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To cite this article: Xin Li, Xin Lan, Shuang Ma, Lu Bai, Fanbao Meng & Mei Tian (2014) Synthesis and characterisation of imidazolium-based ionic liquid crystals bearing a cholesteryl mesogenic group, Liquid Crystals, 41:12, 1843-1853, DOI: 10.1080/02678292.2014.951884

To link to this article: http://dx.doi.org/10.1080/02678292.2014.951884

Published online: 21 Aug 2014.

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Synthesis and characterisation of imidazolium-based ionic liquid crystals bearing a cholesteryl mesogenic group

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(Received 31 March 2014; accepted 2 August 2014)

A series of cholesteryl-containing imidazolium chlorides and imidazolium tetrachloroaluminates were synthesised, and the chemical structure, liquid crystalline behaviour and ionic conductivity were characterised by several technical methods. Whereas the imidazolium chlorides show chiral smectic A (SmA*) phase on heating and cooling cycles, the imidazolium tetrachloroaluminates display chiral nematic (N*) phase, which is uncommon for ionic liquid crystals (ILCs). The imidazolium chlorides display similar phase transition temperature and entropy, indicating the cholesteryl component influence predominately on the phase transition rather than the different alkyl substituent groups. The imidazolium tetrachloroaluminates show lower melting point temperatures and lower clear point temperature than the imidazolium chlorides. The mesophases exist at rather moderate temperatures. Non-mesomorphic imidazolium tetrachloroaluminates(III) salts with short alkyl substituents have been known for a long time, and the synthesised imidazolium tetrachloroaluminates are the first examples of tetrahalogenoaluminates(III)-containing ILCs. For the imidazolium tetrachloroaluminates, imidazolium cations combine loosely with AlCl4− ions because AlCl4− ions are large and occupy more space in spite of the hydrogen bond and electrostatic attraction interaction, indicating that the layer structure can be destroyed easily to form N* phase on heating.

Keywords: liquid crystals; ionic; chiral; phase behaviour

1. Introduction

Recently, ionic liquids (ILs) have attracted considerable interest as soft materials because they exhibit a lot of unique properties including low volatility, good solubility of other materials, wide liquid temperature range, negligible vapour pressure, high thermal stability, high ionic conductivity and so on.[1–4] Many of the potentially advantageous properties of ILs are actually highly dependent on their precise structure. The ILs have the potential for various applications such as catalyst, solvents for chemical synthesis and ionic conduction over the past decade.[5–7] Liquid crystals (LCs) are some kinds of soft materials for applications with a long time, and they are usually regarded as the fourth state of matter, apart from the solid, isotropic liquid and gas states. LCs with chiral units have presented large potential for various applications because they show a marvellous variety of LC phases such as chiral smectic phase, cholesteric phase and blue phase.[8–10] Ionic liquid crystals (ILCs) have become a fascinating class of functional soft materials because they combine the properties of ILs and LCs. That is, ILCs can show some outstanding features in comparison with normal LCs. For example, they can exhibit high ionic conductivity. Thus, ILCs have attracted considerable attention from both fundamental and applied points of view.[11–14] Some kinds of ILCs have been reported, and it is claimed that the liquid crystalline behaviour strongly depends on the nature of both the cation and the anion, but also on the length of the alkyl chain of the organic cation.[15] Many other cations and anions have been used to obtain ILCs. The reported cations include pyridinium,[16,17] imidazolium,[18,19] pyrrolidinium,[20,21] quaternary ammonium and quaternary phosphonium salts,[22,23] and the anions include halide ion, BF4−, PF6−, CF3SO3− and so on.[24–26] Some ILs can show mesomorphic properties and become liquid crystalline materials. For example, some imidazolium-based ILCs can be generated simply by increasing the alkyl chain length to increase the self-organisation character.[27,28] However, it is interesting to introduce functional groups into IL category to construct ILCs when one seeks to obtain other mesophase types than a smectic A (SmA) phase, which is most commonly observed for simple ionic mesogens. Because ILCs containing imidazolium cations show particular advantages such as low melting points, high chemical and electrochemical stability, excellent anisotropic ionic conductivity, organised reaction media or ordered

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solvents, these types of ILCs with functional groups have attracted considerable attention recently. [29–32]

