Switching of ionic conductivities in columnar liquid-crystalline anilinium salts: effects of alkyl chains, ammonium cations and counter anions on thermal properties and the switching temperatures

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Complete List of Authors:	Kuo, Daniel; University of Tokyo, Department of Chemistry and Biotechnology Soberats, Bartolome; Universitat de les Illes Balears, Chemistry Sunil Kumar, K.; The University of Tokyo, Department of Chemistry and Biotechnology, School of Engineering Yoshio, Masafumi; Busshitsu Zairyo Kenkyu Kiko Ichikawa, Takahiro; Tokyo University of Agriculture and Technology, Department of Biotechnology Ohno, Hiroyuki; Tokyo University of Agriculture and Technology, Department of Biotechnology Zeng, Xianbing; University of Sheffield, Department of Materials Science and Engineering Ungar, Goran; The University of Sheffield, Dept of Engineering Materials Kato, Takashi; University of Tokyo, Chemistry and Biochemistry

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Design, System, Application

Recent advances of liquid-crystalline (LC) technologies have permitted the development of a new generation of functional materials which are potentially applied to energy and environment fields. The nanostructured ion transport materials, which can be used as electrolytes for battery devices, have been exploited for new, stable and efficient electrolytes. Molecular engineering of these ionic liquid crystals has enabled preparation of anisotropic and efficient ion-transport in self-assembled nano-channels. We have found some columnar liquid crystals provide 1D ion-transport with thermal switching in ionic conductivities. It is expected that these materials can be used as new electrochemical devices. We here demonstrate basic molecular design and engineering of ionic liquid crystals that exhibit stimulus responsive switching in ion conductivities.

Journal Name

ARTICLE

Switching of ionic conductivities in columnar liquid-crystalline anilinium salts: effects of alkyl chains, ammonium cations and counter anions on thermal properties and the switching temperatures

Daniel Kuo,[a] Bartolome Soberats,[ab] K. R. Sunil Kumar,[a] Masafumi Yoshio,[ac] Takahiro Ichikawa,[d]

Hiroyuki Ohno,[d] Xiangbing Zeng,[e] Goran Ungar[e] and Takashi Kato*[a]

Switching one-dimensional ion conductivities in organic materials is a challenging task. Recently we found that a liquid-crystalline (LC) *N,N,N*-trimethyl-3,4,5-tridodecyloxy-anilinium salt showed a remarkable change in the conductivities of about four orders of magnitude, which is triggered by a thermotropic LC phase transition between rectangular (Col$_r$) and hexagonal (Col$_h$) columnar phases. In the present study, we have succeeded in tuning the switching temperature by changing the length of the alkyl chains attached to the anilinium ring of LC materials. The size of the *N,N,N*-trialkylanilinium cations that is, trimethyl, dimethylethyl and diethylmethyl, and the counterion (BF$_4$, PF$_6$ or CF$_3$SO$_3$) play a crucial role for the formation of successive Col$_r$ and Col$_h$ LC phases, which affect the switching behaviour. We have found that the temperature of the Col$_r$-Col$_h$ phase transition and the switching of ion conductivity is tuned in *N,N,N*-trimethylanilinium tetrafluoroborates by changing the length of the alkyl chains. These results give new insights in design of ion-conductive self-assembled molecular materials.

Introduction

Molecular self-assembly is a powerful approach for the development of functional materials.[1-8] Liquid crystal is an ordered molecular self-assembled material. Liquid-crystalline (LC) materials have attracted attention because they exhibit ordered and mobile phases for constructing functional materials.[3,4,8,9] For example, ordered 1D, 2D, and 3D nanostructures have been used for transport of ions,[4,13-22] proton,[23-25] electrons,[26-28] and water molecules.[29,30] Moreover, transport properties in liquid crystal could be switched by external stimuli of light[31-34] and temperature[34-36] Early work of Kimura and co-workers showed that an LC material based on a crown ether and azobenzene moieties

