Ionic liquid crystals based on viologen dimers: tuning the mesomorphism by varying the conformational freedom of the ionic layer

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ABSTRACT
We investigated the liquid crystal behaviour of newly synthesised bistriflimide salts of symmetric viologen dimers. A smectic A phase was observed for intermediate spacer lengths and for relatively long lateral alkyl chains. The systems were characterised by thermal analysis, polarised optical microscopy, X-ray scattering and solid-state NMR. An intermediate ordered smectic phase was also exhibited by the compounds (except for systems with very short lateral chains) consisting of molten layers of alkyl chains and partially ordered ionic layers. These results, relating to the mesomorphic behaviour of viologen salts, are qualitatively compared to those of the more common imidazolium salts, highlighting the importance of the conformational degrees of freedom of the anions and of the cationic core. It appears that fine tuning of the conformational degrees of freedom of the ionic layer is an important component of mesophase stabilisation.

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Introduction
Ionic liquid crystals (ILCs) have recently attracted the attention of the chemistry and materials science communities as systems with the potential to combine the many applications and features of liquid crystals (LCs) and ionic liquids (ILs); see Ref. [1] for a comprehensive review and Refs. [2,3] for more recent updates on the subject. ILCs are usually obtained from organic salts of quaternised nitrogen as imidazolium, [4–8] piperidinium, [9] pyridinium, [10,11] bipyridinium (also known as viologens), [12–14] pyrrolidinium, [15] phenantrolinium, [16] and guanidinium [17–19] with common inorganic anions, such as halides, bistriflimide, tetrafluoroborate and hexafluorophosphate. These salts usually form ILs but when one or more alkyl chains is sufficiently long they also exhibit mesomorphism. Since the driving force is micro-segregation between the hydrophobic chains and the ionic layers, a
smectic phase (for calamitic systems) is frequently obtained, though rare cases of ionic nematic phases have been reported. [20–23] Besides the effect of these chains, the role of head groups has received some attention recently. [24]

Computer simulations, either coarse-grained [25–29] or fully atomistic, [30,31] and theoretical models [32] have tried to shed light on the relation between molecular structure (size, shape and charge of both cations and anions) and the type and thermal range of stability of the mesophase formed. This is, however, a formidable challenge: prediction of the type of mesophases formed and their transition temperatures is still beyond our reach. For example, in a review concerning the various empirical methods and protocols for the prediction of the melting points of ILs, [33] those exhibiting LC phases, that is ILCs, were purposely left out of the set of compounds investigated because they were deemed too difficult to treat, due to the limited understanding and modelling currently available.

On the other hand, the huge amount of literature and the vast knowledge base concerning the structure–property relationships of non-ionic LCs, though essential for a comparison, might be hard to apply directly in the case of ionic compounds because the electrostatic interactions (not the key factor in LC science) are instead dominant for ILCs. Excluded volume effects, already important for the stabilisation of LC smectic phases, [34] might be even more important in regard to ILCs due to the presence of two kinds of particle (cation and anion) of very different shape and size.

A deeper understanding of the relationship between structure and phase properties of ILCs would be highly desirable: ILCs have been used recently for applications in the field of solar cells, [35] membranes for water desalination, [36] battery materials, [37] electrochemical sensors [38,39] and electrofluorescence switches. [40] In these applications, the microscopic structure of the ILC molecules and the conductive properties of the ionic mesophase were found to have a significant impact on the performance of ILC-based devices compared with analogous devices based on isotropic ILs. The only way to improve the performance is thus to learn how to design a particular cation–anion combination in order to obtain the relevant mesophase with tailored properties.

Our interest has been focused more recently toward viologen-based ILCs that have added value due to the interesting red–ox chemistry of the viologen unit. [41,42] Non-symmetric viologen monomers, [12] symmetric tetramethylviologens [43] and symmetric viologen dimers with a short lateral ethyl chain [44] have been synthesised and characterised by a range of experimental techniques. Interestingly, a SmA phase has been found only recently [45] by dimerisation of viologen salts which, in their monomeric form, exhibit either a crystal–to-isotropic transition or an intermediate ordered mesophase, labelled as SmX, the detailed nature of which has not been completely elucidated to date.