It is interesting to know the liquid crystalline phases of cholestery-containing ILCs, because normal cholestery-containing low-molecular-weight LCs can show chiral smectic phase, cholesteric phase, blue phases, and so on. Some cholestery-containing low-molecular-weight ILCs have been reported previously. A glassy liquid crystalline phase can be formed by a cholesteryl hydrogen phthalate and its complex salts with normal aliphatic amines.[33] Goossens et al. have prepared the first imidazolium-based ILCs with one or two cholesteryl substituents connected via a flexible undecyl spacer to the cationic core, which exhibited a SmA* phase at room temperature.[34] Their compounds incorporate a longer and more flexible alkyl spacer between the cholesteryl mesogens and the imidazolium ion pairs, suggesting a larger extent of decoupling between the ion head group and the mesogenic group. Yousif et al. have prepared cholesteryl-containing ILCs exhibiting cholesteric phase, which were made by quaternisation of cholesteryl isonicotinate with n-alkyl salts \((n = 2–8)\).[35] For these cholesteryl isonicotinate salts, the alkyl spacer between the ion group and the mesogenic group is not long and flexible enough. Usually, the most common method for obtaining ILCs is the attachment of long alkyl chains to the IL cation, and simple long alkyl-substituted imidazolium salts only show SmA phases, but nematic phases are very uncommon for IL crystalline systems.[11] Therefore, it is necessary to study the liquid crystalline phase of cholestery-containing imidazolium-based ILCs with short alkyl spacers between the ion group and the mesogenic group.

In this work, we synthesised a series of imidazolium-based ILCs by introducing cholesteryl mesogenic groups in the chemical structure to obtain novel ILCs with short alkyl spacers between the ionic group and mesogenic group. These chiral ILCs contain cholesteryl groups, different alkyl substituents, imidazolium cations and different anions including \(\text{Cl}^-\) and \(\text{AlCl}_4^-\). Non-mesomorphic imidazolium tetrachloroaluminate(III) salts with short alkyl substituents have been known for a long time, and the cholesteryl-containing imidazolium tetrachloroaluminate is the first examples of tetrahalogenoaluminate(III)-containing ILCs. The effect of the different substituents on the LC behaviour is investigated in structures, thermal behaviours and effect of cation–anion interactions.

2. Materials and methods

2.1 Materials and measurements

3-Chloropropanoyl chloride, cholesterol, 1-methylimidazole, 1-iso-propylimidazole, 1-butylimidazole and aluminium trichloride were purchased from Aldrich (Sigma-Aldrich, Shanghai, China). All other commercially available chemical materials were used without further purification except for 1-methylimidazole, 1-iso-propylimidazole, 1-butylimidazole and aluminium trichloride. \(^1\)H NMR (600 MHz) and \(^{13}\)C NMR (75 MHz) spectra were performed by a Varian Gemini NMR Spectrometer (Varian Associates, Palo Alto, CA) using dimethyl sulfoxide-\(d_6\) (DMSO-\(d_6\)) or CDC\(_3\) as solvent and tetramethysilane as internal standard. Fourier transform infrared (FTIR) spectra were carried out by a PerkinElmer Instruments Spectrum One Spectrometer (PerkinElmer, Foster City, CA). The element analyses were performed by an Elementar Vario EL III instrument (Elementar, Hanau, Germany). Differential scanning calorimetry (DSC) measurements were performed by a Netzsch instrument DSC 204 (Netzsch, Wittelsbacherstr, Germany) at heating and cooling rates of 10°C min\(^{-1}\) under nitrogen atmosphere. The powder X-ray diffraction (PXRD) measurements were performed using a Cu \(K\alpha(\lambda = 1.542\ \text{Å})\) radiation monochromatised with a Rigaku DMAX-3A X-ray diffractometer (Rigaku, Tokyo, Japan) at heating and cooling rates of 10°C C min\(^{-1}\). Optical textures were observed by polarising optical microscopy (POM) using a Leica DMRX (Leica, Wetzlar, Germany) microscope equipped with a Linkam Scientific Instrument THMS-600 hot stage (Linkam, Surrey, England) at heating and cooling rates of 10°C C min\(^{-1}\). Ionic conductivities were obtained by a RTS-9 four-probe meter (Guangzhou four-point probe technology, Guangzhou, China) equipped with a hot stage. A sample wafer (25 mm in diameter, 2 mm in thickness) was prepared using a waferer and was immediately placed on a glass substrate, and the ionic conductivity measurement was performed on the hot stage.

