric compounds for Cl salts or BF4 salts. Unsymmetric 5-8 showed a Col_b mesophase of range 133.5 °C, whereas the mesophase range found for dimeric 2-8,4, 2-8,6 and 2-8,8 are 197.4, 155.7 and 149.5 °C, respectively. Compound 5-12 has a mesophase range of 117.4 °C, which is lower than the corresponding symmetric materials 2-12,4 (140.6 °C), 2-12,6 (120.3 °C) and 2-12,8 (178.9 °C). A similar trend can also be found for BF₄ salts. Here, the mesophase range of symmetric 3-12,4, 3-12,6 and 3-12,8 are 251.7, 240.3 and 162.2 °C, respectively, while a range of 123.5 °C was observed for unsymmetric 6-12. The one exception was 6-8, for which a melting point has not been recorded (vide supra). However, the inability to cause the material to crystallise and the observation of a glass transition at -35.1 °C suggests a useful range of up to 167.8 °C, although it is recognised that this is not a true thermodynamic range.

Conclusion

We have demonstrated that the symmetric dicationic imidazolium ionic liquids (2-n,m and 3-n,m, n = 8, 12; m = 4, 6, 8) and unsymmetric monocationic imidazolium ionic liquids (5-n and 6-n, n = 8, 10, 12, 14) are able to form Col_h mesophases. Their symmetric structure and the presence of the ion moiety leads to a relatively high thermal stability and wide mesophase range. Indeed, an extremely large columnar phase width of more than 200 °C and spanning room temperature was observed for the first time. Spacer length, alkyl length and the nature of ions were all found to influence the mesomorphism. Thus, systems with longer alkyl chain length and short spacer length were found to have large mesophase ranges. In considering the counter anions, Cl⁻ and BF₄⁻ were found to stabilise the formation of mesophases, while the bulky anion, Tf_2N^- , suppressed phase formation. Symmetric, dimeric, dicationic imidazolium ionic liquid crystals therefore represent a versatile platform for molecular design. For example, the coupling of the remarkable mesophase range and the incorporation of ions into the centre of Col_h phase demonstrate the potential for anisotropic ionic conductivity. Exploring their fundamental structure-property relationships also give a guide for the design of high-temperature-range ionic liquid crystals.

Experimental

General procedures and materials

Reagents and solvents were obtained from commercial suppliers and were used without further purification. The compounds were characterised by ¹H and ¹³C NMR spectroscopy recorded on JEOL ECX400, or Bruker AV500 spectrometers. Elemental analysis was carried out on an Exeter Analytical Inc. CE-400 Elemental Analyser. Mass spectra were obtained on a Bruker microTOF instrument. The water content in samples was measured by Karl Fischer (Mettler Toledo DL32 coulometer). Thermal properties of liquid crystal transitions were measured using a Mettler Toledo DSC822e differential scanning calorimeter, equipped with Mettler Toledo TS0801RO sample robot and calibrated against pure indium metal. Heating and cooling rates were 10 °C min⁻¹. Optical textures were recorded using an Olympus BX50 polarising microscope equipped with a Linkam scientific LTS350 heating stage, Linkam LNP2 cooling pump, and Linkam TMS92 controller. Thermogravimetric analysis was performed on a Stanton-Redcroft STA 625 instrument. The heating rate employed was 10 °C min⁻¹ from room temperature (approximately 25 °C).

Synthesis

The synthetic pathways used to obtain symmetric 2-n,m; 3-n,m; 4-n,m and unsymmetric 5-n; 6-n; and 7-n are shown in Scheme 1. Diimidazole compounds (1-m) were first synthesised from imidazole and the corresponding α, ω -dibromoalkanes according to procedures outlined in the literature, 58,62 but with minor modifications to the purification protocol. The mesogenic 3,4,5-tris(alkyloxy)benzyl chlorides (n = 8, 10, 12, and14) were then synthesised by a literature procedure.⁶ Subsequent reaction with 2 equivalents of a 3,4,5-trialkoxybenzyl chloride produced the symmetric dicationic ionic liquids with chloride counterions (2-n,m). Ion-exchange with AgBF₄ or LiTf₂N afforded the related salts 3-n,m and 4-n,m. In a similar way, unsymmetric monocationic 5-n compounds were prepared by quaternisation of N-methylimidazole with mesogenic 3,4,5-tris(alkyloxy)benzyl chlorides. 6-n and 7-n are obtained by metathesis of the chlorides using AgBF₄ and LiTf₂N, respectively.

