Dicationic imidazolium-based ionic liquids and ionic liquid crystals with variously positioned fluoro substituents

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A series of new dicationic imidazolium-based organic salts bearing fluoro substituents on the bent-core unit and/or linker benzene-ring positions has been synthesized and characterized. The properties of these salts, including transition and decomposition temperatures, and density were determined, indicating that their performance is strongly dependent on the positions of the fluoro substituents, the number of carbon atoms in the alkyl group, and the anion present. Examination by polarized optical microscopy showed that the four salts (compounds **4c**, **7a**, **7b** and **8b**, where the alkyl group was $C_{12}H_{25}$–) were mesomorphic and these data were supported by DSC measurements.

Introduction

Liquid crystals (LCs) as soft materials have received considerable attention owing to their fascinating properties[1] and their success in commercial applications.[2] Generally, LCs are fluids showing different mesophases that depend strongly on the combination of ordered and disordered constituent molecules and on the molecular shape. Therefore, the constituent molecular architectures are crucial factors both for mesomorphism and for the physical/chemical properties that characterize LC mesophases.[3] In order to investigate structure–property relationships and generate targeted results, many materials have been prepared,[4–6] but as is ever the case, only a very small percentage of them is of suitable quality for commercial applications.

Among the tools available to synthetic chemists to tune LC properties, selective fluorination is among the most productive,[7] having been extensively developed and explored since the introduction of diversely located fluoro substituents including terminal chain,[8] linking arm,[9] or core position[10] provide an excellent opportunity for investigating the relationship between structures and properties and for modifying and optimizing the physical/chemical properties of compounds. In 20 years every semiconductor and LCD plant will have its own on-site fluorine generator.[7b] Therefore, targeted materials can be generated which may lead to active matrix applications[11] as well as other display applications enabling ferroelectric–antiferroelectric switchable devices,[12] electroluminescence,[13] and semiconductors.[14]

Ionic liquid crystals (ILCs), that are considered to be the combination of LCs and ionic liquids (ILs), are also a class of liquid-crystalline compounds.[15] Owing to the presence of anions and cations, some properties of ILCs, such as ion conductivity, non-volatility, low viscosity, low melting points and tunable polarity, are significantly different from conventional, neutral LCs, but these materials still display mesophases[16] that can allow for ion-conductive materials, organic reaction media or self-assembled nanostructured materials. Imidazolium salts, that have been well-investigated as ionic liquids, have also been introduced into ILCs systems.[16a,17] Some imidazolium-based ILCs including symmetrical and unsymmetrical molecular frameworks were generated and most of them show smectic phases. For example, a series of unsymmetrical monocationic imidazolium-based ILCs which contain rigid cores are known[18] as well as some self-organized imidazolium-based materials that form columnar phases.[19] Their mesomorphic properties and potential applications as solvents, electrolytes, high ion transport materials and templates have also been extensively developed. Considering the potential applications, the introduction of fluoro substituents at diverse positions in compounds as in more conventional, neutral LCs (*vide supra*) is a feasible route. However, although many fluorinated LCs have been synthesized and shown to display excellent modified properties due to the existence of fluoro substituents, investigations involving this kind of ILC-bearing fluoro substituents have been reported only rarely.[20] In this work, we describe the design and syntheses of twelve dicationic imidazolium-based organic salts with fluoro substituents and study the impact of fluoro groups in varying positions, of alkyl chain lengths, and of anions on their properties.

Experimental section

General methods

All the reagents were available commercially and were used as purchased without further purification. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 300 MHz spectrometer (Bruker AMX 300) operating at 300, 282 and 75 MHz, respectively, by using $CDCl_3$ or CD_3CN as locking solvents unless otherwise indicated. Chemical shifts are reported in ppm relative to $CFCl_3$ for ^{19}F NMR spectra and TMS for ^{1}H and ^{13}C NMR spectra. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an autocool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 °C to

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0 °C, heating to 400 °C, cooling from 400 °C to −30 °C at 10 °C min^{-1}, and then heating and cooling again. The transition temperature, T_m, was taken as peak maximum. Density was measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C min^{-1} from 25 °C to 600 °C in a dynamic nitrogen atmosphere. Elemental analyses were determined using an Exeter CE-440 Elemental Analyzer. Analysis by polarized optical microscopy was carried out using an Olympus BX50 polarizing microscope in conjunction with a Linkam LTS350 hot stage and a Linkam TMS92 control unit.

General procedures for the preparation of precursors of 1a–c and 5 (Williamson alkylation method)

A mixture of 4-iodophenol (4.40 g, 20 mmol) for **1a–c** and 4-bromo-2-fluorophenol (3.8 g, 20 mmol) for **5**, K_2CO_3 (5.5 g, 40 mmol) and KI (0.664 g, 4 mmol) in DMF (30 mL) was stirred for 30 min at 25 °C. Then 1-bromooctane (4.6 g, 24 mmol) for **1a**, 1-bromodecane (5.3 g, 24 mmol) for **1b**, and 1-bromododecane (6.0 g, 24 mmol) for **1c** and **5** were added slowly. The reaction mixture was heated at 150 °C for 12 h; then cooled to room temperature, filtered and concentrated to 20 mL. 1 M HCl (15 mL) was added to the concentrated solution, and the mixed solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with 1 M HCl (2 × 20 mL), H_2O (3 × 20 mL), and dried over Na_2SO_4. After the solvents were removed, the residue was purified using recrystallization from methanol to give **1a–c** and **5**.