2.2 Synthesis of chlorine-containing liquid crystal

The synthesis of the target chlorine-containing LC cholesteryl 3-chloropropanoate (CCPA) is outlined in Figure 1. Cholesterol (38.6 g, 0.1 mol) and pyridine (50 mL) were dissolved in tetrahydrofuran (THF, 450 mL) to obtain a solution. 3-Chloropropanoyl chloride (17.8 g, 0.14 mol) was added dropwise to the solution and stirred for 2 h at room temperature (25°C), and the reaction mixture was refluxed and
stirred for 54 h. Then 400 mL of water was added into the reaction mixture, and 380 mL of THF was distilled out. The residue was cooled to room temperature and acidified with 6 N sulphuric acid. The precipitates were separated by filtration, recrystallised by chloroform and dried in a vacuum oven to obtain white crystals of CCPA. Yield 85%. IR (KBr): 2951, 2868, 1728, 1636, 1571, 1467, 1374, 1210, 1188, 1190 cm\(^{-1}\). Elem. analysis: found: 75.32% C, 10.18% H; calc.: 75.51% C, 10.35% H. \(^1\)H NMR (CDCl\(_3\), ppm): 0.66–2.04 (m, 41H, alkyl-\(\textit{H}\)), 2.35 (d, \(J = 7.8\) Hz, 2H, –OCC\(_2\)H\(_2\)=C= in cholesteryl), 2.76–2.78 (m, 2H, –CH\(_2\)=COO–), 3.75–3.78 (m, 2H, Cl–CH\(_2\)CH\(_2\)=COO–), 4.66–4.71 (m, 1H, –OCH\(_2\)=CH in cholesteryl), 5.40 (t, \(J = 4.2\) Hz, 1H, –C=CH– in cholesteryl). \(^1\)C-NMR (CDCl\(_3\), ppm): 12.9, 21.0, 21.3, 22.5, 22.8, 23.8, 24.3, 27.7, 28.0, 28.2, 31.8, 31.9, 35.8, 36.2, 36.6, 36.9, 37.9, 38.1, 39.8, 42.3, 50.1, 56.1, 56.7, 74.7 (OCH– in cholesteryl), 122.8 (C=CH in cholesteryl), 139.5 (C=CH in cholesteryl), 169.6 (C=O in ester linkage).

### 2.3 Synthesis of imidazolium chlorides

The synthesis of the target imidazolium chlorides is shown in Figure 1. The compound CCPA (23.9 g, 0.05 mol) was dissolved in dry acetonitrile (50 mL) under a nitrogen atmosphere to obtain a solution. 1-Butyl-imidazole was purified by distillation over KOH. The freshly distilled 1-butyl-imidazole (22.3 g, 0.18 mol) was added dropwise to the solution under nitrogen atmosphere at room temperature (25°C), and the reaction mixture was refluxed and stirred for 92 h under nitrogen atmosphere. The solvent and excess 1-butyl-imidazole were distilled out under reduced pressure, and the residue was washed three times using diethyl ether, dried under high vacuum for 24 h to obtain 1-cholesteryloxycarbonylethyl-3-butylimidazolium chloride ([C mim]Cl). Yield 93%. IR (KBr): 2936, 2867, 1723, 1635, 1466, 1375, 1213, 1188 cm\(^{-1}\). Elem. analysis: found: 73.53% C, 10.03% H, 4.68% N; calc.: 73.90% C, 10.22% H, 4.66% N. \(^1\)H NMR (DMSO-\(_d_6\), ppm): 0.68–2.01 (m, 48H, alkyl-\(\textit{H}\)), 2.34 (t, \(J = 8.4\) Hz, 2H, –OCC\(_2\)H\(_2\)=C= in cholesteryl), 2.66–2.76 (m, 2H, –CH\(_2\)=COO–), 3.73–3.76 (m, 2H, –N=CH\(_2\)CH\(_2\)=COO–), 5.38 (t, \(J = 7.2\) Hz, 1H, –C=CH– in cholesteryl), 7.03–7.23 (m, 2H, –N=CH=CH=N in imidazolyl ring), 8.48 (s, 1H, –N=C–H–N in imidazolyl ring). \(^1\)C-NMR (DMSO-\(_d_6\), ppm): 12.8, 18.7, 19.1, 19.3, 21.0, 22.8, 23.8, 24.2, 27.7, 28.0, 30.2, 31.8, 31.9, 35.7, 36.2, 36.6, 36.9, 37.9, 38.0, 39.1, 39.5, 39.7, 42.3, 50.0, 56.1, 56.6, 74.7 (OCH– in cholesteryl group), 119.6 (C=N in imidazole ring), 122.8 (C=CH in cholesteryl), 129.0, 130.2 (C=N in imidazole ring), 139.4 (C=CH in cholesteryl), 169.7 (C=O in ester linkage).

