

Viologen-based ionic liquid crystals: induction of a smectic A phase by dimerisation†

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The stability of thermotropic ionic liquid crystals is essentially due to micro-phase segregation between the ionic heads and the long alkyl chains. Here we show, using newly synthesized viologen dimers, that the structure of the central core is another key parameter to play with in order to tune the mesomorphic behaviour.

Ionic liquid crystals (ILCs) have recently attracted the attention of the chemistry and materials science communities as systems with the potential to combine together the many applications and features of liquid crystals (LCs) and ionic liquids (ILs); see ref. 1 for a comprehensive review and ref. 2 and 3 for more recent updates on the topic. ILCs are usually obtained from organic salts of quaternized nitrogen, the same class of compounds forming ILs, after a sufficient lengthening of the alkyl chain(s).^{4,5} In a recent paper, the role of the chains in driving the formation of imidazolium ILCs has been highlighted by MD simulations, and the emergence of a smectic phase for chains longer than C12 was nicely reproduced.⁶ Since the driving force is believed to be the micro-segregation between the hydrophobic chains and the ionic layers, a smectic phase (for calamitic systems) is almost invariably obtained,⁷ although rare cases of ionic nematic phases have been reported.^{8–10}

The modulation of the thermal range of stability and type of the ILC phase is very important for the optimization of their performance, together with the tuning of properties like viscosity and conductivity. ILCs have been successfully tested recently for applications in the field of solar cells,¹¹ membranes for water desalination,¹² battery materials¹³ and electrochemical sensors.^{14,15}

The conductive properties of the ionic mesophase have been found to have a significant impact on the performance of the ILC-based devices compared to the analogous devices based on isotropic ILs. Recent MD simulations have highlighted the role played by pore-like defects in enhancing the diffusion, and therefore the conductivity, along the director in smectic ILCs.^{16,17} Nevertheless, our understanding of the properties of ILCs is still poor.

The design of novel ILCs with improved properties (notably lower viscosity and lower melting temperature) has, in most cases, regarded the exploration of the type of cationic head, the length and type of chain and the type of counter-anion but often remaining within the paradigm of an amphiphilic organic cation, with an ionic head and an alkyl chain, paired with a roughly spherical inorganic anion. Notable digressions with respect to this route have been pursued by Ringstrand *et al.*¹⁰ and Laschat and co-workers¹⁸ who focussed on different kinds of “mesogenic” anions.

In this work, starting from our previous investigations,^{19–21} we present a series of symmetric viologen dimers **n.m.n**, where *n* and *m* indicate the number of carbon atoms in the lateral and middle (spacer) alkyl chains, respectively (see Fig. 1). We found that they exhibit rich polymorphism including the ionic smectic A phase and an ordered smectic phase, SmX, which we believe to be characteristics of ionic liquid crystals with a poly-cationic core. Moreover, the viologen core is a key component that imparts solvatochromic and redox properties in view of possible applications of these materials.²²

Synthetic procedures are described in the ESI.† Two routes are available. (i) First the central core is obtained by reacting an

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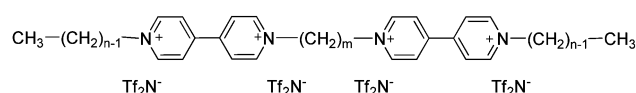


Fig. 1 Structure of the tetracationic viologen dimers investigated, **n.m.n** = *n*BP*m*BP*n*(Tf₂N)₄, where BP is the bipyridinium core. For *n*, *m* pairs see Table 1. Tf₂N[−] is (CF₃SO₂)₂N[−] (bistriflimide). Dicationic monomers, **n.m**, contain a single bipyridinium unit.