Compounds 1a and 1c. 1a: yellow liquid (4.8 g), yield 72%; **1c**: white solid (6.3 g), yield 81%; ^{1}H NMR ($CDCl_3$) analysis was in good agreement with the literature.[21]

Compound 1b. Yellow liquid (6.8 g), yield 94%; ^{1}H NMR ($CDCl_3$): δ 7.52 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 3.89 (t, J = 15.0 Hz, 2H), 1.74 (m, J = 30.0 Hz, 2H), 1.25 (m, 14H), 0.86 (t, J = 12.0 Hz, 3H).

Compound 5. White solid (5.0 g), yield 70%; ^{1}H NMR ($CDCl_3$): δ 7.22–7.18 (m, J = 12.0 Hz, 1H), 7.16–7.12 (m, J = 12.0 Hz, 1H), 6.81 (t, J = 21.0 Hz, 1H), 3.97 (t, J = 12.0 Hz, 2H), 1.78 (m, J = 30.0 Hz, 2H), 1.28 (m, 18H), 0.86 (t, J = 15.0 Hz, 3H); ^{19}F NMR: δ −131.2 (t, J = −19.7 Hz, 1F).

General procedures for the preparation of precursors of 2a–c and 6 (Ullmann-type coupling reaction)

A mixture of **1a–c** (10 mmol) for **2a–c**, **5** (10 mmol) for **6**, imidazole (1.0 g, 15 mmol), K_2CO_3 (4.1 g, 30 mmol), CuI (0.19 g, 1 mmol) and L-proline (0.23 g, 2 mmol) was stirred in dry DMSO (30 mL) in nitrogen atmosphere at 110 °C for 12 h; then cooled to room temperature and filtered. 1 M $NH_3 \cdot H_2O$ (20 mL) was added to the solution, and then the mixed solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with 1 M $NH_3 \cdot H_2O$ (2 × 20 mL), H_2O (3 × 20 mL), and dried over Na_2SO_4. After the solvent was removed, the residue was purified using column chromatography (SiO_2) to give pure **2a–c** and **6**.

Compound 2a–c. ^{1}H NMR ($CDCl_3$) analyses were in good agreement with the literature.[18,21]

Compound 6. White solid (1.9 g), yield 56%; ^{1}H NMR ($CDCl_3$): δ 7.73 (s, 1H), 7.24 (s, 1H), 7.16 (s, 1H), 7.14 (m, J = 3.0 Hz, 1H), 7.10 (m, J = 6.0 Hz, 1H), 7.06–6.98 (m, J = 24.0 Hz, 2H), 4.04 (t, J = 12.0 Hz, 2H), 1.82 (m, J = 27.0 Hz, 2H), 1.25 (m, 18H), 0.86 (t, J = 12.0 Hz, 3H).

General procedures for the preparation of compounds 3a–c and 7a–c

Imidazole precursors **2a–c** (1.2 mmol) with 1,4-bis(chloromethyl)tetrafluorobenzene (0.5 mmol) for **3a–c**; imidazole precursors **2c** and **6** (1.2 mmol) with α,α'-dibromo-*p*-xylene (0.5 mmol) for **7a** and **7b**, respectively; **6** (1.2 mmol) and 1,4-bis(chloromethyl)tetrafluorobenzene (0.5 mmol) for **7c**; and CH_3CN (5 mL) were placed in a Pyrex glass tube. After the mixture was cooled to −78 °C, the tube was evacuated and sealed, then warmed to room temperature. The reaction mixture was heated to 110 °C and stirred for 12 h. After cooling and carefully opening the tube, the reaction mixture was removed and dried under reduced pressure. The residue was washed three times with hexane and pure compounds **3a–c** and **7a–c** were obtained.

Compound 3a. White solid (0.35 g), yield 89%; ^{1}H NMR ($CDCl_3$): δ 11.00 (s, 2H), 8.73 (s, 2H), 7.61 (d, J = 9.0 Hz, 4H), 7.49 (s, 2H), 6.95 (d, J = 9.0 Hz, 4H), 6.08 (s, 4H), 3.92 (t, J = 15.0 Hz, 4H), 1.75 (m, J = 30.0 Hz, 4H), 1.28 (m, 20H), 0.85 (t, J = 15.0 Hz, 6H); ^{19}F NMR: δ −139.8 (s, 4F); ^{13}C NMR: δ 160.42, 135.81, 127.25, 123.45, 120.65, 115.89, 68.58, 41.49, 31.73, 29.28, 29.26, 29.11, 29.02, 25.91, 22.59, 14.03. Anal. Calcd for $C_{42}H_{52}N_4O_2F_4Cl_2$ (791.79): C, 63.71; H, 6.62; N, 7.13; found: C, 63.70; H, 6.73; N, 7.16%.