In this work, we extend our investigation by presenting a series of symmetric viologen dimers n.m.n.m.m.n, where ‘.’ represents the bipyridinium core while n and m indicate the number of carbon atoms in the lateral and middle (spacer) alkyl chains, respectively. These compounds exhibit a rich polymorphism, including the ionic SmA and SmX phases.

Dimeric systems are also interesting for several other reasons: non-ionic LC dimers have been extensively investigated in the literature for about 30 years when they were proposed as model systems for the mesomorphic behaviour of LC polymers, [46] and the research in this field is still very active. [47] A critical review covering this field was presented by Imrie and Henderson. [48] Recent examples encompass hybrid systems of rod-like and bent-core units exhibiting a biaxial SmA phase, [49] chiral dimers, [50] systems based on isoflavone moiety [51] and dimers with a sulfur–sulfur link in the spacer. [52] The novel twist-bend nematic phase observed in some cyanobiphenyl dimers has very recently contributed to boosting and renewal of interest in the intriguing properties of LC dimers. [53–59]

One of the key properties of LC dimers is a pronounced odd–even effect in thermodynamic transitional properties, that is a dependence on the length, and especially the parity, of the spacer: higher clearing points and larger enthalpy and entropy changes are observed for the even members. [48] Significant theoretical [60–62] and computational [63] work has been devoted to a rationalisation of this behaviour in order to overcome the oversimplified view where only the all-trans arrangement of the spacer is considered.

The second interesting feature of LC dimers is the somehow unexpected dependence of the stability of the smectic phase on the length of the spacer. Since micro-phase segregation is also the driving force for the formation of smectic phases in non-ionic LCs, it comes as no surprise that smectic phase stability generally increases with increased length of the terminal chains of monomeric LCs. Similarly, for main-chain polymeric LCs the stability of the smectic phase also increases with increased length of the chains connecting the mesogenic units. [48] For symmetric dimers the stability of the smectic phase increases with increased length of the terminal chains but, at variance with other cases, it is diminished and the smectic phase
suppressed when the spacer is too long. Luckhurst and co-workers found that, in order to have a smectic phase, the number of carbon atoms in the terminal chains, \( n \), should be greater than \( m/2 \), where \( m \) is the number of carbon atoms in the spacer of the symmetric dimers. [64]

In contrast to non-ionic LC dimers, ILC dimers have been less investigated. ILCs based on imidazolium dimers were described by Bara et al., [65] where a significant effect of the length and type of spacer (alkyl vs. oligo (ethylene glycol)) was observed. A marked dependence of the stability of the smectic phase on the spacer is indeed expected since for ionic systems, micro-phase segregation is significantly stronger than for the analogous non-ionic LCs. Gin and co-workers studied imidazolium trimers exhibiting rich mesomorphism. [66, 67]

**Results and discussion**

The compounds investigated are shown in Figure 1. Synthetic protocols are described in the Supplemental Information. One option is to first prepare the dimeric core, 1,1′-(alkane-1,3-diyl)bis(4-pyridine-4-yl)pyridinium) dihalide by refluxing an excess of bipyridine with \( \text{X} \) followed by quaternisation with \( \text{C}_n\text{H}_{2n+1}^- \cdot \text{X} \). The second option is a multi-step quaternisation of bipyridine, first with \( \text{C}_n\text{H}_{2n+1}^- \cdot \text{X} \) to obtain the 1-alkyl-4-(pyridine-4-yl)pyridinium halide (\( \text{X} = \text{Br}, \text{I} \)), followed by reflux with excess X–CH\(_{2n}^-\cdot\text{X} \) to yield the dimeric viologen halide. In both cases a final metathesis with LiTf\(_2\)N yielded the desired salt. The compounds were structurally characterised by \(^1\text{H} \) and \(^{13}\text{C} \) NMR, ESI-MS and elemental analysis. Details are in the supplemental information.