Table 1 Thermodynamic properties of the samples investigated. Transition temperatures $T_n/^\circ\text{C}$ ($\Delta H/\text{kJ mol}^{-1}$). H: 1st heating; C: 1st cooling

n.m.n		H T_1 (ΔH_1)		H T_2 (ΔH_2)		H T_3 (ΔH_3)	
		C T_1 (ΔH_1)		C T_2 (ΔH_2)		C T_3 (ΔH_3)	
14.2	Cr	71 (6.7)	Iso				
		61 (6.5)					
12.4.12	Cr	88 (23.6)	SmX	154 (17.7)	SmA	183 (7.3)	Iso
		24 (7.1)		148 (16.8)		174 (5.8)	
14.4.14	Cr	84 (23.2)	SmX	153 (20.0)	SmA	229 (10.0)	Iso
		19 (32.0)		143 (16.8)		209 (2.6)	
16.4.16	Cr	79 (20.6)	SmX	152 (18.2)	SmA	264 (6.8)	Iso
		19 (37.8)		143 (15.9)		248 (3.9)	
14.14	Cr	42 (49.1)	SmX	218 (15.2)	Iso		
		33 (30.3)		214 (13.2)			

excess of α,ω -dihaloalkane with bipyridine; the intermediate is then dialkylated with the long-chain haloalkane. (ii) First a monoalkylated bipyridine is synthesised, which is then reacted with the α,ω -dihaloalkane to obtain the monomer; a second reaction with the monoalkylated bipyridine affords the final product. The latter route allows the synthesis of non-symmetric viologens. In Table 1 we report the thermodynamic data for the viologen dimers with a spacer of four carbons plus two monomers useful for a direct comparison. In particular, **14.2** is formally the monomeric unit of the dimer **14.4.14**, while **14.14** is the analogous symmetric monomer with the same lateral chain. The histograms of the thermal range of stability of the phases are shown in Fig. 2. As noted in ref. 20 strongly non-symmetric monomeric viologen salts of bistriflimide do not exhibit any mesophase, rather they behave as ILs. This is the behaviour observed here for **14.2**; see the typical crystal textures in the ESI† (Fig. S27). In contrast, when the number of carbon atoms increased, an ordered smectic phase, SmX, was found that was not completely identified: POM, XRD²⁰ and solid-state NMR²¹ studies ruled out a smectic A phase and suggested an ordered, layered mesophase. This behaviour has been confirmed here for the sample **14.14** whose optical textures are of mosaic type and striated fan-shaped type (see ESI,† Fig. S24),²³ thus suggesting an ordered smectic phase.

We now turn our attention to the dimeric viologen systems, particularly the **14.4.14** salt which can be directly compared with either its formal monomeric unit, **14.2** or the symmetric monomer with the same lateral alkyl chain length, **14.14**.

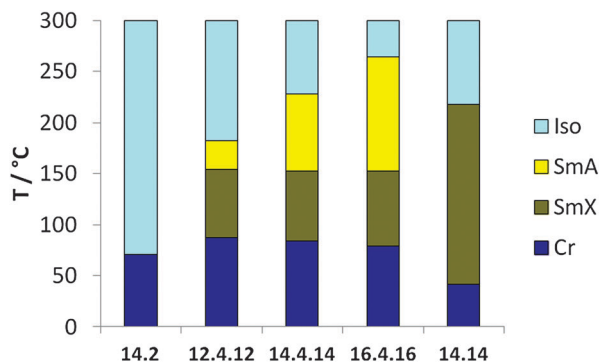


Fig. 2 Thermal range of stability of the systems investigated.

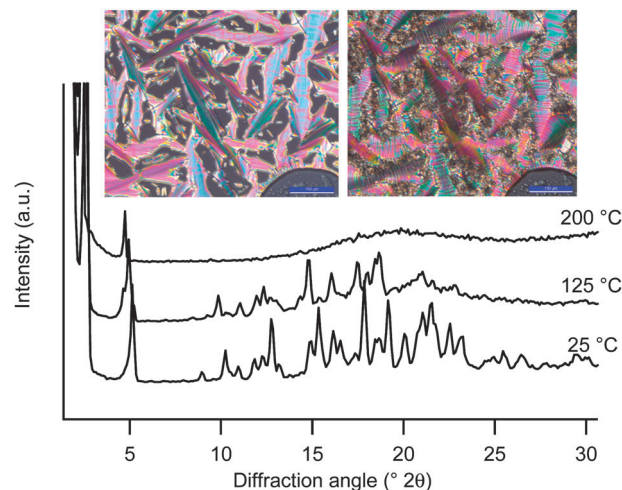


Fig. 3 XRD traces of **14.4.14** at three different temperatures corresponding to the Cr, SmA and SmX phases. Inset: (left) fan-shaped textures of the SmA phase at 150 °C; (right) striated fan-shaped textures of the ordered SmX phase at 120 °C. The blue bar is 100 μm .