Other imidazolium chloride salts such as 1-cholesteryloxycarbonylethyl-3-methylimidazolium chloride ([C mim]Cl) and 1-cholesteryloxycarbonylethyl-3-iso-propylimidazolium chloride ([C pim]Cl) were synthesised using 1-methylimidazole and 1-iso-propylimidazole, and CCPA by the same method.

1-Cholesteryloxycarbonylethyl-3-methylimidazolium chloride ([C mim]Cl): yield 90%. IR (KBr): 3062, 2938, 2865, 2833, 1725, 1636, 1571, 1467, 1374, 1210, 1190 cm\(^{-1}\). Elem. analysis: found: 72.89% C, 9.82% H, 4.94% N; calc.: 73.02% C, 9.91% H, 5.01% N. \(^1\)H NMR (DMSO-\(_d_6\), ppm): 0.66–2.03 (m, 41H), 2.38 (t, \(J = 8.1\) Hz, 2H), 2.64–2.71 (m, 2H), 3.75 (s, 3H), 4.15–4.21 (m, 1H), 4.25–4.32 (m, 2H), 5.36 (t, \(J = 7.8\) Hz, 1H), 7.08–7.36 (m, 2H), 8.49 (s, 1H). \(^1\)C-NMR (DMSO-\(_d_6\), ppm): 12.9, 18.9, 19.0, 19.4, 21.2, 22.9, 23.9, 24.1, 27.9, 28.1, 30.5, 31.7, 31.8, 35.6, 36.4, 36.7, 36.8, 37.9, 38.1, 39.3, 39.6, 42.3.
2.4 Synthesis of imidazolium tetrachloroaluminates

The synthesis of the target imidazolium tetrachloroaluminates is shown in Figure 1. The purchased analytical reagent was sublimated under a nitrogen atmosphere to obtain pure aluminium trichloride. The compound [Cmim][Cl] (12.1 g, 0.02 mol) was put in a flask under a nitrogen atmosphere and was cooled to 0°C. Dry fresh-purified aluminium trichloride (2.66 g, 0.02 mol) was added to the flask in small portions at 0°C and stirred acutely under nitrogen atmosphere for 0.5 h to obtain 1-cholesteryloxycarboxyethyl-3-methylimidazolium tetrachloroaluminate ([Cmim][AlCl4]). No further purification was attempted, and the product was then transferred to a N2-atmosphere glovebox for storage to avoid moisture absorption. IR (KBr): 3067, 2936, 2865, 2836, 2423, 1724, 1641, 1568, 1468, 1377, 1192, 843, 607 cm\(^{-1}\). Elem. analysis: found: 59.39% C, 8.55% H, 3.89% N; calc.: 59.75% C, 8.64% H, 3.87% N. \(^1\)H NMR (DMSO-d6, δ, ppm): 0.64–2.00 (m, 48H), 2.34 (t, J = 7.6 Hz, 2H), 2.63–2.75 (m, 2H), 4.07–4.13 (m, 1H), 4.18–4.29 (m, 2H), 5.39 (t, J = 7.6 Hz, 1H), 7.54–7.72 (m, 2H), 9.13 (s, 1H). \(^13\)C-NMR (DMSO-d6, δ, ppm): 12.9, 18.3, 19.1, 19.2, 21.1, 21.4, 24.7, 24.6, 24.7, 24.8, 24.9, 27.9, 28.0, 28.1, 32.8, 32.9, 36.2, 36.4, 37.6, 37.7, 37.8, 37.9, 39.9, 41.8, 42.6, 46.4, 50.8, 56.6, 56.8, 74.9, 121.9, 122.7, 131.1, 132.8, 140.1, 171.1.

3. Results and discussion

3.1 Syntheses

The chlorine-containing cholesteryl-based LC monomer CCPA is synthesised using cholesterol and 3-chloropropanoyl chloride by one-step esterification reaction. The synthesis and liquid crystalline properties of CCPA have been characterised in the previous report.[36] The imidazolium chlorides ([Cmim][Cl], [Cmim][Cl] and [Cmim][Cl]) are synthesised using 1-butyl-imidazole, 1-methylimidazole and 1-iso-propylimidazole and chlorine-substituted CCPA according to the reported procedure.[37,38] The imidazolium tetrachloroaluminates are synthesised using imidazolium chlorides and fresh AlCl3 in a 1:1 mol ratio in one-step reaction according to the earlier reports. [39,40] The chemical structures of all these novel materials are characterised by FTIR spectra, \(^1\)H and \(^13\)C NMR spectra.