Compound 3b. White solid (0.39 g), yield 92%; ^{1}H NMR ($CDCl_3$): δ 11.05 (s, 2H), 8.77 (s, 2H), 7.62 (d, J = 9.0 Hz, 4H), 7.44 (s, 2H), 6.97 (d, J = 9.0 Hz, 4H), 6.09 (s, 4H), 3.94 (t, J = 12.0 Hz, 4H), 1.74 (m, J = 30.0 Hz, 4H), 1.26 (m, 28H), 0.85 (t, J = 12.0 Hz, 6H); ^{19}F NMR: δ −139.8 (s, 4F); ^{13}C NMR: δ 160.43, 135.84, 127.22, 125.05, 123.45, 120.63, 115.93, 68.58, 41.48, 31.88, 29.54, 29.34, 29.30, 29.04, 25.94, 22.67, 14.11. Anal. Calcd for $C_{46}H_{60}N_4O_2F_4Cl_2$ (847.89): C, 65.16; H, 7.13; N, 6.61; found: C, 65.10; H, 7.38; N, 6.71%.

Compound 3c. White solid (0.39 g), yield 86%; ^{1}H NMR ($CDCl_3$): δ 11.04 (s, 2H), 8.77 (s, 2H), 7.60 (d, J = 9.0 Hz, 4H), 7.45 (s, 2H), 6.97 (d, J = 9.0 Hz, 4H), 6.09 (s, 4H), 3.94 (t, J = 15.0 Hz, 4H), 1.76 (m, J = 27.0 Hz, 4H), 1.25 (m, 36H), 0.85 (t, J = 12.0 Hz, 6H); ^{19}F NMR: δ −139.7 (s, 4F); ^{13}C NMR: δ 160.45, 135.88, 127.25, 125.07, 123.40, 120.58, 115.94, 68.60, 41.50, 31.87, 29.63, 29.59, 29.57, 29.56, 29.52, 29.32, 29.04, 25.93, 22.65, 14.05. Anal. Calcd for $C_{50}H_{68}N_4O_2F_4Cl_2$ (904.00): C, 66.43; H, 7.58; N, 6.20; found: C, 65.75; H, 7.61; N, 6.31%.

Compound 7a. White solid (0.40 g), yield 86%; ^{1}H NMR (d_6-DMSO): δ 9.86 (s, 2H), 8.20 (s, 2H), 7.95 (s, 2H), 7.65 (d, J = 12.0 Hz, 4H), 7.55 (s, 4H), 7.14 (d, J = 9.0 Hz, 4H), 5.47 (s, 4H), 4.01 (t, J = 15.0 Hz, 4H), 1.70 (m, J = 15.0 Hz, 4H), 1.21 (m, 36H), 0.82 (t, J = 15.0 Hz, 6H); ^{13}C NMR: δ 159.93, 135.71, 129.53, 128.02, 123.92, 123.41, 122.35, 115.99, 68.52, 52.29, 31.68, 29.41, 29.38, 29.36, 29.12, 29.08, 28.91, 25.82, 22.45, 14.33. Anal. Calcd for $C_{50}H_{72}N_4O_2Br_2$ (920.94): C, 65.21; H, 7.88; N, 6.08; found: C, 65.40; H, 7.95; N, 6.19%.

Compound 7b. White solid (0.40 g), yield 82%; ^{1}H NMR (d_6-DMSO): δ 9.88 (s, 2H), 8.23 (s, 2H), 7.96 (s, 2H), 7.81 (d, J = 3.0 Hz, 2H), 7.77 (d, J = 3.0 Hz, 2H), 7.54 (s, 4H), 7.40 (t, J = 18.0 Hz, 2H), 5.46 (s, 4H), 4.01 (t, J = 15.0 Hz, 4H), 1.72 (m, J = 15.0 Hz, 4H), 1.21 (m, 36H), 0.81 (t, J = 12.0 Hz, 6H); ^{19}F NMR: δ −139.7 (t, J = 28.2 Hz, 2F); ^{13}C NMR: δ 153.10, 150.51, 147.99, 136.04, 135.47, 129.58, 123.48, 122.31, 118.96, 115.96, 111.46, 111.15, 69.64, 52.38, 31.70, 29.41, 29.36, 29.07, 28.82, 25.73, 22.49, 14.35. Anal. Calcd for $C_{50}H_{70}N_4O_2F_2Br_2$ (956.92): C, 62.76; H, 7.37; N, 5.85; found: C, 61.78; H, 7.42; N, 5.76%.