was able to switch the ion transport upon light irradiation.[31-33] However, this conductivity switch was only one order of magnitude and the ion conductivities were relatively low. Recently we showed that azobenzene-containing smectic ionic liquid crystals changed their direction of ionic channels from parallel to perpendicular by combination of thermal stimuli and light irradiation.[34] In this case, the switching of the directional ion-conductivity was achieved.[34] Thermal stimuli that induced phase transition were also used for switching of ion conductivities. The sharp increase of ionic conductivity from crystal to Col$_h$ was reported.[21] The ionic conductivities increased from 10^{-12} to 10^{-8} S cm^{-1} in the heating process. We observed reversible changes of ionic conductivities of LC materials from LC-isotropic,[20] micellar cubic-columnar,[36] and LC-crystalline[20] phase transitions. In our preliminary work,[35] we found that the remarkable switching of ion conductivities based on the thermally activated columnar rectangular-columnar hexagonal (Col$_r$-Col$_h$) phase transitions in wedge-shaped *N,N,N*-trimethylanilinium BF$_4$ and PF$_6$ liquid crystals which were compounds **1(12/BF$_4$)** and **1(12/PF$_6$)** (Fig. 1). It should be noted that such behaviour has only been observed in these two compounds[15] among ion transport liquid crystals based on ammonium,[18,19] imidazolium,[20,21,34-37] phosphonium[12] and betaines[23,38] developed in the last two decades. The switching of conductivities with compound **1(12/BF$_4$)** was achieved from 1×10^{-8} S cm^{-1} at 130 °C (Col$_r$) and 1×10^{-4} S cm^{-1} at 150 °C (Col$_h$). We hypothesized that the ions are less

a. *Department of Chemistry and Biotechnology, School of Engineering The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan E-mail: kato@chiral.t.u-tokyo.ac.jp*
b. *Present address: Department of Chemistry, Universitat de les Illes Balears Cra. Valldemossa km. 7.5 07122 Palma de Mallorca, Spain*
c. *Present address: Research Center for Functional Materials, National Institute for Materials Science, Namiki, Tsukuba, Ibaraki 305-0044, Japan*
d. *Department of Biotechnology, Tokyo University of Agriculture and Technology, Nakacho, Koganei, Tokyo 184-8588, Japan*
e. *Department of Materials Science and Engineering, University of Sheffield, Sheffield S13JD, United Kingdom*
† Footnotes relating to the title and/or authors should appear here.
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mobile in the ionic channels of more ordered Col_r phase despite that movability drastically increases in the low ordered Col_h phase.

Our intention was to examine how tuning of the molecular structures for **1(12/BF₄)** and **1(12/PF₆)** affected the phase behaviour and the properties of ion switching. Moreover, we aimed at the systematic control for the ion-conductivity switching behaviour by molecular design and engineering.