**Material characterisation**

Previous TGA studies on the thermal stability of monomeric [12] and dimeric [44] bistriflimide viologen salts revealed the decomposition temperature always to be above 350°C. Such investigation has not been repeated here since the salts are similar in terms of molecular properties.

In Table 1 we report the thermodynamic properties of the dimers investigated. In addition we also include, for the sake of comparison, some dimers with a short end-chain (ethyl) studied previously. [44] The enthalpies of transition at the clearing or melting point into the isotropic phase are also displayed in Figure 2, above the histograms representing the temperature range of the phase of each compound.

We identified four different phases: a crystal phase (Cr), which is observed in all compounds at sufficiently low temperature; an isotropic liquid phase (Iso), which is also observed in all compounds at sufficiently high temperature; and two intermediate phases – at least one mesophase for dimers with long end-chains which appears to be the same as that found in monomeric viologens, here called SmX since its full characterisation turned out to be rather difficult; [12] and two mesophases in some dimers, the higher-temperature examples being an ionic smectic A phase, SmA. This behaviour was previously observed in few selected example reported in Ref. [45], namely 12.4.12, 14.4.14 and 16.4.16. We note that Cr-to-Cr transitions were frequently observed in the DSC differential scanning calorimetry (DSC), but these will not be discussed here.

The enthalpy of melting into the isotropic phase shows a clear pattern: melting from the crystal phase (see the 2.n.2 series) has a relatively high value (in the range of several tens of kJ/mol) and a marked odd–even effect (see also the more detailed discussion in Ref. [44]). Melting from the intermediate SmX phase was accompanied by a much lower enthalpy change, in the range 20–30 kJ/mol. This is, however, still much higher than typical enthalpy of melting of SmA phases. Finally, melting from the SmA phase was characterised by a somewhat lower enthalpy of transition, in the range of a few kJ/mol to even below 1 kJ/mol, typical of SmA-Iso transitions. Entropies of transition at the clearing point, \( \Delta S_m/R \), are also in the expected ranges (i.e. 0.6, 2.4 and 0.6 for 14.3.14, 14.4.14 and 14.5.14, respectively). The higher entropy (and enthalpy) change for dimers with an even spacer is well documented for non-ionic dimers. [48, 64] It is noteworthy that the enthalpy of transition from the Cr to SmX is not too dissimilar to typical values of the enthalpy of melting of alkanes: these range, for example, from \( \Delta H_{\text{melt}}(\text{C}_{10}\text{H}_{22}) = 28.7 \) kJ/mol at 243.5 K to \( \Delta H_{\text{melt}}(\text{C}_{16}\text{H}_{34}) = 51–53 \) kJ/mol at 291 K. [68] This observation is consistent with the mechanism we proposed previously, [45] where the Cr-to-SmX phase transition was ascribed essentially to melting of the hydrophobic layers.

![Figure 1. Structure of the viologen dimers investigated, n.m.n. For n, m pairs see Table 1. Tf2N⁻ is (CF₃SO₂)₂N⁻, bistriflimide.](image-url)
Table 1. Thermodynamic properties of the samples investigated. Transition temperatures $T_n/°C$ ($\Delta H_n/kJ/mol$). h: $1^{st}$ heating; c: $1^{st}$ cooling. In some cases the cooling transition(s) were not observed due to large hysteresis.

