In and out – new ionic mesogens based on a cyanoborate building block and lipophilic or hydrophilic counter ions

Matthias Lehmann, Pascal Weinberger, Maik Finze, Guinevere A. Giffin, Mario Weller, Stephanie Bachmann and Ann-Christin Pöppler

Abstract. New ionic mesogens have been prepared based on a cyanoborate head group, which is tethered to a lipophilic periphery via a short flexible spacer. As counter ions, either tetra-n-butyl ammonium cations or sodium and potassium cations stabilized by 18-crown-6 have been used. Although all compounds realise SmA enantiotropic mesomorphism, X-ray diffraction, modelling and solid-state NMR uncover distinct self-assembly of the LC materials in double layers. While the ammonium ions are located in-between the borate anions and are in contact with spacers and aromatic units, the crown ethers with the coordinated alkali metal cations are completely nanosegregated between two borate anion layers. Homogenous and homotropic alignment has been achieved. Electrical impedance studies confirm two to three orders of magnitude higher conductivity of the correctly aligned samples in the single-ion conductor. Values of ca. $10^4 \text{Sm}^{-1}$ in the SmA phase at 85 °C and $10^4 \text{Sm}^{-1}$ at 40 °C have been obtained.

Introduction

Ionic liquid crystals (ILCs) are currently the focus of intense investigation owing to their potential application as anisotropic electrolytes. They can be polymerized and achieve ionic conductivities of $10^{-2}$-$10^{-3} \text{Sm}^{-1}$.[1] These conductivities vary with temperature, counter ion and the alignment between the electrodes. Anisotropic ion conductivities exceeding $10^{-2} \text{Sm}^{-1}$ (e.g., in systems with mobile fluorohydrogenate anions and at temperatures below 60°C) were obtained, [1-3] showing the potential of ILCs as future solid state ionic conductors. The mesogens frequently consist of a charged unit such as ammonium, imidazolium and pyridinium cations linked to non-polar organic scaffolds. Together with anionic counter ions, these amphiiphiles generate the ILCs. Amphiphiles with anionic groups in ILCs are known and generally contain nucleophilic anionic groups such as sulfonates and carboxylates.[1,4] Weakly coordinating borate anions have been studied as ionic liquids and anionic counter ions of ILCs,[1,5,6] to date they have not been explored as part of the amphiphilic block of the ILCs. Tetraphenylborate anions, non-chiral and chiral α-substituted α-hydroxyethanoato borates, among others, have been investigated as ionic liquids or anions for the study of ion mobilities in non-ionic liquid crystal hosts.[7,8] Furthermore, they were used as anion excluders in ion transporting liquid crystal membranes[9] and in liquid-crystalline anions as fast ion conducting tunnels for application in lithium ion batteries.[10] LC Carba-closododecaborates have been more deeply studied as typical rod-shaped mesogens forming nematic and layered SmA mesophases.[11]

Cyanoborate anions are chemically and electrochemically very stable and typically, their salts are very thermally robust.[12] In particular,
cyanoborate ionic liquids have been the focus of materials research, e.g. for gas separation, extraction processes, polymer chemistry, and electrochemical devices.\textsuperscript{12,13} In addition to the high stability, these ionic liquids (ILs) have both low melting points and viscosity. These properties are, at least in part, due to the weak interaction between cyanoborate anions and organic cations. In contrast, cyanoborate anions coordinate to metal cations via the N atoms of the cyano groups. Due to the advantageous properties of cyanoborate ILs, they have been tested in many practical applications,\textsuperscript{12,13} especially, as electrolyte components in electrochemical devices such as dye-sensitized solar cells (DSSCs, Grätzel cells), supercapacitors, and lithium batteries.\textsuperscript{12,14} The chemistry of the tetracyanoborate anion \([B(CN)]^\text{-} 2\) the prototype cyanoborate anion, has been studied in detail. In addition, mixed-substituted cyanoborate anions, e.g. \([BF_4]_n(CN)_{12-n}^\text{-} \quad (n = 1–3,)^{17–20} \quad [BH_4]_n(CN)_{12-n}^\text{-} \quad (n = 1–3,)^{20,21} \quad [R^\text{I} BF_4]_n(CN)_{12-n}^\text{-} \quad (n = 0–2),^{22} \quad \text{and} \quad [B(OR)]_n(CN)_{12-n}^\text{-} \quad (R = CH_3, C_2H_5)_{23} \) have attracted broad attention.

