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# Fluorinated imidazolium salts having liquid crystal characteristics

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# ABSTRACT

A family of fluorinated imidazolium salts showing liquid–crystalline properties in a wide temperature range was developed. These fluorinated ionic liquid crystals, due to their intrinsic hydrophobicity, high thermal stability and good conductivity, are suitable candidates to be used as electrolytes in electrochemical devices such as Dye Sensitized Solar Cell (DSSC) or lithium batteries.

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## 1. Introduction

Liquid crystal materials have been intensively studied over the years and, thanks to their uncommon optical characteristic, they have found applications in a wide variety of fields: main exploited features are high birefringence (polarizers, laser systems), fast electro-optical response (displays, optical switches, tuneable photonic filters, electrochromic windows) and thermo-optical modification (thermometers, sensors) [1].

Among them, ionic liquid crystals are liquid-crystalline compounds that incorporate anions and cations, combining the typical characteristics of both ionic liquids and liquid crystals. As ionic liquids, they have high electrochemical and thermal stability, low vapour pressure and a relatively high ionic conductivity considering their high viscosity [2–6].

Their use ranges from chemical synthesis to electrolyte systems, with an additional liquid crystal behaviour that opens up to a unique anisotropic current conductivity [7,8].

More specifically, imidazolium ionic liquid crystals show typically a well-defined smectic phase A (SmA), allowing these salts to get liquid crystalline properties in different temperature ranges. As a consequence, their conductivity is better than the usual imidazolium ionic liquids at the same concentration and viscosity, especially when properly oriented in their smectic form. The liquid crystal temperature range can be tailored according to the specific application, and these salts are good candidates for electrolytes in electrochemical devices (e.g. DSSC, electrochemical capacitors and lithium batteries [9,10]) to

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provide a better long-term stability both by themselves and in combination with usual electrolytes [11–13].

The ionic liquid properties can be tuned through the choice of anions and cations to get the desired physicochemical and toxicological characteristics required by the specific application [14,15]. In the last decade environmental impact of ionic liquids have been specifically addressed [16]: toxicity of cations and anions must be studied separately, and overall toxicity of the salts depends also on the concentration [17] and does not always increase with the growth of alkyl side chains [18].

The introduction of poly-fluorinated ionic liquids is a strategy to further improve hydrophobicity of the products [19–23]; the presence of the mesophases can be preserved by proper synthetic strategy previously developed by Daunia Solar Cell [9,24,25].

In the present study we have developed a solvent-free synthesis of fluorinated imidazolium salts with high molecular weight alkyl chains having liquid-crystalline properties. The introduction of long alkyl chains (C1–C10) on the imidazolium core gives amphiphilic properties leading to an increase of both orientational order and layered structure: this is due to the micro phase separation of the hydrophilic and hydrophobic components of cations. At the same time, the molecules exhibit greater hydrophobicity and chemical stability thanks to the high level of fluorinated carbons.

More specifically, due to great environmental and health concerns towards long perfluoroalkylated substances (PFAs) we focused on poly-fluoroalkyl chains involving no more than six carbon atoms (Fig. 1) [26–28].

# 2. Experimental

#### 2.1. Material and methods

All products obtained were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR and ESI-MS spectra; mesophase transition temperatures were

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Fig. 1. General molecular structure of the synthetized fluorinated imidazolium salts; p = 1, 4, 6, 10 and X = I; p = 4 and  $X = BF_4$ .

determined by differential scanning calorimetric (DSC) and by polarized optical microscopy (POM) on heating and cooling stage.

All reactions were carried out under argon using standard Schlenk techniques and flame-dried glassware. Solvents: dichloromethane (DCM), diethyl ether (Et<sub>2</sub>O), petroleum ether referring to a fraction of bp 60–80 °C, acetonitrile (CH<sub>3</sub>CN) were dried and distilled under nitrogen prior to use. The deuterated solvents used after being appropriately dried and degassed, were stored in ampoules under argon on 4 Å molecular sieves. All synthetized products were stored in glove box (MBraun UniLab  $H_2O < 0,1$  ppm  $O_2 < 17,4$  ppm) and treated before analysis for 24 h under vacuum (0.1 mbar) at room temperature.