| n.m.n  | phase | $h T_1 (\Delta H_1)$ c | $T_1 (\Delta H_1)$ | phase | $h T_2 (\Delta H_2)$ c | $T_2 (\Delta H_2)$ | phase | $h T_3 (\Delta H_3)$ c | $T_3 (\Delta H_3)$ |
|--------|-------|------------------------|--------------------|-------|------------------------|--------------------|-------|------------------------|--------------------|
| 2.7.2a | Cr    | 103 (56.4)              | –                  | Cr    | 160 (25.2)              | –                  | Cr    | 193 (7.3)              | –                  |
| 2.8.2a | Cr    | 121 (79.3)              | –                  | Cr    | 152 (24.8)              | –                  | Cr    | 174 (5.8)              | –                  |
| 2.9.2a | Cr    | 91 (66.3)               | –                  | Cr    | 143 (30.5)              | –                  | Cr    | 137 (15.1)             | –                  |
| 2.10.2a| Cr    | 93 (78.6)               | –                  | Cr    | 138 (28.3)              | –                  | Cr    | 149 (32.0)             | –                  |
| 8.8    | Cr    | 67 (47.5)               | SmX                | Cr    | 154 (33.7)              | –                  | Cr    | 139 (28.6)             | –                  |
| 10.4.10| Cr    | 93 (25.7)               | SmX                | Cr    | 149 (32.0)              | –                  | Cr    | 122 (22.9)             | –                  |
| 11.4.11| Cr    | 89 (27.4)               | SmX                | Cr    | 122 (22.9)              | –                  | Cr    | 129 (26.6)             | –                  |
| 12.3.12| Cr    | 65 (4.9)                | SmX                | Cr    | 129 (26.6)              | –                  | Cr    | 143 (30.5)             | –                  |
| 12.4.12b| Cr    | 88 (23.6)               | SmX                | Cr    | 154 (17.7)              | SmA                | Cr    | 183 (7.3)              | Iso               |
| 12.5.12| Cr    | 44 (20.1)               | SmX                | Cr    | 119 (31.1)              | –                  | Cr    | 174 (5.8)              | –                  |
| 12.6.12| Cr    | 38 (16.4)               | SmX                | Cr    | 102 (31.1)              | –                  | Cr    | 151 (21.1)             | –                  |
| 12.7.12| Cr    | 46 (26.7)               | SmX                | Cr    | 195 (22.6)              | –                  | Cr    | 141 (11.1)             | –                  |
| 12.8.12| Cr    | 31 (20.9)               | SmX                | Cr    | 167 (26.9)              | –                  | Cr    | 151 (21.1)             | –                  |
| 14.3.14| Cr    | 77 (8.8)                | SmX                | Cr    | 215 (31.8)              | –                  | Cr    | 151 (21.1)             | –                  |
| 14.4.14b| Cr    | 81 (23.2)               | SmX                | Cr    | 208 (30.9)              | –                  | Cr    | 197 (2.2)              | –                  |
| 14.5.14| Cr    | 32 (16.8)               | SmX                | Cr    | 148 (16.8)              | –                  | Cr    | 161 (26.2)             | –                  |
| 14.6.14| Cr    | 44 (11.0)               | SmX                | Cr    | 119 (31.1)              | –                  | Cr    | 174 (5.8)              | –                  |
| 16.3.16| Cr    | 20 (32.0)               | SmX                | Cr    | 107 (25.2)              | –                  | Cr    | 141 (11.1)             | –                  |
| 16.4.16b| Cr    | 39 (35.0)               | SmX                | Cr    | 122 (22.9)              | –                  | Cr    | 174 (5.8)              | –                  |
| 16.5.16| Cr    | 34 (32.4)               | SmX                | Cr    | 100 (21.9)              | –                  | Cr    | 141 (11.1)             | –                  |
| 16.6.16| Cr    | 34 (32.4)               | SmX                | Cr    | 244 (38.2)              | –                  | Cr    | 178 (1.0)              | –                  |

From Ref. [44]. bFrom Ref. [45]. Reproduced by permission of the PCCP owner societies.

Polarised optical micrographs (POMs) of some of the samples investigated are shown in Figure 3. Focal conic and fan-shaped textures support the identification of the high-temperature mesophase observed in some samples as a SmA. In contrast, samples exhibiting only one mesophase between the crystal and the isotropic liquid showed the mosaic or spherulitic texture (see Figures S31 in SI) indicative of a lamellar morphology in the solid state. The position of the (100) peak allows the calculation, according to the Bragg law, of the distance $d_{100}$ between the lamellae formed by the molecules. This peak shifts to lower angles as the temperature was increased (see Table 2 and Figure S32 in the SI).