Herein we report switching behaviour of LC properties and ion conductive properties of a family of *N,N,N*-trialkyl-3,4,5-trialkyloxyanilinium derivatives (**1**-**3**) bearing *N,N,N*-trimethyl-, *N,N*-dimethyl-*N*-ethyl-, and *N,N*-diethyl-*N*-methyl-ammonium cations forming ionic pairs with BF_4, PF_6 and CF_3SO_3 anions (Fig. 1). We also describe the tuning of switching temperatures in the series of compounds **1(*n*/BF₄)** with various alkyl chain lengths.
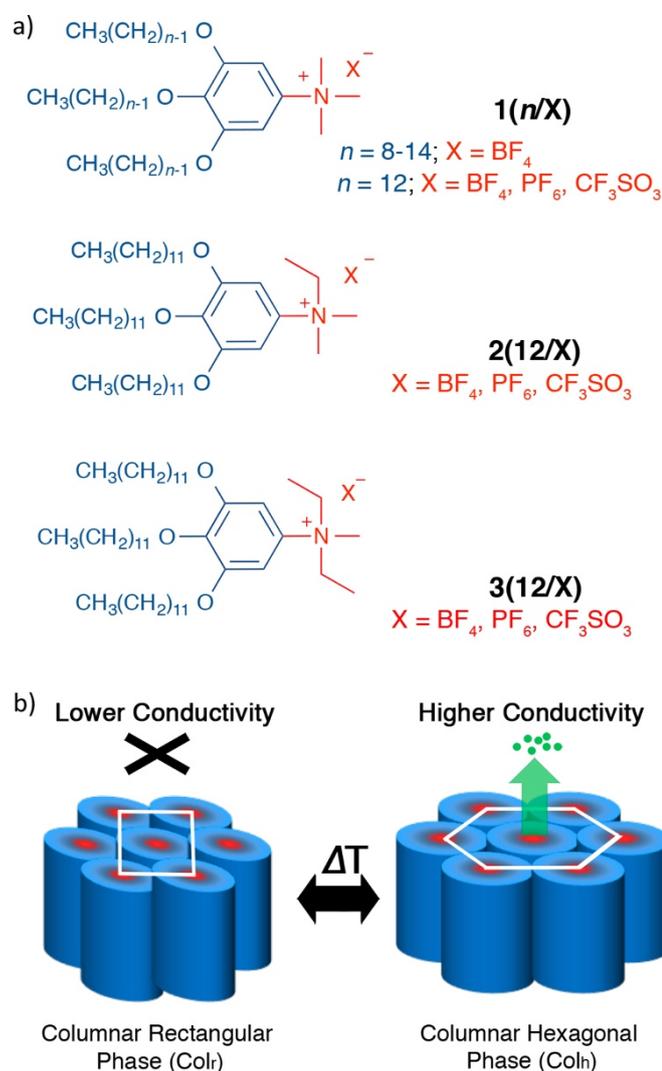
Fig. 1 a) Chemical structures of compounds **1**-**3**. b) Schematic illustration of the switching of ionic conductivities driven by the thermal rectangular-hexagonal columnar liquid-crystalline phase transition.

Results and discussion

Synthesis of compounds 1-3

A series of compounds **1**-**3** were synthesized from the corresponding wedge-shaped 3,4,5-trialkyoxyaniline derivatives (Supporting Information). The series of compounds **1** was prepared via three-fold methylation of the amine group by using iodomethane which yielded the corresponding *N,N,N*-trimethylanilinium iodide. The iodide anion was then exchanged by BF_4, PF_6 or CF_3SO_3 anions by treating with the corresponding silver salt, $AgBF_4$, $AgPF_6$ or $AgCF_3SO_3$, respectively. To prepare compounds **2(12/X)**, 3,4,5-tridodecyloxyaniline was treated with one equivalent of acetaldehyde and followed by the reduction with $NaBH(OAc)_3$ to obtain the corresponding *N*-ethylaniline derivative. Subsequent treatment with excess of iodomethane leads to the formation of the *N*-ethyl-*N,N*-dimethylanilinium iodide. Final compounds **2(12/X)** were obtained after anion exchange with appropriate silver salts. On the other hand, compounds **3(12/X)** were prepared by treating 3,4,5-tridodecyloxyaniline with excess iodoethane, yielding *N,N*-diethylaniline derivative as the major product. Further reactions with iodomethane followed by anion exchange reactions gave final **3(12/X)** compounds. Compounds **1**-**3** were isolated as white solids.

Effects of the tetralkylammonium moieties and the anion on the mesomorphism of anilinium liquid crystals 1-3(12/X)

The LC behaviour as a function of the temperature for compounds **1**-**3(12/X)** (X = BF_4, PF_6 or CF_3SO_3) was examined by differential scanning calorimetry (DSC), polarizing optical microscope observation (POM) and powder X-ray diffraction (XRD) measurements (Supporting Information). Figure 2 summarizes the phase transition behaviour of this library of compounds.