## 2.2. Instruments

## 2.2.1. Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra were recorded at 298 K using Varian Inova 300 (<sup>1</sup>H, 300.1 MHz; <sup>13</sup>C, 75.5 MHz; <sup>19</sup>F NMR, 282.3 MHz) and Varian Mercury Plus VX 400 (<sup>1</sup>H, 399.9; <sup>13</sup>C, 100.6 MHz) instruments for routine analysis and Varian Inova 600 (<sup>1</sup>H, 599.7; <sup>13</sup>C, 150.8 MHz; <sup>19</sup>F NMR, 564.1 MHz) instrument to analyse the purified products; chemical shifts were referenced internally to residual solvent peaks for <sup>1</sup>H (CDCl<sub>3</sub>: 7.26 ppm) and <sup>13</sup>C NMR (CDCl<sub>3</sub>: 77.00 ppm) spectra, and externally to CFCl<sub>3</sub> (0.00 ppm) for <sup>19</sup>F NMR spectra. J. Young valve NMR tubes (Wilmad) were used to carry out NMR experiments under inert conditions. The purity of the commercial starting imidazoles was checked by <sup>1</sup>H NMR (Figs. 1S–5S).

## 2.2.2. Mass spectrometer (MS)

ESI-MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in MeOH.

## 2.2.3. Differential scanning calorimetry (DSC)

Calorimetric data were carried out using DSC1 STRe System (Mettler Toledo). The samples were successively heated under nitrogen atmosphere (50 mL/min) up to 220 °C and cooled down to -100 °C. The cooling-heating cycles were repeated three times at different rates (10, 5, 1 °C/min): the best reproducibility was obtained with a slope of 10 °C/min. DSC experiments were performed on 1–9 mg of the sample, using aluminium pans. The pan was heated initially to 100 °C for 30 min, in order to remove water. The sample pan was then re-weighed and the DSC program was initiated.

#### 2.2.4. Thermogravimetry (TG)

TG analysis was recorded on TG-DSC 111 (Setaram) on 20 mg of the sample: the samples were heated up to 250  $^{\circ}$ C under air flux (10 mL/min) with at a constant heating rate of 5  $^{\circ}$ C/min starting from room temperature.

# 2.2.5. Polarized optical microscopy (POM)

POM analysis was performed using a light microscope (Zeiss Axioskop2) equipped with a polarizing filter and a variable temperature cell controller (Specac.). The sample was heated up to complete fusion then left out to cool down to room temperature. The image of the ionic liquid crystal was acquired using a digital camera (SCC - 833 Samsung).

## 2.2.6. Conductimeter

A PC510 (Eutech Instruments) was used to measure conductivities: a calibration with 0.1 M KCl water solution was performed before the analysis.

## 2.2.7. Karl Fisher titration (KF)

The water content in the C4\_BF4 was determined by KF titration, using a coulometer (Metrohm 831) in glove box.

## 2.3. Synthesis procedures of fluorinated imidazolium salts

## 2.3.1. Synthesis of 1-butyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2H-1λ4,3λ4-imidazol-2-ylium iodide (C4\_I)