In Table 2 we list the observed inter-lamellar distance, $d_{100}$, for each of the phases of the materials (i.e. the layer thickness of the smectic phases) and compare these to the calculated distance between the two methyl ends of the lateral chains of the molecules (i.e. to the full length of the dimers). Even within the same phase, the layer thickness depends on the temperature so comparison can be made only at a qualitative level. However, it is clear that the inter-layer distance obtained by XRD is consistently much lower than the length of the dimer with fully extended lateral alkyl chains. This is indicative of a relevant degree of interdigitation of the alkyl side chains.
Examination of Figure 4 shows that the complexity of the XRD patterns sharply decreases with increasing temperature. Such data confirm the occurrence of the phase sequences identified by thermal analysis and POM (Figures 2 and 3). The Cr phase is characterised by very rich room-temperature XRD patterns, especially in the wide-angle range, indicative of a significant degree of order in the short-distance range. As the temperature was increased, modifications were observed in the XRD pattern: the halo located at about 20 degrees in $2\theta$ became more intense and concurrently the sharp crystalline peaks in the same angular region became weaker. This behaviour is indicative of the formation of a smectic LC phase that retains a significant degree of order (i.e. the SmX phase). [12,67]

The XRD patterns of materials 16.3.16, 16.4.16 and 16.5.16 at 175°C are typical of a smectic A mesophase (see also Figure S32 in the ESI). These show the presence of a long-range order, reflected by a first-order peak and possibly a weak second-order one, with only a broad halo at high angles consistent with the lack of short-range order. [45]

It is worth noting that each of these phase transitions resulted in a decrease in the degree of order of the solid-phase framework. This is evidenced, in the XRD patterns, by both the disappearance of high-order peaks and the looser packing of the molecules, reflected by an increase in the $d_{100}$ interlamellar distance.

To investigate the Cr-to-SmX transition, $^{13}$C CPMAS NMR spectra were also recorded for the series 16.m.16 with $m = 3$–6, and for 14.m.14 with $m = 5, 6$, from room temperatures up to 80°C. For the longer spacers ($m = 5, 6$), an interesting feature emerging from these spectra, and already noted in the solid-state NMR spectrum of the monomer 14.14, [45] is the collapse of cross-polarisation on the methyl signals (the most shielded) upon transition from Cr to SmX (see Figure 5). The disappearance of methyl resonance can be explained by an efficient zero-averaging of C-H dipolar interactions as a result of a liquid-like dynamics, a feature consistent with an almost complete melting of the C16 alkyl chains to form a disordered layer. As counterproof, the N-$^{13}$CH$_2$-spins resonating around 60 ppm and located opposite methyls in the
C16 chains always display an intense cross-polarised signal, since their mobility is hampered both before and after phase transition. The sharpening of pyridine ring signals (120–155 ppm) after phase transition can also be explained by the increased mobility of the bispiridyl moiety. In this case, however, the appearance of intense spinning sidebands (see asterisks in Figure 5) indicates that the motion is not completely isotropic.

Figure 3. (colour online) POM images of 14.n.14, on cooling from the melt, n = 3, 4, 5 and 6 for (a), (b), (c) and (d), respectively. For the first three cases typical SmA textures (either batonnet or fan-shaped) are observed. For the last case a needle-like texture, typical of ordered phase, is observed. The white bar at the bottom is 100 μm and all photographs are the same size.

Figure 4. WAXD patterns of sample 16.3.16 at a) 25°C, Cr; b) 75°C, SmX; c) 175°C, SmA; d) 250°C, Iso.
and is likely to be a rotation along the N–N axis roughly elongated along the director of the smectic phase. As a result, the strong dipolar interactions in the Cr phase are also partially reduced in the SmX phase, and the heteronuclear decoupling during acquisition becomes much more efficient. Similar features are exhibited by the other compounds (see the solid-state NMR spectra in the SI). Therefore the SmX phase of the dimers, whether or not these also exhibit a higher-temperature SmA phase, shares some common features with the SmX phase observed for the viologen monomers discussed in previous works.\[12,44,45\] This appears to correspond to a melting of the hydrophobic layers while the in-plane ordering of the ionic layers does not disappear since clear Bragg’s reflections are observed in the XRD traces.