The liquid crystallinity of compounds **1**-**3** decreases as the volume of the pairing anionic salt increases, considering that BF_4 < PF_6 < CF_3SO_3. As shown in Fig. 2, compounds **1(12/BF₄)** and **1(12/PF₆)** bearing trimethylammonium moieties exhibit two Col_r (Col_{r1} and Col_{r2}) and one Col_h LC phases; in contrast, only a Col_h phase is observed for **1(12/CF₃SO₃)**. The decrease of liquid crystallinity with the increase of anion volume is magnified further in the series of compounds **2**. Compounds **2(12/BF₄)** and **2(12/PF₆)** show Col_h phases, while **2(12/CF₃SO₃)** exhibit no LC phases. For the series of compounds **3**, only **3(12/BF₄)** exhibits an LC phase. The isotropization temperatures of compounds **1**, **2** and **3** increase by decreasing the size of the counter anions. Smaller anions lead to stronger intermolecular interaction between anions and cations, which results in the increase of nanosegregation and the formation of the LC phases.[6,13,14,21,39]
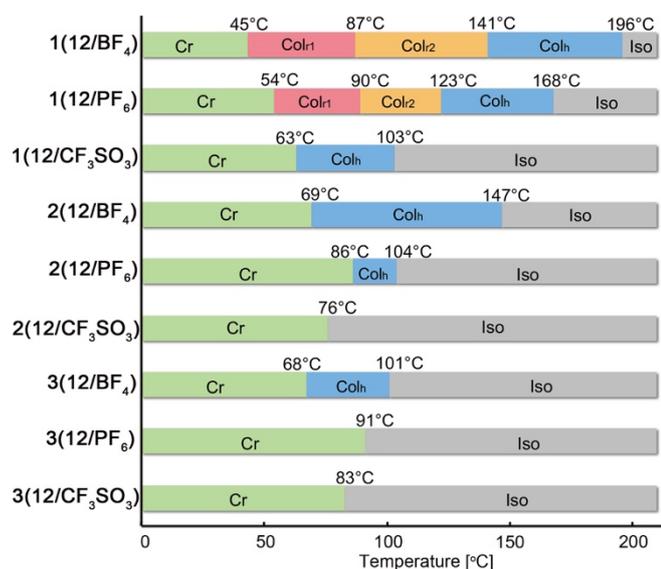
Fig. 2 Phase properties of compounds **1**-**3** with different anions. Cr: crystal phase, Col_r: rectangular columnar phase, Col_h: hexagonal columnar phase, Iso: isotropic phase.
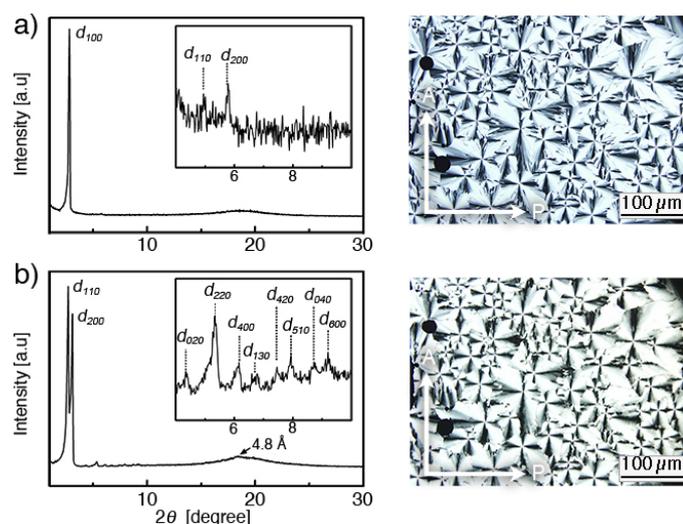
Fig. 3 X-ray diffraction patterns and polarized optical microscopic (POM) images of the Col_h a) and Col_r b) phases for **1(12/BF₄)** (Left: X-ray diffraction patterns, right: POM images).