Compound 7c. White solid (0.36 g), yield 76%; ^{1}H NMR ($CDCl_3$): δ 11.10 (s, 2H), 8.82 (s, 2H), 7.59 (d, J = 6.0 Hz, 2H), 7.50 (m, J = 30.0 Hz, 2H), 7.45 (s, 2H), 7.06 (t, J = 18.0 Hz, 2H), 6.10 (s, 4H), 4.05 (t, J = 12.0 Hz, 4H), 1.82 (m, J = 21.0 Hz, 4H), 1.24 (m, 36H), 0.86 (t, J = 15.0 Hz, 6H); ^{19}F NMR: δ −128.9 (t, J = 19.9 Hz, 2F), −139.7 (s, 4F); ^{13}C NMR: δ 154.08, 150.75, 148.95, 136.16, 126.77, 125.27, 120.29, 118.55, 115.34, 110.87, 69.74, 41.56, 31.83, 29.56, 29.44, 29.25, 28.91, 25.75, 22.59, 14.00. Anal. Calcd for $C_{50}H_{66}N_4O_2F_6Cl_2$ (939.98): C, 63.89; H, 7.08; N, 5.96; found: C, 62.82; H, 7.31; N, 5.96%.

General procedures for the preparation of compounds 4a–c and 8a–c

Compounds **3a–c** or **7a–c** (0.5 mmol) and $LiNTf_2$ (0.43 g, 1.5 mmol) were added into CH_3OH (20 mL). The reaction mixture was stirred at 25 °C for 24 h, then the solvent was evaporated under reduced pressure, and the residue was washed five times with water, and then dried under vacuum. Pure compounds **4a–c** and **8a–c** were generated.

Compound 4a. White solid (0.60 g), yield 93%; ^{1}H NMR ($CDCl_3$): δ 8.86 (s, 2H), 7.54 (s, 2H), 7.44 (d, J = 6.0 Hz, 4H), 7.39 (s, 2H), 6.93 (d, J = 9.0 Hz, 4H), 5.60 (s, 4H), 3.93 (t, J = 15.0 Hz, 4H), 1.75 (m, J = 27.0 Hz, 4H), 1.28 (m, 20H), 0.86 (t, J = 15.0 Hz, 6H); ^{19}F NMR: δ −79.0 (s, 12F), −140.7 (s, 4F); ^{13}C NMR: δ 161.64, 135.29, 127.86, 124.86, 122.61, 116.84, 69.50, 42.06, 32.61, 30.15, 30.10, 30.03, 29.99, 29.90, 23.47, 14.87. Anal. Calcd for $C_{46}H_{52}N_6O_{10}F_{16}S_4$ (1281.17): C, 43.12; H, 4.09; N, 6.56; found: C, 43.70; H, 4.15; N, 6.60%.

Compound 4b. White solid (0.61 g), yield 91%; ^{1}H NMR ($CDCl_3$): δ 8.92 (s, 2H), 7.57 (s, 2H), 7.42 (d, J = 24.0 Hz, 6H), 6.96 (d, J = 9.0 Hz, 4H), 5.63 (s, 4H), 3.94 (t, J = 12.0 Hz, 4H), 1.78 (m, J = 21.0 Hz, 4H), 1.26 (m, 28H), 0.86 (t, J = 12.0 Hz, 6H); ^{19}F NMR: δ −78.9 (s, 12F), −140.6 (s, 4F); ^{13}C NMR: δ 160.88, 134.62, 126.94, 126.03, 124.08, 123.35, 115.92, 68.68, 41.33, 31.88, 29.54, 29.35, 29.30, 29.06, 26.00, 22.64, 14.07. Anal. Calcd for $C_{50}H_{60}N_6O_{10}F_{16}S_4$ (1337.28): C, 44.91; H, 4.52; N, 6.28; found: C, 45.45; H, 4.65; N, 6.50%.

Compound 4c. White solid (0.63 g), yield 90%; ^{1}H NMR ($CDCl_3$): δ 8.89 (s, 2H), 7.56 (s, 2H), 7.42 (d, J = 3.0 Hz, 4H), 7.40 (s, 2H), 6.95 (d, J = 9.0 Hz, 4H), 5.63 (s, 4H), 3.95 (t, J = 12.0 Hz, 4H), 1.77 (m, J = 27.0 Hz, 4H), 1.25 (m, 36H), 0.86 (t, J = 12.0 Hz, 6H); ^{19}F NMR: δ −78.9 (s, 12F), −140.5 (s, 4F); ^{13}C NMR: δ 160.90, 134.56, 126.93, 126.02, 124.10, 121.76, 115.92, 68.69, 41.34, 31.91, 29.65, 29.58, 29.55, 29.36, 29.33, 29.15, 29.06, 25.94, 22.67, 14.08. Anal. Calcd for $C_{54}H_{68}N_6O_{10}F_{16}S_4$ (1393.39): C, 46.55; H, 4.92; N, 6.03; found: C, 46.59; H, 4.94; N, 6.04%.