Synthesis of diimidazole compounds

In a typical procedure, a solution of imidazole (5.0 g, 72.4 mmol) in DMF (25 cm³) in a round-bottomed flask equipped with a stirring bar was deaerated under reduced pressure, and the flask was filled with nitrogen. The deaeration was repeated three times to remove oxygen from the flask thoroughly. The flask was cooled down to about 0 °C with an ice bath. Sodium hydride (1.92 g, 80.0 mmol) was then added slowly into the reaction solution. After that, dibromoalkane (33.35 mmol) was added and the resulting mixture was heated at 70 °C for 4 h with vigorous stirring. When the reaction was over, the crude products were purified either by crystallisation or column chromatography, which depends on the properties of the products. The purification processes are as follows: For 1,1'-(butane-1,4-diyl)diimidazole (1-4), after the reaction was finished, the mixture was cooled down to room temperature and then poured into water (15 cm³). A white, crystalline solid precipitated from aqueous solution after water was evaporated in air for at least 24 h. The same crystallisation was performed twice and 3.68 g (58%) of pure solid product was obtained after dying under decreased pressure at 60 °C for 24 h. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (s, 2H), 7.00 (s, 2H), 6.80 (s, 2H), 3.87 (m, 4H), 1.69 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 136.9, 129.8,$ 118.5, 46.3, 28.1.

For 1,1'-(hexane-1,6-diyl)diimidazole (1-6), the solvent was removed at 80 °C under decreased pressure after the reaction was complete. Chloroform (100 cm³) was then added to the





Scheme 1 Synthesis of dimeric dicationic ionic liquids and unsymmetric monocationic ionic liquids: (i) $Br(CH_2)_mBr$, DMF, NaH (ii) toluene (iii) AgBF₄, MeOH or LiTf₂N, MeOH.

residual and the resulting mixture was dried over anhydrous MgSO₄, filtered through a pad of celite, and concentrated under reduced pressure. The crude solid was purified by silica gel flash-column chromatography eluting with 10% methanol in ethyl acetate to give 6.90 g (95%) of the pure product as a crystalline solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.38 (s, 2H), 6.99 (s, 2H), 6.82 (s, 2H), 3.83 (m, 4H), 1.69 (m, 4H), 1.23 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 137.0, 129.4, 118.6, 46.7, 30.8, 26.0.

For 1,1'-(octane-1,8-diyl)diimidazole (1-8), after the reaction was over, the mixture was poured into a mixture of ethyl acetate and water (10:1). The organic phase was separated; the aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were washed with water and saturated NaCl solution, respectively. The resulting organic phase was dried over anhydrous MgSO₄, filtered through a pad of celite, and concentrated under reduced pressure to give 7.96 g (97%) of the pure product as a viscous liquid.§ ¹H NMR (400 MHz, CDCl₃): $\delta = \delta$ 7.38 (s, 2H), 6.98 (s, 2H), 6.83 (s, 2H), 3.84 (m, 4H), 1.71 (m, 4H), 1.21 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 136.9$, 129.2, 118.7, 46.8, 30.8, 28.7, 26.3.

Synthesis of 1,1'-(1,4-butanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} chloride (2-8,4). To a solution of 3,4,5-tris-(octyloxy)benzyl chloride (10.21 g, 20.0 mmol) in toluene

§ One referee pointed out that this compound has previously been obtained as a solid, but using SciFinder we were unable to find corroborative evidence. Indeed, leaving the sample in a freezer at -20 °C overnight did not cause solidification.

(10 cm³) under nitrogen was added a solution of 1,1'-(butane-1,4-diyl)diimidazole (1-4) (0.95 g, 5.0 mmol) in MeCN (10 cm³) with stirring. After the reaction solution was heated at 80 °C for 48 h, the solvents were removed by a rotary evaporator under reduced pressure. The product was separated and purified by silica gel flash-column chromatography eluting with CH₂Cl₂/ MeOH (10:1) and dried under reduced pressure at 60 °C for 24 h to give the pure product as a white solid (5.30 g, 87.5%). ¹H NMR (400 MHz): δ = 10.61 (s, 2H), 7.89 (t, 2H), 7.06 (t, 2H), 6.58 (s, 4H), 5.31 (s, 4H), 4.55 (t, 4H), 3.93–3.90 (m, 12H), 2.18 (t, 4H), 1.79–1.67 (m, 12H), 1.48–1.26 (m, 64H), 0.87–0.84 (m, 18H). ¹³C NMR (100 MHz): δ = 153.9, 138.9, 136.9, 127.8, 123.2, 121.3, 107.6, 73.5, 69.5, 53.9, 49.1, 32.0, 31.9, 30.4, 29.6, 29.5, 29.4, 26.6, 26.2, 26.2, 22.8, 14.2.