In a 250 mL two-neck round bottom flask equipped with a condenser linked to the vacuum-argon line, *N*-butylimidazole (title 99% w/w, Alfa Aesar) (4.2 g, 33.4 mmol) was charged and after degassing with three vacuum/argon cycles, 1H,1H,2H,2H-perfluorooctyliodide 96% w/w, Aldrich) (23.8 g, 50.1 mmol) was added. After three more vacuum/argon cycles the temperature of the oil bath was increased from 25 °C to 120 °C in 10 min. After heating for 6 h, NMR analysis of the crude reaction mixture (Fig. 6S, ESI) showed that the reaction went to completion and the occurrence, together with the target molecule C4-I, of the by-products N-butyl-imidazolium iodide and 1H,1H,2Hperfluoro-1-octene (Scheme 1) typical of a Hofmann elimination of the imidazolium salts [29–31]. By cooling the presence of two phases was observed: a viscous red liquid (containing C4-I, N-butylimidazolium iodide and  $C_6F_{13}CH = CH_2$ ) at the top and a pale yellow liquid (the unreacted 1H,1H,2H,2H-perfluorooctyl iodide with  $C_6F_{13}CH = CH_2$ ) at the bottom. The phases were separated by decantation and the viscous red liquid washed three times with petroleum ether  $(3 \times 50 \text{ mL})$  and three times with diethyl ether  $(3 \times 50 \text{ mL})$ . The solvent and the volatile by-product  $C_6F_{13}CH = CH_2$  (bp = 102–104°) were eliminated under vacuum (30 °C/53 Pa). After the work-up <sup>1</sup>H NMR of the red oil showed peaks of C4-I (75%) and of N-butylimidazolium iodide (25%). The raw product (20 g) was dissolved in 20 mL of dichloromethane and filtered under argon on anhydrous celite (40 g) previously wetted with 200 mL of dichloromethane. The filtration was repeated two times. Celite was then washed with 80 mL of dichloromethane. Evaporation of the solvent (30 °C/53 Pa) gives a red sticky wax with a yield of 75.1% (15.0 g, 25 mmol).

<sup>1</sup>H NMR (599.7 MHz, CDCl<sub>3</sub>): δ 10.30 (s, 1H, NCHN), 7.52 (bs, 1H, CHim), 7.32 (t, 1H,  ${}^{3}J_{HH} = 1.6$  Hz, CHim), 4.90 (t, 2H,  ${}^{3}J_{HH} = 6.4$  Hz, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 4.30 (t, 2H,  ${}^{3}J_{HH} = 7.5$  Hz, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 2.96 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 1.95 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>H<sub>3</sub>), 1.41 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.99 (t, 3H,  ${}^{3}J_{HH} = 7.4$  Hz, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).</sub>

<sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>): δ 136.5 (NCHN), 122.9 (CHim), 122.4 (CHim), 120-115 (CF), 50.0 (CH<sub>2</sub>), 49.5 (CH<sub>2</sub>), 42.3 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 19.1 (CH<sub>2</sub>), 13.1 (CH<sub>3</sub>). <sup>19</sup>F NMR (564.1 MHz, CDCl<sub>3</sub>): δ – 80.86 (t, 3F,



Scheme 1. Reagents and conditions: 1-butyl imidazole, 1H,1H,2H,2H-perfluorooctyl iodide, 120 °C.

Table 1
Mesophase transition temperatures of the prepared iodide imidazolium salts.

Product	р	Imidazole reagent	T melting (°C)	T clearing (°C)	Enthalpy melting (J/g)	Enthalpy clearing (J/g)
C1_I	1	1-Methyl imidazole	91	188	19.5	2.3
C4_I	4	1-Butyl imidazole	51	65	8.1	3.1
C6_I	6	1-Hexyl imidazole	27	153	6.9	3.6
C10_I	10	1-Decyl imidazole	42	186	8.3	7.3

 ${}^{3}J_{FF} = 10.7$  Hz, CF<sub>3</sub>), -113.36 (m, 2F, CF<sub>2</sub>), -121.86 (m, 2F, CF<sub>2</sub>), -122.92 (m, 2F, CF<sub>2</sub>), -123.17 (m, 2F, CF<sub>2</sub>), -126.22 (m, 2F, CF<sub>2</sub>).

MS-(ESI) (MeOH, *m*/*z*) (+): 471 (100) [Im]<sup>+</sup>; MS-(ESI) (MeOH, m/*z*) (-): 127 (100) [I]<sup>-</sup>.