Compound 8a. White solid (0.67 g), yield 92%; ^{1}H NMR (d_6-DMSO): δ 9.80 (s, 2H), 8.20 (s, 2H), 7.94 (s, 2H), 7.64 (d, J = 9.0 Hz, 4H), 7.54 (s, 4H), 7.14 (d, J = 9.0 Hz, 4H), 5.46 (s, 4H), 4.02 (t, J = 15.0 Hz, 4H), 1.70 (m, J = 12.0 Hz, 4H), 1.22 (m, 36H), 0.81 (t, J = 6.0 Hz, 6H); ^{19}F NMR: δ −78.6 (s, 12F); ^{13}C NMR: δ 160.99, 136.74, 130.54, 129.05, 124.96, 124.44, 123.42, 117.02, 69.55, 53.38, 32.71, 30.44, 30.42, 30.39, 30.15, 30.11, 29.94, 26.85, 23.50, 15.35. Anal. Calcd for $C_{54}H_{72}N_6O_{10}F_{12}S_4$ (1321.42): C, 49.08; H, 5.49; N, 6.36; found: C, 49.28; H, 5.54; N, 6.36%.

Compound 8b. White solid (0.64 g), yield 94%; ^{1}H NMR (d_6-DMSO): δ 9.83 (s, 2H), 8.22 (s, 2H), 7.94 (s, 2H), 7.79 (m, J = 15.0 Hz, 2H), 7.53 (s, 4H), 7.40 (t, J = 18.0 Hz, 4H), 5.45 (s, 4H), 4.10 (t, J = 12.0 Hz, 4H), 1.69 (m, J = 21.0 Hz, 4H), 1.21 (m, 36H), 0.81 (t, J = 15.0 Hz, 6H); ^{19}F NMR: δ −78.6 (s, 12F), −131.5 (s, 2F); ^{13}C NMR: δ 153.34, 150.71, 148.07, 147.93, 136.00, 135.42, 129.53, 127.66, 123.47, 122.33, 118.95, 115.92, 111.44, 69.61, 52.42, 31.66, 29.38, 29.33, 29.07, 29.04, 28.79, 25.70, 22.48, 14.31. Anal. Calcd for $C_{54}H_{70}N_6O_{10}F_{14}S_4$ (1357.41): C, 47.78; H, 5.20; N, 6.19; found: C, 47.43; H, 5.09; N, 6.03%.

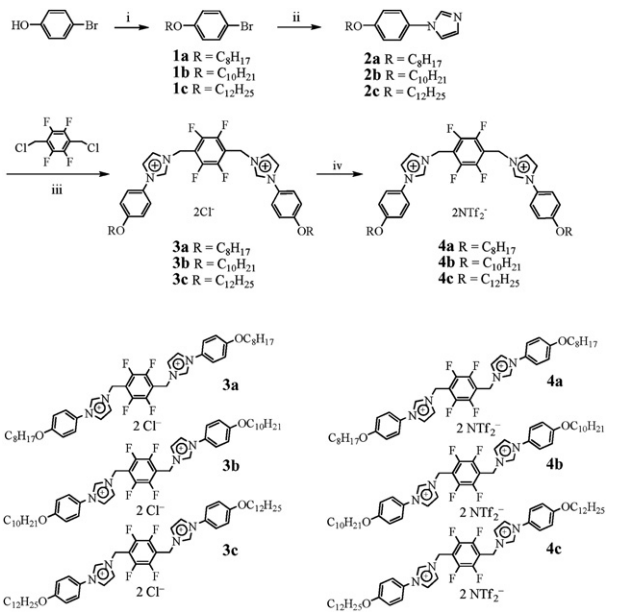
Compound 8c. White solid (0.65 g), yield 91%; ^{1}H NMR ($CDCl_3$): δ 8.90 (s, 2H), 7.57 (s, 2H), 7.42 (s, 2H), 7.26 (m, J = 12.0 Hz, 4H), 7.03 (t, J = 21.0 Hz, 2H), 5.63 (s, 4H), 4.03 (t, J = 15.0 Hz, 4H), 1.82 (m, J = 27.0 Hz, 4H), 1.25 (m, 36H), 0.86 (t, J = 15.0 Hz, 6H); ^{19}F NMR: δ −78.9 (s, 12F), −129.1 (s, 2F), −140.5 (s, 4F); ^{13}C NMR: δ 154.11, 135.04, 123.84, 122.49, 119.33, 115.22, 111.68, 111.37, 69.87, 41.42, 31.91, 29.64, 29.57, 29.52, 29.33, 28.97, 25.82, 22.67, 14.08. Anal. Calcd for $C_{54}H_{66}N_6O_{10}F_{18}S_4$ (1429.37): C, 45.38; H, 4.65; N, 5.88; found: C, 45.67; H, 4.67; N, 5.88%.

