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Columnar Liquid-Crystalline Imidazolium Salts. Effects of Anions and Cations on Mesomorphic Properties and Ionic Conductivities

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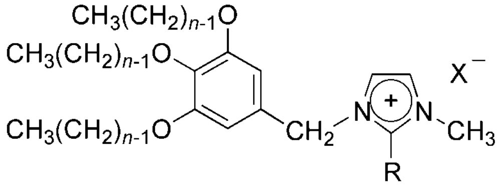
Two series of 1-methyl-3-[3,4,5-tris(alkyloxy)benzyl]imidazolium salts (**1**(n/X$^-$); n = 8, 12, 16, and 18) and 1,2-dimethyl-3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium salts (**2**(12/X$^-$)) containing anions (X$^-$), such as tetrafluoroborate, hexafluorophosphate, trifluoromethylsulfonate, and bis(trifluoromethylsulfonyl)imide, have been synthesized. The thermal properties of these salts were characterized by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The salts form hexagonal columnar liquid-crystalline phases except for **1**(8/X$^-$) and **1**(12/X$^-$) containing $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$, and **2**(12/$(CF_3SO_2)_2N^-$) which melt directly to isotropic ionic liquids. The clearing points show a decreasing trend with an increase in the size of anions. The ionic conductivities of **1**(16/X$^-$) forming columnar phases have been measured by using an alternating current impedance method. The conductivities depend on the nature of anions, suggesting that the predominant conduction mechanism is hopping and/or diffusion of anions in the columnar structures.

Liquid crystals are self-organized materials that form fluid and ordered states.[1] Liquid-crystalline (LC) nanostructures, such as layer (smectic phase) and cylinder (columnar phase), have the potential to be used as anisotropically functional materials for charge, ion, and mass transportation.[2] The self-assembly of LC block molecules composed of two or more covalently bonded immiscible molecular parts leads to the formation of well-defined nano-segregated structures.[3]

Ionic liquids based on organic salts have attracted attention.[4] It is of interest to introduce anisotropic self-assembled structures into ionic liquids for further functionalization. Recently, we have reported on one-dimensional organic ion-conductors using columnar LC imidazolium salts.[5] For example, 1-methyl-3-[3,4,5-tris(alkyloxy)benzyl]imidazolium tetrafluoroborates (**1**(n/BF_4^-)) (Fig. 1) show hexagonal columnar (Col$_h$) LC phases. The aligned columnar materials exhibit anisotropic ionic conductivities. Although there had been several attempts to obtain one-dimensional LC ion-conductors,[6] no anisotropic ion conduction and no macroscopic alignment had been achieved until that time. The salts of **1**(n/BF_4^-) have block molecular structures consisting of ionic and non-ionic moieties. The ionic moieties can self-assemble into the center of the hexagonal columnar structure through ionic interactions and nano-segregation behavior. These columns can be macroscopically aligned in two directions: parallel to the surface of a glass substrate by mechanical shearing and vertical to the surface of amine-functionalized substrates.[5] However, the ionic conductivities of the columnar imidazolium salts are about 10^{-7}–10^{-4} S cm^{-1} in the LC phases. If the conductivity can be increased to the order of 10^{-3} S cm^{-1}, the applicability of the columnar ionic materials as electrolytes will be increased. In addition, improvement in the reduction stability of the imidazolium ring to electrodes is also required for the development of high-performance electrolytes.[7]



1(n/X$^-$): R = H, n = 8, 12, 16, 18
2(12/X$^-$): R = CH_3, n = 12
X$^-$ = BF_4^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$

Fig. 1. Fan-shaped imidazolium salts **1**(n/X$^-$) and **2**(12/X$^-$).