**Figure 1.** Structure of the cyanoborate ionic mesogens (ILCs).

The stability of cyanoborate anions is reflected by the tricyanoborate dianion \([B(CN)]_3^\text{2-}\),\textsuperscript{24} which is obtained, e.g., by deprotonation of the \([BH(CN)]_3^\text{-} \) anion (MHB).\textsuperscript{25} \([B(CN)]_3^\text{2-}\) reacts as a boron-centered nucleophile and thus, provides easy access to many tricyanoborate anions with the general formula \([BR(CN)]_3^\text{-}\).\textsuperscript{24–27} The reaction with \(CO_2\) yields the carboxylate borate anion \([B(CO_2)]_3^\text{(CN)}_4^\text{-}\) that is reversibly protonated to \([B(CO_2H)]_3^\text{(CN)}_4^\text{-}\).\textsuperscript{25} Here, we explore this carboxy-functionalized cyanoborate anion as a non-coordinating and immobile anion in the ILCs. In contrast to many ionic liquid crystals, these anions are bound to the organic non-polar unit of the amphiphile in liquid crystalline films with selected weakly-coordinating counter cations \(Na^+ \subset \text{18-crown-6 (1a), K}^+ \subset \text{18-crown-6 (1b) and [nBuN]^+ (2)} \) (Figure 1).

**Results and Discussion**

**Synthesis**

Conventional ester synthesis has been applied as described in the ESI. The final coupling has been performed between the terminal \(OH\)-group of the spacer and the carboxycyanoborate ammonium and potassium salts.\textsuperscript{12} Although ILC 2 has been obtained in 88 % isolated yield, the potassium salt did not react. Only the addition of stoichiometric amounts of 18-crown-6 furnished an ionic liquid crystal as a mixture of sodium and potassium salts after column chromatography. Subsequent cation exchange via the corresponding sulfates resulted in the sodium ILC 1a and the potassium ILC 1b in 75 % and 88 % yield, respectively. The identity and purity of the compounds were confirmed by \(^1\)H, \(^{13}\)C, \(^{11}\)B NMR and HRMS mass spectrometry (see ESI).

**Thermotropic Properties – POM and DSC**

**Figure 2.** DSC and POM results. A-C: DSC cycles of ILCs 2 (A), 1a (B) and 1b (C). The DSC scanning rate was 10 °/min. D-F: Representative textures of the SmA and Cr1 phases. (D) Bâtonnets at the transition to the SmA phase of ILC 2 at 46 °. (E) After shearing at 40 °C, the thin film is homeotropically aligned. F-G: ILC 2 in a liquid crystal cell (INSTEC 9µm) without (F) and with \(\lambda/2\) compensator plate (G). Left: homogenous aligned focal conic textures at 25 °C; Right: textures at -2 °C. SmA = smectic A phase, Crn (n= 1–3) = crystalline phases, I isotropic liquid.

**Table 1.** DSC results for the ILCs 1 and 2 (rate 10 K / min)

<table>
<thead>
<tr>
<th>compound</th>
<th>onset transition temperatures and enthalpies (2.heating) °C / kJmol(^{-1})</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>Cr1 6.8/5.1 Cr2 20.5/30.7 SmA 37.9/-5.7 Cr3 50.0/4.8 SmA 84.6/1.9 l</td>
</tr>
<tr>
<td>1b</td>
<td>Cr1 0.6/1.0 Cr2 12.4/26.3 SmA 25.1/-20.9 Cr3 65.3/20.2 SmA 82.0/-1 l</td>
</tr>
<tr>
<td>2</td>
<td>Cr1 3.5/13.0 Cr2 8.8/32.9 SmA 42.7/1.1 l</td>
</tr>
</tbody>
</table>

SmA = smectic A phase, Crn (n= 1–3) = crystalline phases, I isotropic liquid.