Results and discussion

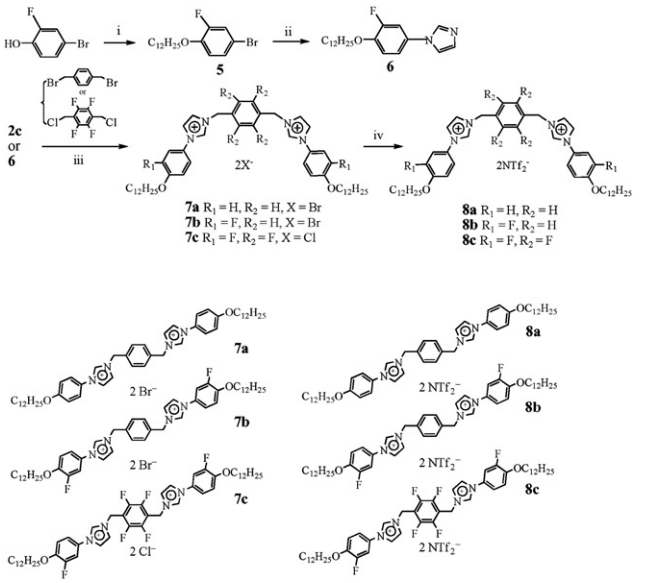
Initially, we synthesized six dicationic imidazolium-based compounds (**3a–c** and **4a–c**) with various alkyl groups (–C_8H_{17}, –$C_{10}H_{21}$ and –$C_{12}H_{25}$), and discovered that the length of the alkyl group plays an important role in the performance properties of the salts, especially on the appearance of mesophases. When the alkyl group is C-12 (compound **4c**), the mesophase may be formed. Then using –$C_{12}H_{25}$ as a substituent group, another six dicationic imidazolium-based compounds (**7a–c** and **8a–c**) were synthesized, in which **7b–c** and **8b–c** were fluorinated with the introduction of fluoro substituents at different positions.

Compounds **7a**, **7b** and **8b** show LC mesophases. All twelve compounds, **3a–c**, **4a–c**, **7a–c** and **8a–c**, were characterized by nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and elemental analysis (EA). Compounds **4c**, **7a**, **7b** and **8b** were also analyzed by polarized optical microscopy (POM). The synthetic routes using standard organic methodology are shown in Schemes 1 and 2.

Compounds **3a–c** and **4a–c** were prepared by the convergent syntheses of 1,4-bis(chloromethyl)tetrafluorobenzene and rigid bent-core imidazole derivatives with different alkyl groups. Compounds **4a–c** were generated from the anion exchange of compounds **3a–c** with $LiNTf_2$ (lithium bis(trifluoromethanesulfonyl)amide) (Scheme 1). The chemical/physical properties of compounds **3a–c** and **4a–c** including transition and thermal decomposition temperatures, and densities are given in Table 1. For the six compounds, changing of the anion from Cl^- to NTf_2^- results in an increase in density and thermal decomposition temperature which demonstrates the positive effect of the stabilizing NTf_2^- anion over that of chloride. Transition temperature is one of the most important properties. Concomitantly with the change in alkyl group from $–C_8H_{17}$, $–C_{10}H_{21}$ to $–C_{12}H_{25}$, the transition temperatures distinctly change. Compounds **3a,b** and **4a,b**, which contain $–C_8H_{17}$ and $–,C_{10}H_{21}$ groups, respectively, display low melting points with the exception for compound **3a** which exhibits not only a low melting point at 56 °C but also a transition arising from supercooling from crystal to crystal at 36 °C. The melting points for salts **3a,b** and **4a,b** are below 100 °C; therefore, they fall into the ionic liquid class. For **3c** and **4c** with $–C_{12}H_{25}$ alkyl substituents, the different anion defines their properties. For example, with chloride ion, compound **3c** is an ionic liquid since only one transition temperature, namely the melting point at 60 °C is



Scheme 1 Syntheses of compounds **3a–c** and **4a–c**. *Reagents and conditions*: (i) RBr, K_2CO_3, KI, DMF, 150 °C, 12 h; (ii) imidazole, K_2CO_3, CuI, L-proline, dry DMSO, 110 °C, 12 h; (iii) CH_3CN, 110 °C, 12 h; (iv) $LiNTf_2$, CH_3OH, rt, 24 h.



Scheme 2 Syntheses of compounds **7a–c** and **8a–c**. *Reagents and conditions*: (i), (ii), (iii) and (iv) are the same as in Scheme 1.

observed; however, when the anion is NTf_2^-, compound **4c** is an ionic liquid crystal and does show liquid crystal properties. Thus, the compound melts at 82 °C (Cr–SmA) and clears at 79 °C (SmA–Iso). The investigation of the six compounds shows that when the alkyl group was $–C_{12}H_{25}$, the mesophase may be present.