Variable-temperature $^{19}$F MAS NMR spectra (368.7 MHz, 10 kHz MAS, see the SI) run on the same sample in the interval 25–80° C also reveal a phase transition between 50° and 55° C (note that any discrepancy in $^{13}$C NMR and DSC data can be attributed to an additional sample heating induced by the fast MAS). In this case, assessing the phase transition from linewidth of the isotropic chemical shift (~79 ppm) is more difficult, as the $\text{TF}_2\text{N}^-$ anion is intrinsically less ordered than its counter-ion.

To summarise, these new data confirm the hypothesis presented in our previous work.\[45\] The layered phases differ in the degree of bidimensional order within the alternating hydrophobic and ionic layers. This 2-D order is in addition to that along the director, which is common to all three phases. Based on comparison of XRD and SSNMR data we can say that in the Cr phase both layers – the ionic and the hydrophobic – are ordered as obviously expected for a crystal; in the SmA phase both layers are disordered and fluid; in the intermediate SmX phase only the hydrophobic layer is liquid-like while the ionic layer retains some degree of in-plane ordering.

We note that a very similar behaviour, featuring the sequence of an ordered low-temperature SmX phase and a fluid high-temperature SmA phase, was recently reported by Gin and co-workers for polycationic salts based on imidazolium trimers.\[66,67\] Therefore, such behaviour may be related to the presence of an ionic layer of significant thickness compared to the hydrophobic layer, while simpler ILCs, such as monocationic imidazolium salts, only exhibit a SmA mesophase. However, at present it is not possible to propose a better-defined description of the ordered SmX mesophase.

**Solution and aggregation behaviour**

In order to unambiguously assign the $^{13}$C NMR resonances of 16.5.16, the following protocol was adopted. Selective TOCSY spectra were first run on a sample of 16.5.16 dissolved in CD$_3$OD. Both inner and outer N-CH$_2$-CH$_2$- resonances were separately excited, and

### Table 2. Geometrical parameters, at the PM3 level and experimental layer thickness, from the first Bragg’s peak at the selected temperatures.

| n.m.n  | D(CH$_3$-CH)$_2$ | Cr $d_{100}$ | SmX $d_{100}$ | SmA $d_{100}$ |
|--------|-----------------|-------------|---------------|---------------|
| 10.4.10 | 42.47           | 29.9        | 31.1          |              |
|        |                 | (25°C)     | (98°C)        |              |
| 11.4.11 | 45.41           | 31.1        | 34.4          |              |
|        |                 | (25°C)     | (137°C)       |              |
| 12.4.12 | 47.06           | 32.5        | 33.3          | 34.6          |
|        |                 | (30°C)     | (125°C)       | (165°C)       |
| 12.8.12 | 50.38           | 38.7        | 38.6          |              |
|        |                 | (25°C)     | (120°C)       |              |
| 14.4.14 | 51.63           | 33.3        | 34.6          | 36.9          |
|        |                 | (25°C)     | (125°C)       | (200°C)       |
| 16.3.16 | 53.51           | 32.6        | 34.6          | 36.8          |
|        |                 | (25°C)     | (120°C)       | (200°C)       |
| 16.4.16 | 56.22           | 34.6        | 37.6          | 37.6          |
|        |                 | (25°C)     | (100°C)       | (200°C)       |
| 16.5.16 | 56.38           | 31.9        | 36.1          | 39.5          |
|        |                 | (25°C)     | (105°C)       | (185°C)       |
| 16.6.16 | 58.23           | 39.2        | –             |              |
|        |                 | (25°C)     | (100°C)       |              |

*aDistance between two methyl carbons of the lateral chains in the all-trans conformation.