* transition only observed with POM. |
Thermotropic properties were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray scattering (XRS). POM and DSC revealed broad range LC behaviour for 1 and 2 (table 1). The LC phases show a very low viscosity, similar to an isotropic liquid. Bâtonnet textures in the transition from the isotropic to the mesophase, homeotropic- and homogenous-aligned focal conic domains are observed, which are typical for smectic phases (Figure 2D,F). Conoscopy on thick films with homeotropically-aligned materials confirm the uniaxial, optical positive nature of the LC phases (see Figure S13ESI). Homeotropic textures generate upon shearing thin films (Figure 2E). The textures in the SmA and the CrI phase are almost identical and differ only in the birefringence (Figure 2F).

Insertion of the λ/2 compensation plate reveals the different orientation of the homogenously-aligned domains in the textures which also remains unchanged upon the SmA-CrI transition. These observations suggest to a structural relationship of both phases. The DSC clearing transitions show very small clearing enthalpies of around 1 kJ/mol indicating an LC phase of low order (Figure 2A-C). All these observations are in complete agreement with typical SmA phases, in which the mesogens stack orthogonal to the layers. Thermal cycling revealed that upon cooling the SmA phases of all compounds, the ILCs crystallise below 20 °C (Cr0, CrI) and melt reversibly to the lamellar phases upon heating. Again, this indicates a structural relationship. However, the compounds 1a and 1b with the more hydrophilic counter ions exhibit a subsequent cold crystallisation of the SmA phase to form crystals (CrI). ILC 1a exhibits a new melting to the SmA phase. For ILC 1b, the SmA phase transforms to a CrI phase, which melts over a broad temperature range (maximum at 72 °C). The SmA-I and I-SmA transitions for compound 1b are invisible by DSC. It can only be observed upon cooling by POM at 82.0 °C upon heating and 79.3 °C at cooling. The SmA phase of ILC 1b is rather instable and crystallises upon annealing at room temperature, while 1a maintains the lamellar structure and shows only cold crystallisation when heated above 30 °C.

**Thermotropic Properties – XRS**

X-ray scattering on extruded fibres was performed to confirm these results. In the smectic A phase, the material can be aligned with the preferential layer direction along the fibres. However, a good alignment is challenged owing to the low viscosity of the SmA phase and in case of compounds 1 to the relative fast crystallisation of this phase at room temperature. The equidistant 001 and 002 reflections and a halo corresponding to the average distance of liquid-like hydrocarbons confirm the layer structure and LC nature of the phase (Figure 3A-C). The c-parameters measured at 25 °C for the ILC compounds are 45.0 Å (ILC 1a), 44.8 Å (ILC 1b) and 44.0 Å (ILC 2). These distances are larger than the total length of a single amphiphilic anion determined from the molecular model (33 Å, see Figure 5B) but much smaller than that of two extended mesogens (minimum 76 Å including the cations). This can be only rationalised when the amphiphiles interdigitate with the non-polar part to form interdigitated bilayer phases (SmA2, c.p. Figure S5C,D).[1-2] The low temperature phases were studied at -10 °C. The LC and CrI phases are assumed to be structurally related since they transform reversibly to the SmA phases. The WAXS pattern of the CrI phase of ILC 2 exhibits a set of equidistant signals and only a more defined and intense signal at the halo. This is rather unusual for a crystalline phase and indicates that there is no perfect positional long-range order of molecules as would be expected in a well-defined crystal. The signals can be attributed to a lamellar phase which increases in the layer spacing by 16.3 Å to 60.3 Å, when compared with the layer spacing of the SmA phase. The change in layer-spacing is approximately the length of a dodecyl chain and thus, this indicates that the aliphatic chains, which are interdigitated in the fluid SmA phase, separate and pack more efficiently. Electron density reconstruction (see Figure S19) is in complete agreement with this structural picture.

