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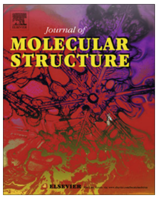

Cholesteryl-containing ionic liquid crystals composed of alkylimidazolium cations and different anions

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HIGHLIGHTS

- Imidazolium-based ionic liquid crystals with cholesteryl mesogens are prepared.
- The ionic liquid crystals include chlorides and tetrachloroaluminates.
- The imidazolium chlorides showed chiral smectic A phase.
- The imidazolium tetrachloroaluminates exhibit chiral nematic phase.

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ABSTRACT

Cholesteryl-containing ionic liquid crystals (ILCs) 1-cholesteryloxycarbonylmethyl(propyl)-3-methyl(butyl)imidazolium chlorides ([Ca-Me-Im]Cl, [Ca-Bu-Im]Cl, [Cb-Me-Im]Cl and [Cb-Bu-Im]Cl) and corresponding imidazolium tetrachloroaluminates ([Ca-Me-Im]$AlCl_4$, [Ca-Bu-Im]$AlCl_4$, [Cb-Me-Im]$AlCl_4$ and [Cb-Bu-Im]$AlCl_4$) were synthesized in this work, and the chemical structure, LC behavior and ionic conductivity of all these ILCs were characterized by several technical methods. The imidazolium-based salts with Cl^- ions showed chiral smectic A (S_A^*) phase on both heating and cooling cycles, while the tetrachloroaluminates exhibited chiral nematic (N^*) phase. The mesophase was confirmed by characteristic LC textures observed by polarizing optical microscopy and typical diffractogram obtained by X-ray diffraction measurements. The samples with similar cholesteryl-linkage component showed similar phase transition temperature and entropy, indicating the cholesteryl component influence predominately on the phase transition rather than alkyl substituents on the imidazole ring. The imidazolium tetrachloroaluminates display relatively low phase transition temperature compared with the precursor chlorides. The functional difference in LC behavior and ionic conductivity were discussed by investigated the structural difference between the Cl^--containing and $AlCl_4$—containing materials. The imidazolium chlorides exhibited layer structure both in crystal and mesophase states, and should be organized with a 'head-to-tail' organization to form interdigitated monolayer structures due to the tight ion pairs. But the imidazolium tetrachloroaluminates displayed layer structure only in crystal phase, and should be organized in 'head-to-head' arrangements form bilayer structures due to loose combination of ion pairs despite of hydrogen-bond and electrostatic attraction interaction.

Introduction

Liquid crystals (LCs) are usually regarded as the fourth state of matter between anisotropic solid and isotropic liquid, and are one kind of soft materials for applications with a long time. Chiral LCs can exhibit a marvelous variety of LC phases including cholesteric phase, chiral smectic phase, and blue phases, and have presented large potential for various applications [1–4]. However, some imperfection (e.g. high melting points) has recently emerged for chiral LCs.

Ionic liquids (ILs) possess a lot of unique properties such as wide liquid temperature range, low volatility, negligible vapor pressure, high thermal stability, good solubility in a wide range of materials, high ionic conductivity, and nonflammability [5–7]. Thus ILs have attracted considerable interest as soft materials for various applications including solvents for chemical synthesis, catalyst, ionic conduction and so on over the past decade [8–10]. Ionic liquid crystals (ILCs) are one kind of ILs exhibiting liquid crystalline properties, which are composed of ionic species and have anisotropic structural organizations in a certain temperature

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range. Both from fundamental and from applied points of view, ILCs are a fascinating class of functional soft materials that combine the properties of ILs and LCs, and have attracted considerable attention recently [11–13]. In fact, ILs can be appropriately designed to obtain liquid crystalline. For example, many imidazolium-based ILCs can be generated simply by increasing the alkyl chain length to increase the self-organization character [14,15]. The structure of ILs goes through a transition from spatially heterogeneous to ILCs due to the increased van der Waals interactions between the increased alkyl length of cationic side-chains, which is observed by Ji et al. using coarse-grained molecular dynamics simulations [16]. For ILCs, the liquid-crystalline behavior 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 [17]. Many types of ILCs have been investigated, which contain different organic cations such as imidazolium [18–20], pyridinium [21–23], pyrrolidinium [24,25], quaternary ammonium and quaternary phosphonium salts [26–28] conjugating different anions such as halide ion, BF_4^-, PF_6^-, $CF_3SO_3^-$ and so on. Most reported ILCs contain single organic cation unit in one ILC molecule. Recently, ILCs containing multiple imidazolium units are reported by Schenkel, which can exhibit smectic A phase [29]; and viologen-based ILCs with bipyridinium cores are reported by Casella, which exhibit rich polymorphism including the ionic smectic A phase and an ordered smectic phase [30]. In particular, imidazolium-based ionic liquids attract considerable attention among these types of ILCs because they give low melting points with high chemical and electrochemical stability, and exhibit excellent ability in anisotropic ionic conductivity, organized reaction media or ordered solvents [31,32]. Usually, the most common long alkyl-substituted imidazolium-based ILCs only show smectic A phases [33]. However, some imidazolium sulphonates ILCs display cubic phases and hexagonal columnar phases [34]. Thus it is interesting to investigate the liquid-crystalline behaviors of imidazolium-based ILCs that contain some functional groups.