![Figure 5](https://example.com/image5.png)

**Figure 5.** 100 MHz $^1$H-$^{13}$C CP-MAS spectra of sample 16.6.16 (a) and 16.5.16 (b) recorded at increasing temperatures and MAS frequency of 5 kHz. Peaks marked with an asterisk are spinning sidebands.
the magnetisation was propagated to the respective spin systems by means of a 100 ms DIPSI-2 isotropic mixing scheme. These preliminary experiments allowed a clear separation of the $^1$H signals stemming from the inner C5 and outer C16 alkyl chains. A $^1$H-$^{13}$C HSQC spectrum was then acquired to extract the corresponding $^{13}$C resonances, which were finally compared to those of the solid-state spectra (see SI for details).

We also studied the aggregation behaviour of a representative sample, 14.6.14, in methanol and dichloromethane by means of DOSY spectroscopy, using stimulated echoes with bipolar gradient pulse pairs and a longitudinal eddy current delay (STE LED-BPP). The results are reported in Table 3.

The analysis of the apparent diffusion coefficients was complicated by the fact that signal broadening was observed upon increasing the concentration of 14.6.14, in both methanol and dichloromethane. Interestingly, the self-diffusion coefficients of the residual protonated solvent lie close to the values found for CH$_3$OH and CH$_2$Cl$_2$ at the same temperature ($2.36 \times 10^{-9}$ and $3.0 \times 10^{-9}$ m$^2$/s, respectively. [69,70] This evidence suggests that the microscopic solvent viscosity is preserved in the different samples, and that the signal broadening likely results from sample inhomogeneity due to micro-segregation of 14.6.14.

### Comparison to imidazolium salts

A rich mesomorphism is exhibited by viologen salts, which has been investigated by both us and others (see the Introduction for references). Precursors salts, bromides and iodides usually display crystal phases stable up to the decomposition temperature, [3,12,44,45] while metathesis with the flexible and conformationally disordered bistriflimide ion (Tf$_2$N$^-$) is responsible for the appearance of smectic phases after destabilisation of the crystal phase. This behaviour is the converse to that observed for imidazolium salts, while bromides and iodides, as well as BF$_4^-$ and PF$_6^-$, usually show smectic mesophases (indeed for sufficiently long alkyl chains, [71,72]) their bistriflimide analogues behave as ILS and the smectic phase is suppressed in favour of the isotropic phase.

For example, we cite here the case of 1,1′-diheptyl and 1,1′dioctylviologen dibromides (HV and OV, respectively, in Figure 6) studied in Ref. [73] These compounds remain in the crystalline phase up to 277 and 275°C, respectively, above which they decompose; therefore no liquid or liquid crystal phase is observed for them. In contrast, replacing the anion with Tf$_2$N$^-$ results in the appearance of a mesophase between 41

![Figure 6](https://example.com/figure6.png)
and 112°C for the former salt and between 37 and 136°C for the latter. Above the clearing point, the systems exhibit an isotropic liquid phase stable up to the decomposition temperature of 360 and 364°C for the heptyl and octyl derivative, respectively. These results should be paired with those of common imidazolium salts (e.g. 1-dodecyl- and 1-tetradecyl-3-methylimidazolium (C12 and C14, respectively, in Figure 6)) studied in Ref. [74] Bromide salts show a liquid crystal phase in the range 33–115 and 46–176°C, respectively. By replacing the Br– anion with Tf2N–, the liquid crystal phase is removed and the crystal directly melts into an isotropic phase at 17 and 35°C, respectively.

The thermal stability range of these systems discussed above is also graphically shown in Figure 6. These results are consistent with the well-known behaviour of the Tf2N– anion, which usually lowers the melting point of ILs because of the disordered structure in the solid state. [75] However, when LC phases are involved, the bistriflimide anion can either uncover a LC phase by destabilising the crystal or extend the thermal range of the isotropic liquid, thus removing the LC phase, depending on the counter-cation. It seems, therefore, that the pairing of spherical and rigid anions with cations lacking a real rigid and anisotropic core – such as the imidazolium cation – is the correct combination with the appropriate amount of conformational freedom in order to exhibit mesomorphism, while increasing the overall degree of conformational freedom of the system by replacing the anions with Tf2N– leads to a stable isotropic phase. In contrast, pairing of spherical and rigid anions with the viologen moiety (also rigid and highly symmetric) favours crystal phases; these can be destabilised in favour of a less ordered mesophase by replacement of the anions with Tf2N–. It appears, therefore, that the total degree of conformational freedom can be modulated independently in the cations and anions in order to meet the requirements for a smectic phase, as schematically illustrated in Figure 7.