Our intention is to obtain columnar LC imidazolium salts exhibiting both higher ionic conductivities and electrochemical stability through the chemical modification of the functional molecular structures. For normal ionic liquids that form isotropic liquid states, the effects of cations and anions on their properties were examined.[8] The ionic conductivities of the ionic liquids depend on the viscosities and the size of cations and anions.[8a] MacFarlane and co-workers reported the ionic conductivities of imidazolium salts depend on the cationic species.[8b] It is of interest to examine the effect of the anions of LC imidazolium salts on their ionic conductivities and self-assembling properties. However, only the salts based on BF_4^- were studied.[5a,b] In the case of the series of **1**, the size of the imidazolium cation is larger than those of normal imidazolium-

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Table 1. Thermal Properties of Compounds **1**(n/X$^-$) and **2**(12/X$^-$)

Compound	1st Cooling[a]					2nd Heating[a]				
1(8/BF$_4^-$)[b]	I	130 (1.0)	Col$_h$	−37	G	G	−29	Col$_h$	133 (1.0)	I
1(12/BF$_4^-$)[b]	I	182 (1.1)	Col$_h$	8 (26)	Cr	Cr	17 (29)	Col$_h$	183 (1.3)	I
1(16/BF$_4^-$)[c]	I	175 (0.7)	Col$_h$	33 (72)	Cr	Cr	74 (42)	Col$_h$	177 (1.5)	I
1(18/BF$_4^-$)[c]	I	145 (1.2)	Col$_h$	60 (88)	Cr	Cr	88 (87)	Col$_h$	148 (1.1)	I
1(8/PF$_6^-$)	I	73 (0.6)	Col$_h$	−38	Cr	G	−33	Col$_h$	78 (0.6)	I
1(12/PF$_6^-$)	I	147 (1.0)	Col$_h$	5 (26)	Cr	Cr	12 (28)	Col$_h$	151 (1.0)	I
1(16/PF$_6^-$)	I	167 (1.0)	Col$_h$	48 (69)	Cr	Cr	55 (63)	Col$_h$	167 (1.0)	I
1(18/PF$_6^-$)	I	162 (1.1)	Col$_h$	60 (92)	Cr	Cr	68 (77)	Col$_h$	161 (1.2)	I
1(8/CF$_3$SO$_3^-$)	I		—	−72	G′	G′	−56 I′	−20 (25)[d]	Cr 1 (25)	I
1(12/CF$_3$SO$_3^-$)	I	73 (0.8)	Col$_h$	10 (39)	Cr	Cr	63 (57)	—		I
1(16/CF$_3$SO$_3^-$)	I	116 (0.9)	Col$_h$	52 (83)	Cr	Cr	78 (90)	Col$_h$	117 (0.9)	I
1(18/CF$_3$SO$_3^-$)	I	115 (1.0)	Col$_h$	60 (90)	Cr	Cr	86 (90)	Col$_h$	119 (1.0)	I
1(8/(CF$_3$SO$_2$)$_2$N$^-$)	I		—	−70	G′	G′	−58 I′	−19 (31)[d]	Cr 2 (31)	I
1(12/(CF$_3$SO$_2$)$_2$N$^-$)	I		—	13 (34)	Cr	Cr	37 (34)	—		I
1(16/(CF$_3$SO$_2$)$_2$N$^-$)	I	55 (0.3)	Col$_h$	52 (78)	Cr	Cr	55 (78)	Col$_h$	60 (0.2)	I
1(18/(CF$_3$SO$_2$)$_2$N$^-$)	I	76 (0.7)	Col$_h$	63 (85)	Cr	Cr	66 (81)	Col$_h$	77 (0.7)	I
2(12/BF$_4^-$)	I	177 (0.7)	Col$_h$	10 (26)	Cr	Cr	19 (27)	Col$_h$	174 (0.7)	I
2(12/PF$_6^-$)	I	157 (0.9)	Col$_h$	5 (23)	Cr	Cr	58 (30)	Col$_h$	155 (0.8)	I
2(12/CF$_3$SO$_3^-$)	I	83 (0.5)	Col$_h$	13 (35)	Cr	Cr	66 (54)	Col$_h$	85 (0.6)	I
2(12/(CF$_3$SO$_2$)$_2$N$^-$)	I		—	14 (82)	Cr	Cr	51 (77)	—		I

a) Transition temperatures (°C) and enthalpies of transition (kJ mol^{-1}, in parentheses) determined by DSC on the heating and cooling rates of 10 °C min^{-1}. The transition temperatures were taken at the onset points of the transition peaks. Cr: crystalline; Col$_h$: hexagonal columnar; G, G′: glassy; I, I′: isotropic. b) Ref. 5a. c) Ref. 5b. d) Cold crystallization.