In Fig. 3 we show the XRD profiles at various temperatures corresponding to the three phases, except for the liquid phase which only shows a broad halo around $2\theta \sim 20^\circ$. These traces indicate a crystal phase at room temperature; an ordered mesophase at 125 °C since, together with a broad halo around $2\theta \sim 20^\circ$, we have several strong reflections indicating the coexistence of short-range order;²⁴ a SmA phase at 200 °C since, apart from a first-order peak and a weak second-order one, there is only the broad halo indicating the lack of the short-range order. The small angle region of the first-order peak due to the layered structure is clearly visible in Fig. S21 in the ESI.† The layer periodicity is found to be 33.3 Å, 34.6 Å and 37.6 Å, which increases as the system goes from the crystal phase into the SmX phase and finally into the high temperature SmA phase. The thickness is much smaller than the full elongation of the cation: for **14.4.14** the distance between the two methyl carbons in the all-trans arrangement is 51.6 Å (semiempirical PM3 calculations). Therefore, a significant degree of interdigitation occurs in all the three phases.

The assignment of the SmA phase is confirmed by the fan-shaped textures observed on cooling from the melt (see Fig. 3) and by the fluidity of the sample under the microscope, while no flow was observed upon lowering the temperature below the SmA–SmX transition; moreover, the textures, once the sample cooled into the SmX phase, changed into a striated fan-shaped type, as observed for **14.14**, which is typical of ordered smectic phases, with a higher degree of order than a SmB.²³ This would also explain the absence, in the XRD traces, of the typical sharp peak around $2\theta \sim 20^\circ$ expected in the hexagonal smectic B phase.

The XRD traces and POM images of **12.4.12** are shown in the ESI† (Fig. S23 and S25) and, again, clearly indicate a SmA phase at higher temperature and an ordered smectic phase at lower temperatures. Similarly to the former compound, the layer thickness is significantly shorter than the molecular length. An analogous behaviour is found for **16.4.16**.

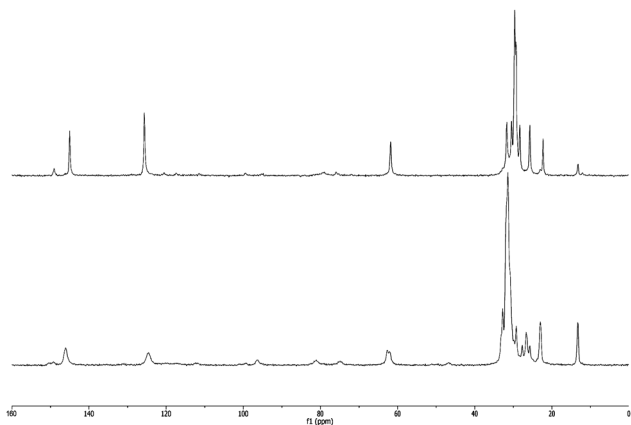


Fig. 4 SSNMR ^1H – ^{13}C CP-MAS spectra of **14.14** (100 MHz).