The range of temperature for 3,4,5-tridecyloxyanilinium derivatives (**1**-**3**) becomes narrower as the volume of the cationic ammonium moiety increases. As shown in Fig. 2, **1(12/BF₄)** exhibits two Col_r and a Col_h phases ranging from 45 to 196 °C, while **2(12/BF₄)** exhibits only a Col_h phase from 69 to 147 °C. Compound **3(12/BF₄)** bearing *N,N*-diethyl-*N*-methyl-ammonium cations shows only a Col_h phase between 68 and 101 °C. The isotropic temperature also decreases as the ammonium volume increases. For example, **1(12/BF₄)** becomes isotropic above 196 °C, while **2(12/BF₄)** and **3(12/BF₄)** melts at 147 and 101 °C, respectively. The order of isotropization temperature is inversely correlated to the volume of the *N,N,N*-trialkylanilinium moiety. This behaviour can be ascribed to a decrease in the nanosegration strength when the molecular volume of the ionic parts increases, and thereby decreases the electrostatic interactions.[21,29,39] These results show that the formation of the Col_r phase in the wedge-shaped anilinium liquid crystals requires a delicate balance between the size of the tetraalkylammonium salt and the counter anion that only occur in the BF₄ and the PF₆ salts of *N,N,N*-trimethyl-3,4,5-tridodecyloxyanilinium. No Col_r phase is observed in compound **2** and **3** series with larger size of the alkylammonium groups. Thus, Col_r LC phases only formed via a compact packing of the ionic moieties in the nanostructured columns. The compact nature of the Col_r phases can be easily deduced from the XRD pattern of **1(12/BF₄)** (Fig. 3). For the Col_r phase, the XRD pattern shows two intense reflections in the small angle region along with eight in the wide-angle region. The presence of ten peaks in the pattern is an indication of the highly ordered structure of the phase.[35] In contrast, the XRD pattern of **1(12/BF₄)** at the Col_h phase shows only two signals corresponding to the 100 and 200 reflections.

Effects of the alkyl chains length in 1(*n*/BF₄) compounds on the mesomorphism of benzenamonium liquid crystals

To control the Col_r-Col_h phase transition at different temperatures, we focus on modifications on the peripherical alkyl chains of compound **1(12/BF₄)**, which exhibits the suitable thermal behaviour and stability. We prepared a series of compound **1(*n*/BF₄)** with the auxiliary alkyloxy chains composed of 8 to 14 carbons (Fig. 1). The LC behaviour of compounds **1(8-14/BF₄)** is shown in the Fig. 4. Compounds **1(9-14/BF₄)** exhibit one or two Col_r (Col_r1 and Col_r2) and a Col_h phases. Only crystalline phase is observed for **1(8/BF₄)**. These results confirm that the molecular design of *N,N,N*-trimethyl-3,4,5-trialkylloxyanilinium tetrafluoroborate provides a suitable balance between anion and cation to stabilize Col_r phases independently of the length of the peripherical chains. For the alkyl chain length of the mesogenic molecules, it is essential to induce and tune LC properties.[3,11,13,14,20,21,41,42] The change of the length of peripheral alkyl chains induces shifts in the phase transition temperatures (Fig. 4). The isotropization temperature and the crystal-Col_r phase transition temperature increase as the alkyl chain is elongated (Fig. 4). The raise in transition temperatures can be ascribed to the increase of intermolecular interactions between aliphatic molecules.[6,13,14,41-44] Lin and co-workers showed that similar trend could also be observed in ionic liquid crystals bearing imidazolium moiety.[43] The isotropic temperature increases from 161 °C for **1(8/BF₄)** to 196 °C for **1(14/BF₄)**. The crystal-Col_r2 phase occurs at 29 °C for **1(9/BF₄)** but the same phase transition increases to 53 °C for **1(14/BF₄)**. The Col_r-Col_h phase transition temperatures decrease as the alkyl chain length increases. As shown in Fig. 4, compound **1(9/BF₄)** has a Col_r-Col_h phase transition temperature at 155 °C, while for **1(14/BF₄)** this transition occurs at 134 °C. The LC-iso and crystal-LC transition temperatures of **1(*n*/BF₄)** are compared with those of the series of **4(*n*/BF₄)** (Fig. 5 and 6). Fan-shaped compounds **4(*n*/BF₄)** bearing imidazolium moieties are representative series of molecules in our study on ion transport