The \(^1\)H and \(^13\)C NMR spectra of 1-butylimidazolium chloride salt [Cmim][Cl] are illustrated in Figure 2. In \(^1\)H NMR spectra, [Cmim][Cl] exhibits characteristic chemical shift at 2.34 ppm (–OCC\(_2\)H\(_2\)=C– in cholesteryl), 2.66–2.76 ppm (–CH\(_2\)COO–), 3.73–3.76 ppm (N–CH\(_2\)(CH\(_2\))\(_2\)CH\(_3\)), 4.12–4.24 ppm (–OCH– in...
cholesteryl), 4.24–4.30 ppm (–N–CH$_2$CH$_2$CH$_2$COO–), 5.38 ppm (–C=CH– in cholesteryl), 7.03–7.23 and 8.48 ppm (imidazolyl–H), as displayed in Figure 2(a).

In $^{13}$C NMR spectra, [Cbim]Cl displays characteristic chemical shift at 74.7 ppm (–OCH– in cholesteryl group), 119.6 ppm (–C=N in imidazole ring), 122.8 ppm (–C=CH in cholesteryl), 129.0 and 130.2 ppm (–C=N in imidazole ring), 139.4 ppm (–C=CH in cholesteryl) and 169.7 ppm (–C=O in ester linkage), as shown in Figure 2(b). [Cbim]Cl exhibits characteristic carbons of imidazolyl hydrogens due to the formation of imidazolium.

The difference in chemical structure of CCPA, the imidazolium chlorides and the imidazolium tetrachloroaluminates is shown in FTIR spectra. Figure 3 illustrates FTIR spectra of CCPA, [Cbim]Cl and [Cbim]AlCl$_4$. CCPA shows characteristic bands at 2951–2937 cm$^{-1}$ (alkyl C–H stretching), 1728 cm$^{-1}$ (C=O stretching in ester linkage) and 687 cm$^{-1}$ (C–Cl stretching) as displayed in Figure 3(a), and [Cbim]Cl exhibits characteristic absorbance peaks at 2936–2867 cm$^{-1}$ (alkyl C–H stretching), 1723 cm$^{-1}$ (C=O stretching in ester linkage), 1635 and 1466 cm$^{-1}$ (C=C and C=N stretching in imidazole group) as displayed in Figure 3(b). In comparison with CCPA, [Cbim]Cl shows C=C and C=N stretching absorbance bands, but does not show C–Cl stretching absorbance bands due to formation of the imidazolium salt. [Cbim]AlCl$_4$ shows characteristic absorbance peaks at 3066, 2937–2867 (alkyl C–H stretching), 2421, 1723 (C=O stretching in ester linkage), 1640, 1565 and 1466 cm$^{-1}$ (C=C and C=N stretching in imidazole group) as displayed in Figure 3(c). The obvious difference of IR absorbance between [Cbim]AlCl$_4$ and [Cbim]Cl emerges at 3066 and 2421 cm$^{-1}$, which can be due to the formation of hydrogen bonds between imidazole–H and chlorine atoms.[41–43]

### 3.2 Liquid crystalline behaviour of the imidazolium chlorides

The LC behaviour of all the synthesised imidazolium chlorides [Cbim]Cl, [Cmim]Cl and [Cpim]Cl is studied by using the technological means including DSC, POM and PXRD, as summarised in Table 1. The phase transition temperatures and enthalpies are obtained by DSC performed on both the first and the second heating/cooling cycles, and the types of mesophase are testified by POM and PXRD. Although all these imidazolium chlorides are synthesised from different N-alkylimidazoles, they exhibit similar mesomorphic properties. Thus the liquid crystalline behaviour of [Cpim]Cl is discussed as a representative compound for these series materials. Figure 4 illustrates the DSC thermograms and optical textures of [Cpim]Cl. When it is investigated by DSC, [Cpim]Cl shows a melting transition (crystal-to-mesophase transition) and an isotropic phase transition at 71.1°C and 124.0°C, respectively, on the first heating scans, as shown in Figure 4(a). On the first cooling scans, [Cpim]Cl displays an isotropic-to-mesophase transition and crystallisation at 108.7°C and 67.7°C, respectively. When it is investigated by POM, [Cpim]Cl shows characteristic chiral smectic A (SmA*) texture upon heating and cooling cycles. As [Cpim]Cl is heated above 71°C, it starts to melt and displays optical textures. A fan-shaped texture of the SmA* phase gradually appears with rise in the temperature, as shown in Figure 4(b). The director basically lay in the plane of the substrate, and the smectic layers are curved across the fans in this fan-shaped texture, and it is the most commonly observed natural SmA* appearance. Then, oily streaks appear when the sample is heated unceasingly, as shown in Figure 4(c). The textures and mesomorphic properties disappear at 125°C. A characteristic bâtonnets is observed when the isotropic liquid is cooled to 108°C, as shown in Figure 4(d), and then the bâtonnets extend to form fan-shaped...
texture on cooling to 82°C (see Figure 4(e)). The phase transition from the isotropic to the SmA* phase can be distinguished from that of isotropic-N* phase transition due to appearance of smectic bâtonnets rather than spherical nuclei which grow from the black background of the isotropic melt.