![Figure 3. XRS results of SmA and CrI phases. A, B: WAXS pattern of partially-aligned SmA phases at 25 °C of ILC 2 (A) and ILC 1b (B). C: Integrated intensity of the WAXS pattern (A,B). D: Integrated intensities of the WAXS patterns of ILC 1 and 2 in the CrI phases. E, F: WAXS patterns of aligned CrI phases. Inset in F exhibits the XRS pattern of the CrI phase.](https://orcid.org/0000-0002-2903-7101 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0)
Å (1a) and 55.7 Å (1b) and thus approach in size the layer spacing of ILC 2. The formation of columns can be rationalised if the volume ratio between the nanosegregating hydrophobic and the polar sections (aliphatic and ionic building blocks) increases in favour of the ionic nanospace.[28] The rather low positional order again supports a structural relationship between the fluid SmA and the Cr₁ phase. Heating the ILC 1a,b to room temperature reversibly generates first the SmA phase and subsequently a Cr₃ phase, which exhibits reflections over the whole angular range indicative of a positional long range order of the molecules (Figure 3F inset).

**Solid-State NMR Spectroscopy**

The distinct self-assembly of ILCs 1 and ILC 2 prompted us to study the origin by solid-state NMR spectroscopy. While the relatively high mobility of the SmA phases complicates analysis in the solid state (reduced signal intensity), the structural relationship between the Cr₁ and SmA phases established through X-ray analysis allows to draw conclusions about the molecular arrangement in the ILC phases based on an analysis of the corresponding Cr₁ phases. Based on the DSC results, careful temperature control during samples preparation as well as during the measurements is necessary to ensure the presence of the desired soft crystal phase Cr₁. Sample temperatures of 253 and 260 K for 1a and 1b or 273 K for 2 were chosen. Frictional heating due to 10 and 8 kHz MAS is included in these estimated sample temperatures. A series of 1D ¹H, ¹³B and ¹³C NMR experiments and 2D ¹H-¹³C FSLG HETCOR experiments with different contact times between 50 μs and 4000 μs was recorded to probe differences in the packing arrangement including differences in mobility, degree of order and key intermolecular interactions (Figures S20-S21). Signal assignment of the solid-state NMR data was done based on 1D and 2D ¹H-¹³C FSLG HETCOR data with a short contact time of 50 μs aided by the assignment from NMR spectroscopy in solution (Chapter S3).

For ILCs 1a and 1b comparison of the ¹³C MAS NMR spectra obtained by direct excitation (DE) and by cross-polarization (CP) shows narrower lines and thus a higher degree of mobility for the crown ether signals in 1a, while the aliphatic chains appear to be more rigid. This agrees with the ¹H NMR data. For 1b, a more pronounced mobility is observed for the aliphatic chains. Compared to 1a, the crown ether units are more rigid. This is also reflected by the presence of multiple signal areas for C₆, C₆’ and the crown ether in 1b. Consequently, the signal overlap in this signal region hampers a straightforward interpretation in the case of 1b. Cross peaks in the 2D data could be either the result of “real” contacts of crown ether molecules with surrounding molecular entities or a result of signals overlap with carbons C₆ and C₆’. Therefore, and because the presence of an additional metastable crystalline phase Cr₁ (Figures S22-S23), the subsequent spectral analysis will focus on ILCs 1a and 2.

For ILC 1a, already at 500 μs and 1000 μs contact time multiple through-space contacts can be observed in the 2D ¹H-¹³C FSLG HETCOR data (Figure 4, Figure S21). While the aromatic, carbonyl and spacer carbons show various cross peaks to other moieties, the crown ether lacks such close intermolecular contacts (Figure 4, top). At higher contact times of 2000 μs, a weak cross peak with the aliphatic chains at 1.7 ppm is observed, which cannot be clearly assigned to the signal of the crown ether but rather to C₆’.