Therefore, using $–C_{12}H_{25}$ as the long alkyl group, we synthesized six additional dicationic compounds (**7a–c** and **8a–c**) with the concomitant introduction of fluoro substituents (Scheme 2), and investigated the effect of this phenomenon on the property–structure relationship. The transition and thermal decomposition temperatures, and densities of **7a–c** and **8a–c** are shown in Table 1. As reported for **3a–c** and **4a–c**, the densities and thermal

Table 1 Thermal behavior of the new compounds

Compound	Density/g cm^{-3}	Transition	T/°C	T_d/°C
3a	1.22	Cr–Cr′	36	194
		Cr′–Iso	56	
4a	1.38	Cr–Iso	64	317
7a	1.25	Cr–SmA	106	250
		SmA–Iso (dec)	299	
8a	1.36	Cr–Iso	85	325
3b	1.28	Cr–Iso	50	198
4b	1.39	Cr–Iso	74	318
7b	1.31	Cr–Cr′	75	250
		Cr′–M	133	
		M–SmA	145	
		SmA–Iso (dec)	289	
8b	1.38	Cr–Iso	81	320
		(SmÃ–Iso)	(33)	
3c	1.21	Cr–Iso	60	215
4c	1.36	Cr–Cr′	63	334
		Cr′–Iso	82	
		(SmA–Iso)	(79)	
7c	1.21	Cr–Iso	77	195
8c	1.40	Cr–Cr′	43	324
		Cr′–Iso	84	

decomposition temperatures of compounds **8a–c** which contain NTf_2^- are much higher than the corresponding compounds **7a–c** with Cl^-/Br^- anions. The thermal decomposition temperature data show that the compounds containing NTf_2^- anions have very high stability which is beneficial for possible applications. The densities of compounds bearing fluoro substituents are higher than those of their congeners without such substituents. As we had shown earlier, it is not surprising that compounds exhibiting higher densities are those with the larger amounts of fluorine.[22]

Thermal behavior

The most important property is the transition temperature determined by optical microscopy and DSC. The thermal behavior is given in Table 1 and shows that with the exception of compounds **7a** and **7b**, all compounds melt below 100 °C and so can formally be considered as ionic liquids. Structurally, **7a** and **7b** differ by having the central ring as a 1,4-phenylene and by having a halide counter-anion, whereas all the other compounds have the much more sterically demanding bis(trifluoromethanesulfonyl)amide (NTf_2^-) anion and/or and 2,3,5,6-tetrafluorophenylene ring. With the exception of these two compounds and **8b** and **4c**, which are liquid-crystalline, the compounds melt between 50 and 85 °C with little systematic variation in melting point. Some of the compounds show solid-state polymorphism.

Closer examination of **4c**, **7a**, **7b** and **8b** by polarized optical microscopy (POM) revealed that they were ionic liquid crystals. Compounds **7a** and **7b** behaved in a similar fashion. Thus, **7a**, melted at 106 °C to give a highly viscous fluid that was clearly birefringent and could, with difficulty, be spread by the application of mechanical strain. As the temperature was increased, the viscosity of the sample gradually dropped and it was clear that the material was in a liquid crystal mesophase. On approaching 280 °C, the viscosity was such that the preparation was now quite free flowing and it was possible to see textural features characteristic of an SmA phase, including focal-conic and homeotropic regions. Cooling from these temperatures allowed quite well-developed textures to form. However, on heating further to 299 °C, the compound began to clear and showed distinct signs of decomposition, confirmed by the fact that cooling the cleared material did not lead to any signs of the SmA phase seen on heating. Decomposition at such a temperature is not surprising.

Compound **7b** behaved in a broadly similar manner, except that on heating a transition was seen at 133 °C at which temperature the sample visibly softened and could be persuaded to flow when subjected to mechanical strain, although its viscosity was very high. Then, at 145 °C, a second transition was seen which could be identified as an SmA phase on further heating as described for **7a**. Clearing at 289 °C was again accompanied by extensive decomposition so that no texture could be observed on further cooling. The identity of the phase observed between 133 and 145 °C (represented as M in Table 1) is not at this stage obvious. Rather few mesophase types are found for truly ionic liquid crystals, being mainly SmA and SmB with, occasionally, less common phases such as the tetragonal T phase described by Skoulios and co-workers.[23] Textural changes on cooling through the transition were minimal, although it was not possible to obtain a very well-developed SmA texture from which to observe. On balance, it is considered most likely that this is an SmB phase, but the label M is retained in the absence of a definitive identification.

For compound **4c**, the phase behavior was different. Thus on heating, a Cr–Cr′ transition was seen at 63 °C and then at 82 °C the compound melted directly to the isotropic liquid. It was necessary to take care when observing this behavior for just below the melting point at 79 °C, a monotropic SmA phase was seen. Observed between normal glass cover slips, it was not easy to pick out a texture, but using 5 μm cells treated with nylon to give planar alignment, the phase was readily identifiable. Thus, the cell was filled at 90 °C and then allowed to cool—the characteristic texture is seen in Fig. 1.