The same procedure as for C4\_I was used for the other products as in Table 1, by heating in neat the suitable N-alkyl-imidazole with 1H,1H,2H,2H-perfluorooctyl iodide.

## 2.3.2. Synthesis of 1-methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2H-1λ4,3λ4-imidazol-2-ylium iodide (C1\_I)

Starting reagent *N*-methyl imidazole (>99%, Alfa Aesar).

<sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>): 10.37 (s, 1H, NCHN), 7.42 (bs, 1H, CHim), 7.29 (bs, 1H, CHim), 4.86 (t, 2H,  ${}^{3}J_{HH} = 7.0$  Hz, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 4.11 (s, 3H, NCH<sub>3</sub>), 2.97 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>).

2.3.3. Synthesis of 1-hexyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2H-1λ4,3λ4-imidazol-2-ylium iodide (C6\_I)

Starting reagent N-hexyl imidazole (> 98%, Iolitec).

<sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>): 10.26 (s, 1H, NCHN), 7.61 (bs, 1H, CHim), 7.35 (bs, 1H, CHim), 4.90 (t, 2H,  ${}^{3}J_{HH} = 6.5$  Hz, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 4.29 (t, 2H,  ${}^{3}J_{HH} = 7.5$  Hz, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 2.95 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 1.93 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.31 (m, 6H, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 0.86 (m, 3H, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>).

2.3.4. Synthesis of 1-decyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2H-1λ4,3λ4-imidazol-2-ylium iodide (C10\_I)

Starting reagent N-decyl imidazole (>98%, Iolitec).

$$\label{eq:horder} \begin{split} ^{1}\text{H}\ \text{NMR}\ (399.9\ \text{MHz}\ \text{CDCl}_3)\ &:\ 10.0\ (s,\ 1\text{H},\ \text{NCHN}),\ 7.75\ (bs,\ 1\text{H},\ \text{CHim}), \\ 7.45\ (bs,\ 1\text{H},\ \text{CHim}),\ 4.85\ (t,\ 2\text{H},\ ^3J_{\text{HH}} = 7.5\ \text{Hz},\ \text{NCH}_2\text{CH}_2\text{C}_6\text{F}_{13}),\ 4.28\ (t,\ 2\text{H},\ ^3J_{\text{HH}} = 7.0\ \text{Hz},\ \text{NCH}_2(\text{CH}_2)_8\text{CH}_3),\ 2.93\ (m,\ 2\text{H},\ \text{NCH}_2\text{CH}_2\text{C}_6\text{F}_{13}),\ 1.92\ (m,\ 2\text{H},\ \text{NCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3),\ 1.31\ (m,\ 4\text{H},\ \text{NCH}_2\text{CH}_2(\text{CH}_2)_2(\text{CH}_2)_5\text{CH}_3),\ 1.20\ (m,\ 10\text{H},\ \text{NCH}_2\text{CH}_2(\text{CH}_2)_2(\text{CH}_2)_5\text{CH}_3),\ 0.82\ (m,\ 3\text{H},\ \text{NCH}_2(\text{CH}_2)_4\text{CH}_3). \end{split}$$

2.3.5. Procedures for anion exchange reaction of 1-butyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2H-1 $\lambda$ 4,3 $\lambda$ 4-imidazol-2vlium tetrafluoroborate (C4 BF<sub>4</sub>)

In a two- neck 250 mL schlenck linked to the vacuum-argon line, C4-I (25.6 g, 42.8 mmol) was charged and was completely dissolved in 20 mL of anhydrous dichloromethane. Then HBF<sub>4</sub> · (Et<sub>2</sub>O) (title 51,0–57,0%, Aldrich) (7,6 mL, 55.6 mmol,  $\rho = 1,19$ ) was added at room temperature and during the reaction bubbling of HI was observed. The <sup>1</sup>H NMR analysis in CD<sub>3</sub>CN showed that the metathesis reaction was finished after 1 h. As described in Scheme 2, three products were present in the crude reaction mixture: the expected C4-BF<sub>4</sub> and the by-products N-butylimidazolium BF<sub>4</sub> (ca. 21%) and 1H,1H,2H-perfluoro-1-octene.