**Figure 4.** 2D ¹H-¹³C FSLG HETCOR spectra of 1a and 2 recorded at 14.1 and 9.4 T. The spectrum of 1a was obtained at 250 K with 10 kHz MAS, 1000 μs contact time, 2 s recycle delay and 100 transients co-added for each of the 100 t₁ FIDs. For processing, forward linear prediction of 100 additional t₁ FIDs was used. For 2, the measurement was performed at 273 K with 1000 μs contact time, 1.5 s recycle delay and 96 transients co-added for each of the 200 t₁ FIDs. Counter ion signals are highlighted by red boxes.
No other contacts can be found for the crown ether carbon atoms. This points to an assembly, in which the crown ethers are expelled from the ionic layer and form a separate interlayer. While there are fewer contacts visible for the aromatic and carbonyl carbon atoms in ILC 2, the carbons of the ammonium cations, especially the signals at 19.7 and 59.0 ppm, show cross peaks to aromatic, aliphatic and spacer protons at a contact time of 1000 μs (red boxes in Figure 4, ILC 2). Thus, they are located in close proximity to each other.

**Electron Density Reconstruction**

The lipophilic cation "In" and hydrophilic cation "Out" situation is finally also reflected in the intensity profile of the SmA diffraction pattern. When carefully integrating the 001 and 002 reflections for ILC 1a, 1b and 2 it becomes evident that the ratios $I_{001} : I_{002}$ for both crown ether materials 1a, 1b are large with values of 32 and 34, while for ILC 2 this ratio is only 2 (Figure 5). This affects the electron density (ED) distribution in the phases. A smaller ratio indicates a more rapid and larger change of electron density in the structure. This can be rationalised by a partial interdigitation of the hydrocarbons including the chains and the gallic acid unit but excluding the spacer area in ILC 2 which results in a dense hydrocarbon section in the middle of the double layer while the ionic periphery is less densely packed. The density of the hydrocarbon section should not exceed the density of crystalline polyethylene which is 1.005 g cm$^{-3}$.[29] The difference in ED of the two sections reaches a maximum value of 0.14 eÅ$^{-3}$. The lowest ED coincides with the aliphatic spacer area and increases again in the borate ion section. For ILCs 1, a complete interdigitation of all hydrocarbon units decreases the density and ED in the center of the layer. The hydrophilic crown ethers are expelled from the spacer area and the density and electron density increases in the ionic sublayer. The average ED difference between the sections decreases by a factor of 2 to only 0.06 eÅ$^{-3}$ as expected for the experimental $I_{001} : I_{002}$ intensity ratios. The density and electron density is smallest in the ionic nanophase, which might be favourable for ion transport owing to a smaller steric repulsion.

**Ionic Conductivity**

The ionic conductivity has been probed in commercial LC cells by temperature-dependent electrical impedance spectroscopy.
(EIS). The EIS data was transformed into permittivity data using the WinFit software (Novocontrol Technologies, Montabaur, Germany) and fit as described in references [30,31] to determine the conductivity values shown in Figure 6. It is expected that only the cations are sufficiently mobile to make a significant contribution to the ionic conductivity, making these ILCs single-ion conductors. All cells exhibited homogenous alignment (Figure 6A, Figures 2F,G and Figure S2B). For ILC 1a the material could be also homeotropically aligned (Figure 6A, and ESI). In this case, the ion transport should be lower than for the homogenous-aligned materials since the charge would need to cross the aliphatic layers as the ion channels are oriented parallel to the electrodes. This is shown in Figure 6C for the sodium ILC 1a. The ionic conductivity reaches values of 0.98×10⁻⁵ S cm⁻¹ at 80 °C in the homogenous-aligned material (blue and red lines) and is 2-3 orders of magnitude higher compared with the homeotropically aligned SmA phase (0.87×10⁻⁷ S cm⁻¹ at 80°C, black line). ILC 2 is the only material which does not show any crystallisation to a Cr₃ phase and therefore the same conductivity values are obtained in the cooling and the second heating curve (Figure 6B). The stability of the SmA phase decreases from 1a to 1b. In the heating curve, the ionic conductivity in the Cr₂ phase is low but increases by more than an order of magnitude in the fluid SmA phase. Upon cooling the SmA phase is stable and the conductivity decreases only slowly with decreasing temperature for 1a until the material transforms to the Cr₂ and Cr₃ phases below 20 °C, where the ion transport is poor. For the potassium salt 1b, the Cr₃ phase is generated more rapidly. Consequently, the conductivity drops by more than three orders of magnitude below 40 °C.