To get further insights into the structure of the SmX phase we acquired solid-state ^{13}C NMR spectra (SSNMR) of **14.14**, whose Cr–SmX transition occurs at sufficiently low temperature, as shown in Fig. 4. The spectra obtained just before and after the Cr–SmX transition (see full data in the ESI,[†] Fig. S5 and S6) show the same features reported in ref. 21 for the room temperature crystal and the SmX phase of **8.8** and **7.10**, respectively. In the crystal phase we observe broad signals in the aromatic region and an almost unnoticeable signal of the CF_3 carbon of the anion. In the high temperature SmX phase the aromatic resonances are much sharper, indicating an enhanced mobility, although anisotropic, and the two central lines of the 1:3:3:1 quartet of CF_3 at 118 ppm are now resolved, although weak; the increased mobility is also confirmed by the reduction of the intensity of the spinning side bands due to partial averaging of the chemical shift anisotropy. Moreover, the intensity of the resonance of the methyl group at 13 ppm is strongly reduced, after the transition, suggesting an almost complete isotropic melting of the alkyl region. In fact the liquid-like phase of the alkyl region averages the C–H dipolar coupling responsible for the cross-polarisation of the methyl resonances. Despite this, the XRD traces of **14.14** (see Fig. S22 in the ESI[†]) clearly indicate that the smectic phase is not a SmA phase since short-range order is present, together with the broad halo, in perfect agreement with the behaviour of the monomeric viologens studied in ref. 20; since the hydrophobic layers of the lateral alkyl chains are highly disordered, such order is likely due to a partial structure of the ionic layers.

The overall picture that emerges from these observations is that of rich mesomorphism exhibited by bistriflimide viologen salts, which is summarised in the schematic representation of Fig. 5.

Besides the low temperature crystal phase and the high temperature isotropic phase, two smectic phases have been identified. For dimers, a SmA phase exists whose thermal range of stability grows into the isotropic phase region upon increasing the length of the lateral chains, as usually observed for ILCs. However, the lateral alkyl chains alone are not sufficient to stabilise a SmA phase: comparing the dimer **14.4.14** with the monomer **14.14** we note that the central poly-cationic and

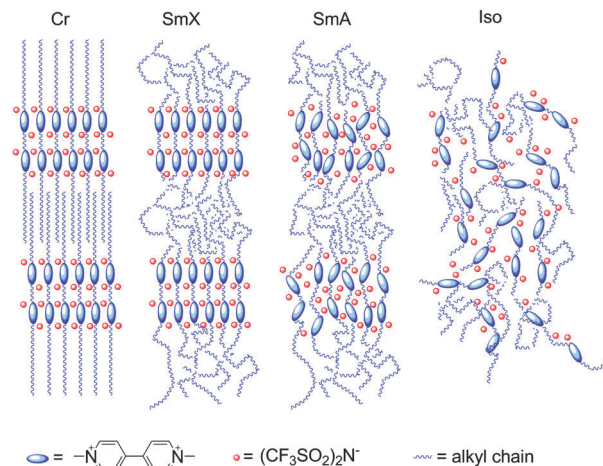


Fig. 5 Schematic representation of the four phases formed by viologen bistriflimide salts. The arrangement of the crystal phase and the ionic layer of the SmX phase is purely qualitative.

flexible core is necessary to induce a fluid SmA phase. An ordered smectic phase is observed for the dimer **14.4.14** at lower temperature, whose thermal range of stability has a very little dependence on the length of the alkyl chains. The long chain symmetric monomer **14.14** only exhibits the ordered smectic phase in a similar temperature range. This latter phase, in turn, is completely destabilized in favour of the isotropic liquid, if one of the chains is replaced by a short ethyl group, as in **14.2**.

The evidence we have collected indicates that the SmX phase is characterized by molten hydrophobic layers alternating with ionic layers which still retain a relatively large degree of order. The packing of the ionic layers, which have, in poly-cationic systems, a considerable thickness, is not a simple hexagonal packing as might be expected in a SmB phase, which is the ordered smectic phase, usually found in non-ionic LCs; rather a different lattice, depending on the type of quaternized nitrogen salt, will be formed giving rise to a complex XRD pattern. Striated fan-shaped type textures support an ordered smectic phase. Remarkably, a similar sequence of high temperature SmA and low temperature ordered SmX phases was very recently reported for imidazolium trimers,²⁴ suggesting that this might be a general behaviour of poly-cationic and symmetric ILCs.

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