The crude material was washed three times with 45 mL of diethyl ether  $(3 \times 15 \text{ mL})$  and evaporated under vacuum (30 °C/53 Pa). The

crude product was then dissolved in acetonitrile (15 mL) and filtered under argon through 40,0 g of anhydrous alumina (previously wetted with 80 mL of acetonitrile). The alumina was then washed twice with 100 mL of acetonitrile. Evaporation under vacuum (30 °C/53 Pa) gave pale yellow oil with a yield of 58% (13,8 g, 24.8 mmol). The purity of the final product has a purity > 98% (NMR) with a water content < 0.1% (evaluated by KF titration) [32].

<sup>1</sup>H NMR (599.7 MHz, CD<sub>3</sub>CN): δ 8.66 (s, 1H, NCHN) 7.51 (bs, 1H, CHim) 7.45 (bs, 1H, CHim), 4.52 (t, 2H,  ${}^{3}J_{HH} = 7.1$  Hz, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 4.15 (t,  ${}^{3}J_{HH} = 7.3$  Hz, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 2.84 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>), 1.80 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.30 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t, 3H,  ${}^{3}J_{HH} = 7.4$  Hz, NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>): δ 137.3 (NCHN), 123.9 (CHim), 123.8 (CHim), 120-110 (CF), 50.7 (CH<sub>2</sub>), 42.9 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 31.9 (t, CH<sub>2</sub>CF<sub>2</sub>, <sup>2</sup>*J*<sub>CF</sub> = 21.1 Hz), 20.0 (CH<sub>2</sub>), 13.7 (CH<sub>3</sub>).

<sup>19</sup>F NMR (564.1 MHz, CD<sub>3</sub>CN):  $\delta$  – 81.57 (t, 3F, <sup>3</sup>*J*<sub>FF</sub> = 9.6 Hz, CF<sub>3</sub>), -114.47 (m, 2F, CF<sub>2</sub>), -122.36 (m, 2F, CF<sub>2</sub>), -123.33 (m, 2F, CF<sub>2</sub>), -124.14 (m, 2F, CF<sub>2</sub>), -126.63 (m, 2F, CF<sub>2</sub>), 151.71 (s, 4F, BF<sub>4</sub>).

## 3. Result and discussion

All synthesized salts are in accordance with the expected composition and structures data.

The synthetized iodide salts showed a SmA liquid crystal phase. As already reported in the literature the length of the non-fluorinated alkyl chain is the main parameter for tuning the mesophase temperature range [34], having strong effect especially on the clearing temperature. The phase diagram plotted in Fig. 2 shows a significant variation of the clearing points for intermediate lengths of the hydrogenated alkyl chain, giving evidence of an abrupt destabilisation in the molecular packing. The reason for this non-linear variation is probably due to the incompatibility of the hydrocarbon and fluorocarbon segments [35].

The thermal transitions were determined by DSC heating ramps (Fig. 3), showing the clearing and melting temperatures as first and last exothermic peaks.

A typical large enthalpy is measured for the crystal/SmA liquid crystal phase transition and small enthalpy for SmA/isotropic transition (Table 1).

Among the fluorinated imidazolium salts developed, the product C4\_I looked as a potential interesting component for electrochemical devices, showing the minimum isotropic transition temperature in the investigated alkyl chain length range substituents.

The purity of these final product is essential for its application as solvent and electrolyte: <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR and ESI-MS analyses



**Scheme 2.** Reagents and conditions: C4\_I, HBF<sub>4</sub> · (Et<sub>2</sub>O)  $\geq$  99,5%, room temperature.



Fig. 2. Phase diagram of the prepared imidazolium salts having anion I- as a function of the non-fluorinated alkyl chain length p = 1, 4, 6, 10.

confirm that the product C4\_I has a purity > 98% with a water content < 0.1% (evaluated by NMR [36,37]).