At 40 °C, the conductivity values of the three salts in the SmA phase are 3.03×10⁻⁵ S cm⁻¹ (2), 1.07×10⁻⁵ S cm⁻¹ (1a), and 8.31×10⁻⁶ S cm⁻¹ (1b). When compared with other potassium ion/crown ether-containing liquid crystals, which reach maximum values of 1×10⁻⁴ S cm⁻¹, these values are significantly higher. The transport mechanism for the alkali metal ions in a nematic phase is proposed to be the transfer from one complexing site to the next, which was confirmed by the addition of metal-free crown ethers, and thus vacant sites, which increased the ionic conductivity.[33] However, the low ionic conductivities obtained in columnar phases with crown ethers covalently attached in the column center, where the anion was assumed to dominate the ion transport, were taken as an argument that the alkali ion-crown ether complexes are too strong for a cation transport.[34] The alkali cations were thought to be immobilised and thus did not take part in the ion conduction. The values with 1a and 1b obtained in this work are two orders of magnitude larger than those in reference.[34] However, the ionic conductivity of the relatively large ammonium ion is still a factor of 3-4 larger than that of the crown ether complexes. Since the crown ether units are not covalently fixed in 1a and 1b, they might migrate as the crown ether-alkali metal complexes and the mobility might be correlated with the size of the cations complexes. The cation volume can be estimated to be 432 Å³ (ILC 2), 380 Å³ (ILC 1b) and 366 Å³ (ILC 1a).[35] While the small difference in conductivity between 1a and 1b might result from the smaller size of the sodium crown ether complex, the higher conductivity of 2 with the tetrabutylammonium cation, and in general the higher conductivity compared with other crown ether ILCs, must have a different origin. The difference might be attributed to: (i) the low nucleophilicity of the cyanoborate counter ions; and (ii) the low density calculated for the ionic nanophases (Figure 5). The smallest density is calculated for ILC 2 (0.583 g/cm³) followed by ILC 1a (0.697 g/cm³) and ILC 1b (0.793 g/cm³). The order of these values corresponds well with the sequence of ionic conductivities.

Conclusions

New ionic liquid crystals have been prepared with robust cyanoborate anions as the mesogenic building blocks and lipophilic and hydrophilic counter ions. The mesogen structure results in a nanosegregation of interdigitated lamellar SmA₂ liquid crystal phases, which freeze at low temperature to lamellar and columnar crystals, in which no interdigitation is observed. The lipophilic or hydrophobic nature of the cations are important for the materials self-assembly. Lipophilic ammonium ions are “In” between the cyanoborate anions, while the hydrophilic sodium and potassium crown ether complexes form a separated interlayer “Out” of the cyanoborate section. This model is confirmed by X-ray, solid state NMR and electron density reconstruction. The ionic conductivity is highest for the homogenously-aligned material in commercial liquid crystal cells and amounts to 10⁻⁴ S cm⁻¹ at 40 °C. It is two to three orders of magnitude lower in the unfavourably-aligned (homeotropic) material. Nonetheless, the conductivity is two orders of magnitude higher than in previously published crown ether ILCs. The data suggests that this is mainly a result of the small density in the ionic nanophases of these ILCs and the low nucleophilicity of the borate anions.

Author Contributions

M.L writing and correction of the manuscript, XRS studies, interpretation of thermotropic and XRS data, electron density reconstruction; P.W. synthesis and molecular analysis, POM, DSC, XRS studies, preparation of the samples for solid-state NMR and EIS, M.F. writing of the manuscript, supply of the cyanoborate anions, G.G. writing and correction of the manuscript, measurement of EIS, data fitting and interpretation, M.W. measurement of EIS, S. B. measurement of solid-state NMR spectra, A.C.P. writing and correction of the manuscript, measurement of solid-state NMR and interpretation of the data

Conflicts of interest

There are no conflicts to declare.