liquid crystals.[4,20,21,41] Both series of compounds show similar trends that the LC-iso and crystal-LC transition temperature increase as the carbon number of alkyl chains increases. The transition temperatures of **1(*n*/BF₄)** are higher than those of **4(*n*/BF₄)** except for the crystal-LC transition for **1(14/BF₄) and 1(14/BF₄)**.
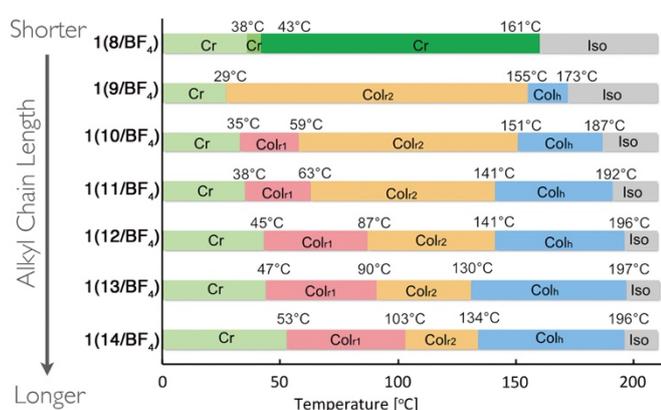
Fig. 4 Phase behaviour of compounds **1(*n*/BF₄)** with different alkyl chain lengths. Cr: crystal phase, Col$_r$: rectangular columnar phase, Col$_h$: hexagonal columnar phase, Iso: isotropic phase.
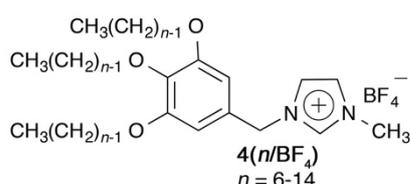
Fig. 5 Molecular structure of the series of compounds **4(*n*/BF₄)**.
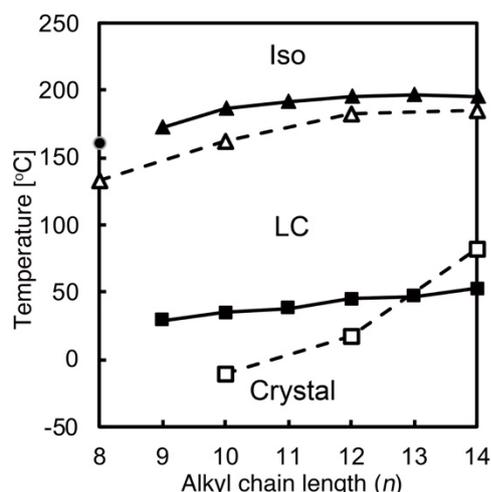
Fig. 6 Comparison of phase transition behaviour for the series of compounds **1(*n*/BF₄)** and **4(*n*/BF₄)**. ▲: LC-isotropic temperature for **1(*n*/BF₄)**; △: Isotropization temperature for **4(*n*/BF₄)**; ●: crystal-isotropic temperature for **1(8/BF₄)**; ■: crystal-LC transition temperature for **1(*n*/BF₄)**. □: crystal-LC transition temperature for **4(*n*/BF₄)**.

Ionic conductivities as a function of temperature for the series of compounds 1-3(12/X) and 1(*n*/BF₄)

The ionic conductivities of **1-3(12/X)** and **1(*n*/BF₄)** were measured by alternating current impendence at variable temperature.[20] As shown in Fig. 7, compounds **1(12/BF₄)** and **1(12/PF₆)** exhibit sudden increase in the ionic conductivities from 10^{-8} to 10^{-4} S cm^{-1} on heating at 139 and 120 °C, respectively. These changes are caused by the Col$_r$-Col$_h$ LC phase transitions. On the other hand, **1(12/CF₃SO₃)** only show modest increase of conductivities from 10^{-7} to 10^{-5} with increasing temperature. For the compounds of the series that exhibit only a Col$_h$ phase (**1(12/CF₃SO₃), 2(12/BF₄), 2(12/PF₆)** and **3(12/BF₄)**), the ionic mobility decreases as the size of the alkylammonium moiety increases. No abrupt increase in conductivity is observed for the liquid-crystalline phases of **1(12/CF₃SO₃), 2(12/X)** and **3(12/X)**.