The thermal stability of the imidazolium salts was studied by carrying out thermo-gravimetric measurements (see Figs. 17S–20S). The temperature dependence of the weight loss for C4\_I, in the temperature range extended from 25 °C to 250 °C, is reported in Fig. 4.

A slight inflection of the weight loss was observed at about 52 °C whose extent, however, does not exceed the 0.1% value of the initial sample mass and thus could be ascribed to a poor residual water content as revealed by ESI-MS analysis. Conversely, a strong decrease of the weight loss (higher than 0.7% of the initial sample mass) was observed at temperatures above 183 °C. This evidence indicated a progressive decreasing of the thermal stability of the sample, which presumably could be associated to the thermal decomposition at 230 °C, in agreement with what previously reported by Pereiro et al. on similar molecules [14].

According to the DSC and TGA results, it is possible to assert that C4\_I showed a good thermal stability in its mesophase temperature range that extended well below its decomposition temperature.

Optical polarized microscopic analysis of C4\_I was performed on cooling from the isotropic phase down to room temperature by means of a polarized microscope. This instrument was equipped with a hot stage and a camera to capture the image of the liquid-crystalline product during the transition between two phases. On cooling from the isotropic phase, C4\_I showed the development of bâtonnets, which coalesce to give a focal conic fan texture (Fig. 5). This arrangement implies the presence of a layered structure and suggests the assignment



**Fig. 3.** Differential Scanning Calorimetry analysis of the prepared imidazolium salts having anion I-: p = 1 (black), 4 (blue), 6 (green), 10 (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. C4\_I thermo-gravimetric analysis.

of this phase to a Smectic A phase. Thus, we can ascribe the clearing temperature revealed by DSC measurements to the transition from the Smectic A to isotropic phases. Very interestingly, this Smectic A texture remains unchanged on cooling down to room temperature confirming a remarkable thermal stability of this structure just in the range of usual employment of electrolytes for electrochemical devices.

Finally, the room-temperature conductivity of C4\_I was measured. As the melting temperature is well above 25 °C a poorly conductive co-solvent (sulfolane,  $35 \ \mu S \ cm^{-1} \ @25 \ °C$ ) was added to the product (Fig. 23S). The measured conductivity of the liquid mixture (C4\_I: sulfolane,  $3:1 \ w/w$ ) is  $0.5 \ m S \ cm^{-1}$ , i.e. comparable to what reported on shorter alkyl chain ionic liquids, like 1-butyl-3-methylimidazolium iodide ( $0.37 \ m S \ cm^{-1}$ ) and 1-methyl-3-propylimidazolium iodide ( $0.58 \ m S \ cm^{-1}$ ) [38], typically used as electrolytes in DSSC.

The nature of the anion has also a relevant influence on mesomorphic properties of the imidazolium salts [10,39,40]. To further reduce the melting temperature of the products we exchanged anion I<sup>-</sup> with fluorinated non-nucleophilic anion BF<sub>4</sub><sup>-</sup>, however this product C4\_BF<sub>4</sub> did not show any mesophase but only a glass transition temperature at -30 °C (Fig. 6), while the stability was improved, showing thermal decomposition over 300 °C (see Fig. 20S).

## 4. Conclusion

A class of thermally stable fluorinated imidazolium salts was prepared using an environmentally safer solvent free-procedure and liquid-crystal SmA phases were demonstrated over a large variation of non-fluorinated alkyl chain length C1-C10. In particular, C4\_I presented a lower clearing temperature associate with good thermal stability in its mesophase temperature range, which extended well below its degradation temperature.

The synthetic feasibility of this class of fluorinated imidazolium salts might represent a key point for their applications in several fields other



Fig. 5. Mesophase texture of C4\_I under crossed polarized light at 25 °C.





than the electrochemical one such as catalysis [39,41–43], surfactants [44,45], and gas separations [46].