The SmA* mesophase of [Cpim]Cl is also testified by PXRD. PXRD of the synthesised imidazolium chlorides ([Cbim]Cl, [Cmim]Cl and [Cpim]Cl) are performed at different temperature in order to confirm the mesophase behaviour and to understand the molecular arrangement in crystal and mesophase. All these imidazolium chlorides display layered structures in both the crystal and liquid crystalline phases. The layer spacings determined by PXRD measurements are listed in Table 2. For the imidazolium chlorides, the d spacings of crystalline phase and mesophase display a little increment with increase of chain length from [Cmim]Cl to [Cbim]Cl, indicating a similar structure for all these salts in the series. There is also some increment of layer thickness from crystal to mesophase for these ILCs, which can be attributed to a decrease in the tilting angle of the molecular rod with respect to the plane normal.[44] Some typical PXRD diffractograms of mesophase for the imidazolium-based salts are illustrated in Figure 5. Figure 5(a) displays a PXRD diffractogram of SmA* mesophase for [Cpim]Cl. [Cpim]Cl shows a strong small-angle diffraction peak (3.1° of 2θ) and a diffuse band (16.4° of 2θ) in the diffractogram. The sharp strong low-angle peak suggests a highly ordered lamellar structure with the layer thickness (28.5 Å), and the diffuse band at wide angle band (d spacing 5.4 Å) indicates melted molecular chains with an average

<table>
<thead>
<tr>
<th>Sample</th>
<th>The second heating run</th>
<th>The first heating run</th>
<th>The second cooling run</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cmim]Cl</td>
<td>Cr 83.9/18.9 SmA* 129.4/0.6 I</td>
<td>Cr 83.0/34.1 SmA* 129.3/0.9 I</td>
<td>I 118.4/−0.9 SmA* 71.0/−18.8 Cr</td>
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<tr>
<td></td>
<td>Cr 75.1/18.8 SmA* 124.3/0.6 I</td>
<td>Cr 73.9/33.9 SmA* 124.0/1.0 I</td>
<td>I 114.3/−0.7 SmA* 68.3/−21.3 Cr</td>
</tr>
<tr>
<td>[Cpim]Cl</td>
<td>Cr 72.2/18.3 SmA* 124.0/0.6 I</td>
<td>Cr 71.1/31.4 SmA* 124.0/0.7 I</td>
<td>I 108.7/−0.8 SmA* 67.7/−19.6 Cr</td>
</tr>
<tr>
<td>[Cmim]AlCl₄</td>
<td>Cr 71.8/17.7 N* 123.0/1.0 I</td>
<td>Cr 70.6/22.8 N* 122.9/1.5 I</td>
<td>I 113.9/−1.3 N* 65.6/−17.8 Cr</td>
</tr>
<tr>
<td>[Cbim]AlCl₄</td>
<td>Cr 70.8/15.6 N* 124.2/0.8 I</td>
<td>Cr 69.5/25.5 N* 124.2/1.1 I</td>
<td>I 113.8/−1.1 N* 61.6/−16.5 Cr</td>
</tr>
<tr>
<td>[Cpim]AlCl₄</td>
<td>Cr 69.6/22.9 N* 118.8/0.7 I</td>
<td>Cr 67.6/22.9 N* 118.6/0.7 I</td>
<td>I 105.1/−0.4 N* 58.7/−15.5 Cr</td>
</tr>
<tr>
<td>[Cmim]Cl</td>
<td>Cr 71.8/17.7 N* 123.0/1.0 I</td>
<td>Cr 70.6/22.8 N* 122.9/1.5 I</td>
<td>I 113.9/−1.3 N* 65.6/−17.8 Cr</td>
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</tr>
</tbody>
</table>

Table 1. Phase transitions and enthalpies of the synthesised imidazolium chlorides and imidazolium tetrachloroaluminates.