A similar synthesis procedure was used to produce **2**-8,6, **2**-8,8, **2**-12,4, **2**-12,6 and **2**-12,8 and the relevant data are listed in the Supporting Information.

Synthesis of 1,1'-(1,4-butanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} tetrafluoroborate (3-8,4). To a solution of 2-8,4 (2.42 g, 2.0 mmol) in CH₂Cl₂ (15 cm^3) was added a solution of silver tetrafluoroborate (AgBF₄) (0.86 g, 4.4 mmol) in MeOH (15 cm^3) with stirring at room temperature. The mixture was stirred at room temperature for 2 h. The insoluble AgCl was filtered off through a pad of celite by using a suction funnel. The filtrate was concentrated by using a rotary evaporator. The crude product was purified by flash-column chromatography on silica gel (eluent: $CH_2Cl_2/MeOH = 10:1$) and dried under reduced pressure at 60 °C for 24 h to give the pure product as a white solid (2.22 g, 84.4%). ¹H NMR (500 MHz): $\delta = 8.81$ (s, 2H), 7.40 (t, 2H), 7.11 (t, 2H), 6.58 (s, 4H), 5.17 (s, 4H), 4.22 (t, 4H), 3.96-3.90 (m, 12H), 1.97 (t, 4H), 1.80-1.68 (m, 12H), 1.48–1.26 (m, 64H), 0.88–0.84 (m, 18H). ¹³C NMR (100 MHz): $\delta = 154.0, 139.0, 135.6, 128.9, 122.8, 121.7, 107.5, 73.5, 69.4,$ 54.2, 49.2, 32.0, 31.9, 30.4, 29.6, 29.5, 29.4, 26.2, 22.8, 14.2. ESI-MS (methanol, m/z): 1337.9449 (1337.9493 calculated $[M] + C_{72}H_{124}B_2F_8N_4NaO_6$).

Similarly, the synthesis procedure of **3**-8,6, **3**-8,8, **3**-12,4, **3**-12,6 and **3**-12,8 is shown in Supporting Information.

Synthesis of 1,1'-(1,4-butanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} bis(trifluoro-methylsulfonyl)imide (4-8,4). To a solution of 2-8,4 (0.61 g, 0.5 mmol) in MeOH (50 cm^3) was added a solution of LiTf₂N (0.32 g, 1.1 mmol) in MeOH (15 cm^3) with stirring at room temperature. The mixture was stirred at room temperature for 10 min. After removal of the solvents at 60 °C under decreased pressure, the residual was dissolved in CH_2Cl_2 (10 cm³) and poured into water (5 cm³). The organic phase was separated, washed with water for 2 times and dried over anhydrous MgSO4, filtered through a short pad of celite, concentrated by a rotary evaporator. The crude product was purified by flash-column chromatography on silica gel (eluent: $CH_3Cl_3/MeOH = 10:1$) and dried under decreased pressure at 60 °C for 24 h to give the pure product as a very viscous liquid (0.61 g, 74.4%). AgBF₄ test shows no Cl⁻ remaining. ¹H NMR (500 MHz): $\delta = 8.77$ (s, 2H), 7.41 (t, 2H), 7.12 (t, 2H), 6.52 (s, 4H), 5.14 (s, 4H), 4.25 (t, 4H), 3.94-3.90 (m, 12H), 2.01 (t, 4H), 1.75-1.68 (m, 12H), 1.46-1.26 (m, 120H), 0.88–0.84 (m, 18H). ¹³C NMR (100 MHz): $\delta = 154.1$,

139.3, 135.1, 126.7, 123.0, 122.0, 121.4, 118.2, 107.5, 73.6, 69.4, 54.3, 49.4, 32.0, 30.4, 29.6, 29.5, 29.4, 26.7, 26.2, 26.1, 22.8, 14.2.

The synthetic procedures for 4-8,8, 4-12,4 and 4-12,8 and all unsymmetric monocationic ionic liquids are given in the Supporting Information, along with data for elemental analysis for all compounds.

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