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2016.08.101.

## References

- [1] J. Beeckman, K. Neyts, P. Vanbrabant, Opt. Eng. 50 (2011) 081202-081217.
- [2] C.A. Angell, N. Byrne, J.-P. Beliers, Acc. Chem. Res. 40 (2007) 1228–1236.
- [3] K. Ueno, H. Tokuda, M. Watanabe, Phys. Chem. Chem. Phys. 12 (2010) 1649–1658.
- [4] N.S.M. Vieira, P.M. Reis, K. Shimizu, O.A. Cortes, I.M. Marrucho, J.M. Araujo, J.M.S.S. Esperanca, J.N. Canoogia Lopes, A.B. Pereiro, L.P.N. Rebelo, RSC Adv. 5 (2015) 65337–65350.
- [5] R.D. Rogers, K.R. Seddon, Science 302 (2003) 792-793.
- [6] K. Gossens, K. Lava, C.W. BielawsKi, K. Binnemans, Chem. Rev. 116 (2016) 4643–4807.
- [7] K. Binnemans, Chem. Rev. 105 (2005) 4148–4204.
- [8] K.V. Axenov, S. Laschat, Materials 4 (2011) 206–259.
- [9] A. Abate, A. Petrozza, V. Roiati, S. Guarnera, H. Snaith, F. Matteucci, G. Lanzani, P. Metrangolo, G. Resnati, Org. Electron. 23 (2012) 2474–2478.
- [10] A.N. Tran, T.-N. Van Do, L.-P. My Le, T.N. Le, J. Fluor. Chem. 164 (2014) 38-43.