In this work, we synthesized a series of imidazolium-based ILCs containing cholesteryl mesogenic groups. Goossens et al. have reported the first imidazolium-based ILCs containing cholesteryl substituents which are connected with a flexible undecyl spacer to the cationic core [35]. Their compounds incorporate a longer and more flexible alkyl spacer between the cholesteryl mesogens and the imidazolium ion pairs, exhibiting chiral smectic A phases at room temperature. In comparison to these cholesteryl-containing ILCs, it is interesting to study the liquid-crystalline behaviors of these kinds of ILCs containing short alkyl spacers between the cholesteryl mesogens and the imidazolium ion pairs. A series of cholesteryl-containing imidazolium-based ILCs with different short chain lengths and anions of Cl^-, and $AlCl_4^-$ were synthesized in this work. The effect of the different substituent was studied by comparing the structures, thermal behaviors, and cation–anion interactions of the cholesteryl-containing imidazolium salts.

Experimental

Materials and methods

Cholesterol, 1-methylimidazole, 1-butylimidazole, aluminum trichloride, 2-chloroacetyl chloride and 4-chlorobutanoyl chloride were obtained from ALDRICH. All commercially available chemicals were used without further purification except 1-methylimidazole and 1-butylimidazole. FT-IR spectra of the synthesized materials were obtained by the KBr method performed on Perkin-Elmer instruments Spectrum One Spectrometer (PerkinElmer, Foster City, CA). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained with a Varian Gemini 300 NMR Spectrometer (Varian Associates, Palo Alto, CA) with fourier transform with dimethyl sulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. The element analyses (EA) were carried out by using an Elementar Vario EL III (Elementar, Germany). Differential scanning calorimetry (DSC) analyses were carried out on a NETZSCH instruments DSC 204 (Netzsch, Wittelsbacherstr, Germany) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Polarizing optical microscopy (POM) was carried out with a Leica DMRX (Leica, Wetzlar, Germany) microscope coupled with a Linkam Scientific Instrument THMSE-600 hot stage and a TMS94 temperature controller (Linkam, Surrey, England). X-ray diffraction (XRD) studies were carried out on a Cu Kα ($\lambda = 1.542$ Å) radiation monochromatized with a Rigaku DMAX-3A X-ray diffractometer (Rigaku, Japan). Ionic conductivities were measured with a RTS-9 four-probe meter (Guangzhou four-point probe technology, Guangzou, China) equipped with a hot stage and temperature controller.

General procedure for the synthesis of cholesteryl chloro-alkylcarboxylic esters

To a solution of cholesterol (0.05 mol, 19.3 g) and pyridine (20 mL) in tetrahydrofuran (THF, 100 mL) was added dropwise with 0.06 mol of 2-chloroacetyl chloride (or 4-chlorobutanoyl chloride), and the reaction mixture was refluxed and stirred for 48 h. Then the mixture was cooled to room temperature, poured into cold water (100 mL) and acidified with 6 N sulfuric acid. The precipitates were isolated by filtration and dried in a vaccum oven, and white crystals of crude product were obtained by recrystallization of the precipitates in chloroform.

Cholesteryl 2-chloroacetate (Ca-Cl)

Yield 87%. IR (KBr): 2941, 2867, 1726, 1468, 1375, 1196, 686. Elem. analysis: found: 75.33% C, 10.15% H; calc.: 75.21% C, 10.23% H. ^1H NMR ($CDCl_3$, δ, ppm): 0.71–2.01 (m, 41H), 2.38 (t, $J = 6$ Hz, 2H), 3.78–3.84 (m, 2H), 4.66–4.73 (m, 1H), 5.41 (t, $J = 6$ Hz, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.9, 18.3, 21.1, 23.3, 23.5, 24.5, 24.6, 24.8, 28.0, 28.1, 31.1, 35.9, 36.0, 36.1, 37.4, 37.5, 38.7, 39.1, 39.2, 41.5, 41.7, 46.2, 50.3, 53.5, 56.3, 74.7, 121.8, 140.1, 172.8.

Cholesteryl 4-chlorobutanoate (Cb-Cl)

Yield 83%. IR (KBr): 2947, 2863, 2835, 1722, 1465, 1190, 683. Elem. analysis: found: 75.53% C, 10.34% H; calc.: 75.80% C, 10.47% H. ^1H NMR ($CDCl_3$, δ, ppm): 0.64–2.02 (m, 43H), 2.36 (t, $J = 6$ Hz, 2H), 2.75–2.79 (m, 2H), 3.76–3.81 (m, 2H), 4.65–4.71 (m, 1H), 5.39 (t, $J = 7$ Hz, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.8, 18.4, 19.1, 21.2, 23.4, 23.6, 24.7, 24.8, 24.9, 28.1, 28.2, 28.3, 31.3, 35.9, 36.0, 36.1, 36.2, 37.4, 37.5, 38.8, 39.0, 39.1, 41.6, 41.7, 46.3, 50.2, 53.6, 56.2, 56.5, 74.8, 121.9, 140.2, 172.4.

Synthesis of imidazolium chloride salts

1-Methylimidazole (0.06 mol, freshly distilled over KOH) was added to a solution of 0.05 mol cholesteryl chloro-alkylcarboxylic ester (Ca-Cl or Cb-Cl) in dry acetonitrile (50 mL) under a nitrogen atmosphere. The solution was refluxed and stirred for 72 h. The solvent was removed under reduced pressure, and the crude product was washed three times with diethyl ether, dried under high vacuum for 24 h to obtain methylimidazolium chloride salts. The product was then transferred into a glovebox for storage.

1-Cholesteryloxycarbonylmethyl-3-methylimidazolium chloride ([Ca-Me-Im]Cl)

Yield 95%. IR (KBr): 2936, 2867, 1723, 1466, 1376, 1182. Elem. analysis: found: 72.53% C, 9.73% H, 5.18% N; calc.: 72.69% C,