To obtain information on relationship between switching properties and molecular structures in the Col$_r$-Col$_h$. The phase transitions of **1(*n*/BF₄)** were examined. Compound **1(8/BF₄)** was not examined due to no observation of the LC phase. In the case of **1(9-14/BF₄)** exhibiting the Col$_r$-Col$_h$ phase transitions, they show drastic changes in ionic conductivities at the phase transition temperature (Fig. 7). The Col$_r$-Col$_h$ phase transition and the conductivity switching for **1(9/BF₄)** occurs at around 155 °C. Elongation of the alkyl chains decreases the Col$_r$-Col$_h$ phase transition temperature and accordingly the ionic conductivity switching for **1(14/BF₄)** occurs at lower temperature around 134 °C. It should be noted that for the series of compounds **1(*n*/BF₄)**, the ionic conductivities switch consistently increased by three orders of magnitude (Fig. 8).
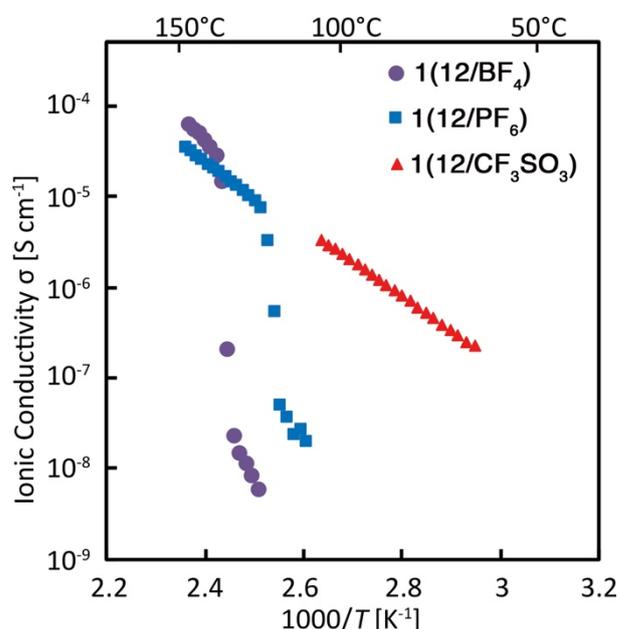
Fig. 7 Ionic conductivities of compound **1(12/BF₄)**, **1(12/PF₆)** and **1(12/CF₃SO₃)**.
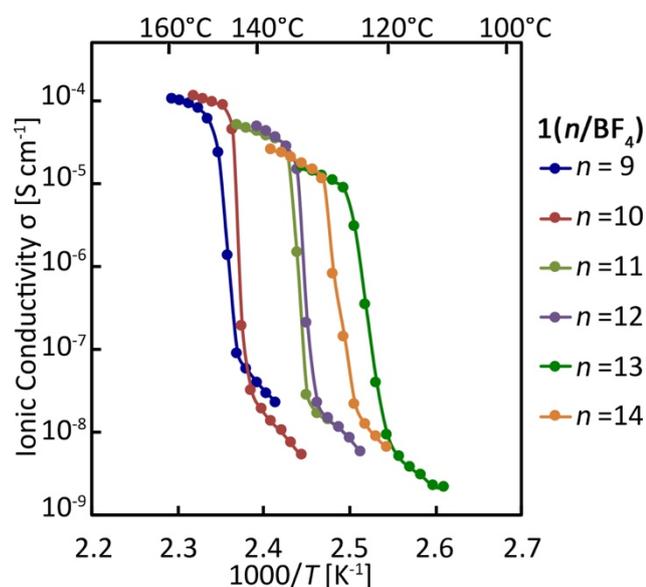
Fig. 8 Ionic conductivities as a function of temperature for compounds **1(9**-**14/BF₄)**.
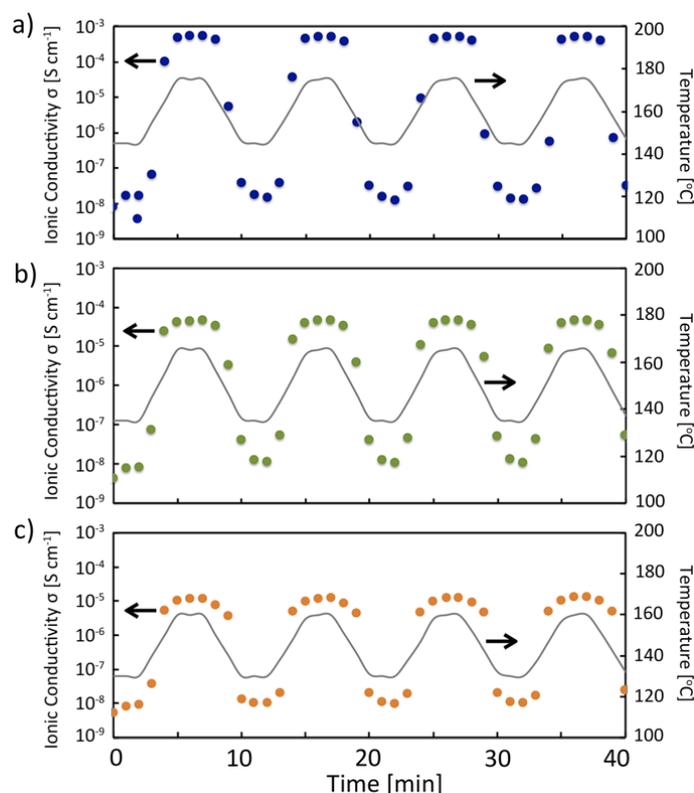
Fig. 9 Ionic conductivities as a function of temperature and time for a) **1(9/BF₄)**, b) **1(11/BF₄)** and c) **1(14/BF₄)**. The dots represent ionic conductivity value and the grey line represent the corresponding temperature.