- [11] N. Yamanaka, R. Kawano, W. Kubo, N. Masaki, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, J. Phys. Chem. B 111 (2007) 4763–4769.
- [12] M. Anouti, L. Timperman, M. Elhilali, A. Boisset, H. Galiano, J. Phys. Chem. C 116 (2012) 9412–9418.
- [13] J. Sakuda, Adv. Funct. Mater. 25 (2015) 1206–1212.
- [14] A.B. Pereiro, J.M.M. Araujo, S. Martinho, F. Alves, S. Nunes, A. Matias, C.M.M. Duarte, L.P.N. Rebelo, I.M. Marrucho, Sust. Chem. Eng. 1 (2013) 427–439.
- [5] R.P. Singh, S. Manandhar, J.M. Shreeve, Tetrahedron Lett. 43 (2002) 9497–9499.
- [16] J. Ranke, S. Stolte, R. Stormann, J. Aming, B. Jastorff, Chem. Rev. 107 (2007) 2183–2206.
- [17] R. Biczak, B. Pawlowska, P. Balczewski, P. Rychter, J. Hazard. Mater. 274 (2014) 181–190.
- [18] Y. Zhao, J. Zhao, Y. Huang, Q. Zhou, X. Zhang, S. Zhang, J. Hazard. Mater. 278 (2014) 320–329.
- [19] T.L. Merrigan, E.D. Bates, S.C. Dorman, J.H. Davis, Chem. Commun. (2000) 2051–2052.
- [20] B.R. Caes, J.B. Binder, J.J. Blanck, R.T. Raines, Green Chem. 13 (2011) 2719–2722.
- [21] D. Almantariotis, T. Gefflaut, A.A.H. Paudua, J.-Y. Coxam, M.F. Costa Gomes, J. Phys. Chem. 114 (2010) 3608–3617.
- [22] M. Skalicky, M. Rybackova, O. Kysilka, M. Kvicalova, J. Cvacka, J. Kvicala, J. Fluorine, Chemistry 130 (2009) 966–973.
- [23] H. Xue, J.M. Shreeve, Eur. J. Inorg. Chem. 13 (2005) 2573-2580.
- [24] A. Abate, S. Biella, F. Meyer, H. Neukirch, P. Metrangolo, T. Pilati, G. Resnati, G. Terraneo, J. Fluor. Chem. 130 (2009) 1171–1177.
- [25] G. Resnati, P. Metrangolo, A. Abate, F. Matteucci, Patent (2010) EP2440532 (2010) JP5738852.
- [26] L. Vierke, C. Staude, A. Biegel-Engler, W. Drost, C. Schulte, Environ. Sci. Eur. 24 (2012) 16–26.
- [27] M.P. Krafft, J.G. Riess, Chemosphere 129 (2015) 4-19.
- [28] M.P. Krafft, J.G. Riess, Curr. Opin. Colloid Interface Sci. 20 (2015) 192-196.
- [29] L. Xu, W. Chen, J.F. Bickley, A. Steiner, J. Xiao, J. Organomet. Chem. 598 (2000) 409-416.
- [30] C.S. Rondestvedt, G.L. Thayer, J. Organomet. Chem. 42 (1977) 2680-2683.
- [31] H.B. Alhanash, A.K. Brisdon, J. Fluorine, Chemistry 156 (2013) 152–157.
- [32] The Karl Fisher analysis can be carried out only on imidazolium salts with anions other than the iodide. See for example. A. Stark, P. Behrend, O. Braun, A. Muller, J. Ranke, B. Ondruschka, B. Jastorff, Green Chem. 10 (2008) 1152–1161 (M. Castaneda Uggarteburu, Assessment of the water content in several ionic liquids using the coulometric Karl Fischer technique, 2015 http://hdl.handle.net/10902/6697).
- [33] P. Migowski, J. Dupont, Chem. Eur. J. 13 (2007) 32–39.
- [34] J. De Roche, C.M. Gordon, C.T. Imrie, M.D. Ingram, A.R. Kennedy, F. Lo Celso, A. Triolo, Chem. Mater. 15 (2003) 3089–3097.
- [35] A. Abate, A. Petrozza, G. Cavallo, G. Lanzani, F. Matteucci, D.W. Bruce, N. Houbenov, P. Metrangolo, G. Resnati, J. Mater. Chem. A 1 (2013) 6572–6578.
- [36] V. Gallo, P. Mastrorilli, C.F. Nobile, G. Romanazzi, G.P. Suranna, J. Chem. Soc. Dalton Trans. 44 (2002) 4339–4342.
- [37] J.-M. Andanson, X. Meng, M. Traikia, P. Husson, J. Chem. Thermodyn. 94 (2016) 169–176.
- [38] Y. Bai, Y. Cao, J. Zhang, M. Wang, R. Li, P. Wang, S.M. Zakeeruddin, M. Grätzel, Nat. Mater. 7 (2008) 626–630.
- [39] F. Xu, S. Matsubara, K. Matsumoto, R.J. Hagiwara, J. Fluor. Chem. 135 (2012) 344–349.
- [40] A.E. Bradley, C. Hardacre, J.D. Holbrey, S. Johnstonm, S.E.J. McMath, M. Nieuwenhuyzen, Chem. Mater. 14 (2002) 629–635.
- [41] T. Fukuyama, M. Arai, H. Matsubara, I. Ryu, J.O.C. 69 (2004) 8105-8107.
- [42] H. Matsubara, L. Maeda, I. Ryu, Chem. Lett. 34 (2005) 1548–1549.
- [43] J. Xiao, W. Chen, Patent 2000 US20030181767.
- [44] T.L. Merrigan, E.D. Bates, S.C. Dorman, J.H. Davis Jr., Chem. Commun. (2000) 2051–2052.
- [45] K.A. Fletcher, S. Pandey, Langmuir 20 (2004) 33-36.
- [46] J.E. Bara, C.J. Gabriel, T.K. Carlisle, D.E. Camper, A. Finotello, D.L. Gin, R.D. Noble, Chem. Eng. J. 147 (2009) 43–50.