Notes: *Cr, crystal; N*, chiral nematic phase; SmA*, chiral smectic A phase; I, isotropic.
3.3 Liquid crystalline behaviour of the imidazolium tetrachloroaluminates

The LC behaviour of the imidazolium tetrachloroaluminates ([Cbim]AlCl$_4$, [Cmim]AlCl$_4$ and [Cpim]AlCl$_4$) are investigated by DSC, POM and PXRD analysis. The transition temperatures and enthalpies obtained from DSC measurements on both the first and the second heating/cooling cycles are shown in Table 1. For the imidazolium tetrachloroaluminates and the imidazolium chlorides, the clearing enthalpy values are very small compared to conventional low molar mass LCs. On the one hand, this is due to the persistence of aggregates into the isotropic phase.[47] On the other hand, these compounds may be considered to be relatively biaxial due to the bulky cholesteryl-based groups, and this reduces the change in orientational order at the transition and hence reduces the entropy change.[48,49]

In order to illustrate the difference of phase transition temperature of imidazolium tetrachloroaluminates and imidazolium chlorides, a comparison chart is given in Figure 6. It is observed that the imidazolium tetrachloroaluminates ([Cbim]AlCl$_4$, [Cmim]AlCl$_4$ and [Cpim]AlCl$_4$) show a little lower temperature of phase transitions and lower enthalpies than those of the corresponding precursors ([Cbim]Cl, [Cmim]Cl and [Cpim]Cl), suggesting that the AlCl$_4^-$ ion reduces the molecular organisation order in comparison with Cl$^-$ ion. Furthermore, the N* phase of imidazolium tetrachloroaluminates are testified by optical textures and PXRD data that are summarised in Table 2. This result indicates that these two types of imidazolium-based salts containing different anions show different mesophases. All the imidazolium salts containing Cl$^-$ ions show SmA* phase, but those containing AlCl$_4^-$ ions display N* phase in both heating and cooling cycles. The mesophase behaviour of these ILCs is strongly dependent on the type of anion.

Since these imidazolium tetrachloroaluminates show similar liquid crystalline behaviour, the discussion begins with [Cpim]AlCl$_4$ as a representative compound for these series materials. Figure 7 displays DSC thermograms and optical textures of [Cpim]...
AlCl₄. [Cpim]AlCl₄ shows a melting transition at 67.6°C and a mesogenic–isotropic phase transition at 118.6°C on the first heating cycle, and an isotropic–mesogenic phase transition at 105.1°C and a mesogenic–crystal transition at 58.7°C are observed on the first cooling scan, as shown in Figure 7(a). The type of mesophase is investigated by the optical textures observed by POM, and some characteristic textures of [Cpim]AlCl₄ are displayed in Figure 7. When [Cpim]AlCl₄ is heated, fan-like texture (see Figure 7(b)) appears in the eyesight. This kind of fan-like texture is a natural texture that is often observed in N* phase, which can be observed for strongly twisted materials. With the rise in the temperature, an oily streak texture (Figure 7(c)) is observed. When it is heated continuously, the sample is in isotropic state and the eyesight becomes black. The N* phase of [Cpim]AlCl₄ is recognised by the appearance of spherical nuclei in Figure 7(d) when the sample is cooled from the isotropic liquid, which is different from bâtonnets of SmA* phase observed for [Cpim]Cl. When the sample is cooled continuously, the fan-like texture appears as shown in Figure 7(e). The nature of the N* phase of [Cpim]AlCl₄ is testified by X-ray diffraction. [Cpim]AlCl₄ shows a typical chiral nematic diffractogram with diffuse bands at both small-angle area and wide-angle area (d spacing 5.4 Å) as shown in Figure 5(b), which coincides with the previous report.[50] Compared with [Cpim]Cl, [Cpim]AlCl₄ displays no strong sharp peaks at small angle due to disappearance of the layer structure, indicating that the AlCl₄⁻ ions reduce the molecular organisation order in the mesophase.