Switching of conductivities in 1(*n*/BF₄)

To examine the reversibility of switching behaviour of ionic transport in the series of **1(*n*/BF₄)**, the ionic conductivities were measured with oscillating temperature over a period of time. The temperature ranges were controlled to include the Col$_r$-Col$_h$

phase transition in several heating-cooling cycles. The rate of measurement was 10 °C/min. All compounds exhibiting Col$_r$ and Col$_h$ phases show the reversible switching behaviour in ionic conductivity (Fig. 9). For example, the difference of reversible conductivities for **1(9/BF₄)** are between *ca.* 10^{-3} and *ca.* 10^{-8} S cm^{-1} when temperatures are controlled between 145 and 175 °C for several cycles.

Conclusions

Molecular design of wedge-shaped *N,N,N*-trialkylanilinium liquid crystals has been studied as ion switches. It is demonstrated that modification of the anilinium cationic moiety pairing with BF₄, PF₆ and CF₃SO₃ anions can drastically affect the liquid-crystalline behaviour. The series of **1(*n*/BF₄)** is shown to be the most suitable design for developing switching of conductivities based on rectangular-hexagonal columnar (Col$_r$-Col$_h$) phase transitions. The selection of the length of the peripheral alkyl chains from 9 to 14 carbons allows the tuning of the Col$_r$-Col$_h$ phase transition temperatures and subsequently tunes the temperatures of ionic conductivity switching for about 30 degrees. These compounds show reversible switching of conductivities in several cycles. The results provide new insight in the molecular design of organic ion-conductive nanostructured materials.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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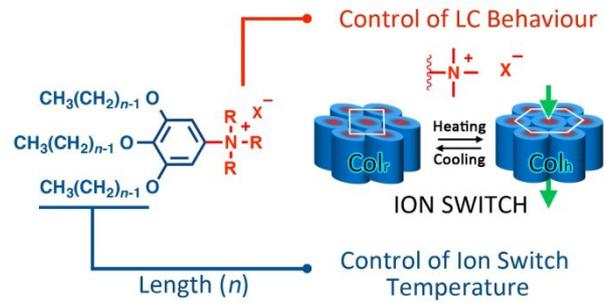
Effects of molecular structures on the thermal switching behavior of ion conductivities for columnar anilinium liquid crystals have been examined.