Besides this effect of cation–anion combination, in this study we explored the effect of modulating the conformational freedom of the tethered bis(viologen) cationic core. Increased flexibility of the cationic core is obtained by dimerisation; this, on the one hand doubles the size and charge, but, on the other hand, makes the whole cationic moiety more flexible. That is, the amount of conformational freedom of the ionic layer is increased, in the dimers, compared with the monomers. This increased flexibility accounts for the appearance of a fluid smectic A phase in the dimers compared to the monomer, where only an ordered smectic X phase was observed. [12,45] Not surprisingly, if the spacer of the dimers is sufficiently long, the two tethered viologen moieties behave again as independent units and multiple layers (hydrophobic and ionic) are present in the smectic phase. Such a phase, however, is again an ordered SmX phase since the ionic layers do not possess the required degree of freedom to allow for a smectic A phase.

**Experimental section**

Variable-temperature 1H–13C CP-MAS spectra (100.7 MHz 13C, 1 ms contact time, 5 kHz MAS) were run in the interval 25–80°C on a Varian 400 spectrometer equipped with a 4 mm MAS probe.
Solution-state NMR spectra were collected at 25°C on a Bruker AVANCE III 500 (500.13 MHz 1H) equipped with a 5 mm z-gradient BBI probe. For diffusion-ordered spectroscopy, 32 transient spectra were collected by means of a standard STE-LED-BPP pulse scheme (Δ = 100 ms, δ = 1.5 ms). Data inversion (fitting and ILT) was performed with Bruker Dynamics Center 2.2.3 software.

Polarised optical microscopy: the textures of the samples were studied with a Leica DM4000 M polarised light microscope. The samples were placed between a glass slide and a cover slip. A Mettler FP82HT hot stage was used to control the temperature. The samples were heated at 10°C/min beyond the melting temperature determined by DSC experiments, and subsequently cooled at 10°C/min to room temperature. The photomicrographs were taken between crossed-polarisers with a Leica DFC280 digital camera.

DSC: all measurements were carried out with a TA Instruments model 2920 calorimeter operating under N2 atmosphere. Samples weighing about 5 mg enclosed in aluminium pans were used throughout the experiments. Indium of high purity was used for calibrating the DSC temperature and enthalpy scales. Four ramps were included in the temperature programme: one heating from room temperature to 160°C at 10°C/min, followed by a cooling step to room temperature at 10°C/min and by another analogous heating/cooling cycle. The repetition of two similar heating/cooling ramps was done to assess the repeatability of the phase transitions.

The XRD patterns were recorded in the diffraction angular range 2–60° 2θ by a Philips X’Pert PRO diffractometer, working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (CuKα radiation). When gathering temperature-dependent XRD spectra, an Anton Paar TTK450 temperature control cell was used and the diffraction angular range was limited to 2–30° 2θ.

Conclusions
We present the characterisation of a series of viologen dimers with bistriflimide as counter-ions; the systems exhibited a rich mesomorphism. We analysed the dependence of mesomorphism on the length of both spacer and lateral chains. Short lateral chains resulted in the suppression of any LC phases; for intermediate lateral chains we observed only an ordered smectic phase; for lateral chains longer than C12 a fluid smectic A phase was found when the length of the spacer was below six carbon atoms, otherwise only an ordered smectic phase was observed.

Comparison of the phase behaviour of alkyl-tethered viologens cations to that of similarly tethered imidazolium cations when paired with two different kinds of anions (rigid and spherical anions, such as halides, and flexible and disordered bistriflimide) revealed interesting insights. A qualitative rationalisation is presented of the variation in behaviour based on the total amount of conformational degree of freedom introduced in the ionic layers of the smectic phases.

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Disclosure statement
No potential conflict of interest was reported by the authors.

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