To give more information about the molecular arrangements of these ILCs in crystalline phase, the molecular organisation structures are conceived according to the PXRD data of [Cpim]Cl and [Cpim]AlCl₄, as shown in Figure 8. In crystalline phase, [Cpim]Cl shows a strong small-angle
diffraction peak corresponding to the layer spacing (28.3 Å) accompanied by a set of diffraction peaks at wide-angle regions (see Figure 8(a)). Similarly, [Cpim] AlCl₄ displays a small strong small-angle diffraction peak corresponding to the layer spacing (39.8 Å) accompanied by a set of diffraction peaks at wide-angle regions as shown in Figure 8(b). For these kinds of imidazolium-based ILCs, a ‘head-to-head’ arrangement is usually expected, [34] as illustrated in Figure 8(c). For these molecules, the molecular area of an ionic cluster can be deduced by

\[ A_M = V_M / L \]  

where \( L \) is the measured layer thickness, and \( V_M \) is the molecular volume which can be calculated using the equation [34]:

\[ V_M = fM / 0.6022 \]  

where \( M \) is the molecular mass (g mol⁻¹), and \( f \) is a temperature correcting factor which can be determined by [51]

\[ f = 0.9813 + 7.474 \times 10^{-4}T \]

where \( T \) is temperature in °C.

For the crystalline phase of [Cpim]Cl and [Cpim] AlCl₄ at 25°C, the measured layer thickness is, respectively, 28.3 and 39.8 Å, thus the molecular area is found to be 34.6 and 30.1 Å², respectively. These values are less than 38.3 Å² of 1-(11-cholesteryloxy) undecyl-3-methylimidazolium bromide (5a),[34] indicating a different extent of interdigitation of the mesogenic groups in both [Cpim]Cl and [Cpim] AlCl₄. The [AlCl₄⁻] salt is interdigitated much more than the [Cl⁻] salt because it possesses less molecular area than the [Cl⁻] salt. In this head-to-head structure, imidazolium cations combine loosely with AlCl₄⁻ ions because AlCl₄⁻ ions are large and more space occupied in the systems. When [Cpim]AlCl₄ is heated in this case, this layer should be destroyed easily due to the loose combination among the imidazolium cations and AlCl₄⁻ ions. Therefore, [Cpim] AlCl₄ displays N* phase when the sample is heated, as shown in Figure 5(b).

### 3.4 Conductivities of the imidazolium-based ILCs

Ionic conductivities of the imidazolium-based ILCs are also investigated to elucidate influence of meso-phase and salification of the imidazolium-based materials which contain different anions. Table 2 shows the ionic conductivities of the synthesised imidazolium chlorides and the imidazolium tetrachloroaluminates in mesogenic phase and isotropic phase. All these imidazolium-based salts display the same order of magnitudes of ionic conductivities in both SmA* phase and N* phase, but they show a magnitude greater conductivity in isotropic phase than in mesophase due to decrease in viscosity.[52] Furthermore, the imidazolium tetrachloroaluminates ([Cpbim]AlCl₄, [Cmim]AlCl₄ and [Cpim]AlCl₄) show higher conductivity than imidazolium chlorides. This result is similar to the conductivity in normal imidazolium-based ILs.[39]

### 4. Conclusions

Cholesteryl-containing imidazolium-based ILCs with Cl⁻ ions and AlCl₄⁻ ions are investigated in this work. The imidazolium chlorides ([Cmim]Cl, [Cbim] Cl and [Cpim]Cl) display SmA* phase and similar phase transition temperature and entropy, indicating the cholesteryl component influence predominately on the phase transition rather than alkyl substituent groups on both heating and cooling cycles. The imidazolium tetrachloroaluminates ([Cmim]AlCl₄, [Cbim]AlCl₄ and [Cpim]AlCl₄) show N* phase on both heating and cooling cycles. These imidazolium tetrachloroaluminates display a little lower melting point temperatures and lower clear point temperature than the imidazolium chlorides. The molecular organisation is studied by PXRD analysis. The imidazolium tetrachloroaluminates display layer structure in crystal phase, but the layer structure is destroyed when they are heated to mesophase. Besides, the imidazolium tetrachloroaluminates ([Cbim]AlCl₄, [Cmim]AlCl₄ and [Cpim]AlCl₄) show higher conductivity than imidazolium chlorides ([Cmim]Cl, [Cbim] Cl and [Cpim]Cl).

### Funding

This work was supported by the National Natural Science Foundation of China under Grant 51273035 and Fundamental Research Funds for the Central Universities under Grant N130405001.

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