On heating, compound **8b** melted directly to the isotropic liquid at 81 °C and, on cooling between glass slides showed some evidence of a monotropic transition close to room temperature. However, the sample was very weakly birefringent and so it was difficult to discern what the texture was. Therefore, the sample was prepared in 5 μm cells in both planar and homeotropic (lecithin) alignment by filling in the isotropic state and then cooling. In the planar cells, a transition was observed at about 25 °C; re-heating the sample showed a clearing point of 33 °C. The discrepancy between the temperature at which the texture appears on cooling and the observed thermodynamic clearing point is much larger than one would normally expect to see. In this case, the hysteresis is attributed to the very high viscosity of the sample at these temperatures and support for this assertion comes from the observation that on standing at 29 °C having cooled from the isotropic state, a texture is observed (Fig. 2a). The texture that is seen is not characteristic of an SmA phase and indeed shows features more commonly associated with a columnar phase. However, on viewing the sample as a preparation under homeotropic alignment, the texture shown in Fig. 2b was observed, namely Maltese crosses. This is characteristic of the SmÃ phase, a modulated ribbon phase with *c*2*mm* symmetry; the molecular organization in such a phase is shown as Fig. 3. The same organization is characteristic of the Col_r and B1 phases and it is this that explains the similarity with the texture of a columnar phase.

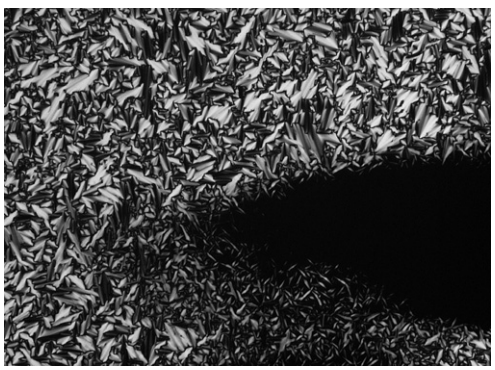
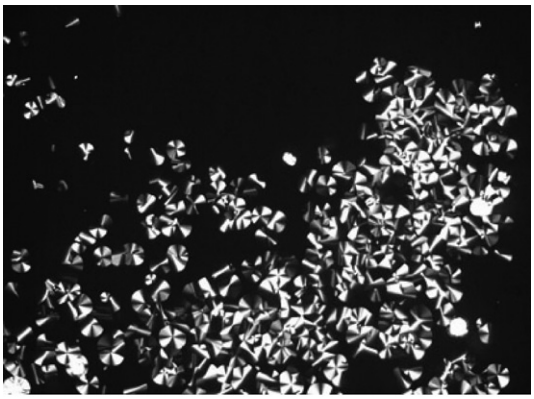
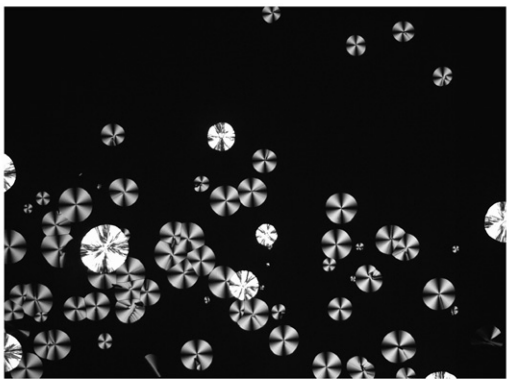


Fig. 1 Representative POM texture of **4c**: a typical focal-conic LC texture in smectic A phase at 76 °C on cooling with some homeotropic area (black).



(a)



(b)

Fig. 2 Some representative textures of **8b**. (a) A typical fan-like LC texture in a planar cell obtained at 29 °C on standing isothermally; (b) some Maltese crosses in a homeotropic cell at 29 °C.

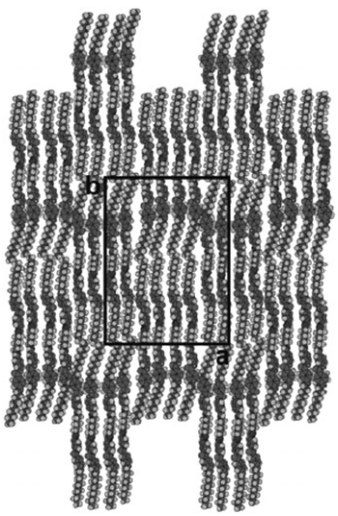


Fig. 3 An undulating ribbon phase with *c2mm* symmetry in **8b**. This is taken from ref. 24 (reproduced by permission of The Royal Society of Chemistry).

Conclusions

In summary, we have successfully synthesized and characterized a new series of dicationic imidazolium-based organic salts (ionic liquids and ionic liquid crystals) by employing fluorine-containing substituents in different positions, with long-chain alkyl groups ($-C_8H_{17}$, $-C_{10}H_{21}$ and $-C_{12}H_{25}$), and varying anions. The investigation reveals that (a) the introduction of fluoro substituents into the linker or core benzene-ring positions of the compounds such as **4c** and **8b** in comparison with **8a** and **8c**, respectively, is a feasible route for the synthesis of ionic liquid crystals, and for the investigation of property–structure relationships; and (b) the long alkyl groups and different anions are also crucial factors for modifying the chemical/physical properties.

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