based ionic liquids. We expect the anionic species exert more effects on the ionic conductivities of the series of the LC materials of **1** than normal ionic liquids. It is also of interest to study the property–structure relationship of the imidazolium salts as ionic LC materials.[9,10]

Here, we report on the mesomorphic properties and ionic conductivities of 1-methyl-3-[3,4,5-tris(alkyloxy)benzyl]imidazolium salts (**1**(n/X$^-$)), $n = 8$, 12, 16, and 18, X$^- =$ hexafluorophosphate (PF$_6^-$), trifluoromethylsulfonate (CF$_3$SO$_3^-$), and bis(trifluoromethylsulfonyl)imide ((CF$_3$SO$_2$)$_2$N$^-$), and 1,2-dimethyl-3-[(3,4,5-tris(dodecyloxy)benzyl]imidazolium salts (**2**(12/X$^-$)) including a tetrafluoroborate anion (BF$_4^-$) (Fig. 1).

Experimental

Compounds **1**(n/X$^-$) and **2**(12/X$^-$) containing perfluorinated anions were synthesized by a quaternization reaction of 1-methylimidazole and 1,2-dimethylimidazole with 3,4,5-tris(alkyloxy)benzyl chloride, followed by anion exchange using silver tetrafluoroborate, potassium hexafluorophosphate, silver triflate, or lithium bis(trifluoromethylsulfonyl)imide in methanol (see Supporting Information). These salts were purified by column chromatography on silica gel (eluent: chloroform/methanol = 10/1). ^{1}H NMR spectra were recorded using a JEOL JNM-LA400 at 400 MHz in CDCl$_3$ relative to tetramethylsilane.

Thermal properties of the materials were examined by differential scanning calorimetry (DSC) using a Netzsch DSC204 *Phoenix*®. The heating and cooling rates were 10 °C min^{-1}. Transition temperatures were taken at the onset points of the transition peaks. A polarizing optical microscope, Olympus BX51, equipped with a Mettler FP82HT hot stage was used for visual observation. X-ray diffraction measurements were carried out on a Rigaku RINT 2500 diffractometer using a Cu Kα radiation.

Ionic conductivities were measured by using an alternating current impedance method using a Schlumberger Solartron 1260 impedance analyzer (frequency range: 10 Hz–10 MHz, applied voltage: 0.3 V) and a temperature controller. The samples of imidazolium salts were heated up to the isotropization temperatures in the glass measurement cell with comb-shaped gold electrodes and then cooled to the temperature at which the columnar LC phase is formed. The columnar materials were oriented by mechanical shearing in the directions parallel and perpendicular to the applied electric field to measure ionic conductivities parallel and perpendicular to the columnar axis, respectively.[5] The heating rate of the measurements was fixed at 3 °C min^{-1}. Ionic conductivities were calibrated with a KCl aqueous solution (1.00 mmol L^{-1}) as a standard conductive solution.

Results and Discussion

Liquid-Crystalline Properties. The thermal properties of compounds **1**(n/X$^-$) and **2**(12/X$^-$) are presented in Table 1. The phase-transition behavior of the series of **1**(n/BF$_4^-$) was reported in previous papers.[5a,b] These salts form enantiotropic hexagonal columnar LC phases except for the salts containing CF$_3$SO$_3^-$ and (CF$_3$SO$_2$)$_2$N$^-$ having octyl and dodecyl chains. The series of compounds **1**(n/BF$_4^-$) and **1**(n/PF$_6^-$) exhibit wider LC temperature ranges. Room-temperature columnar LC phases are seen only for **1**(n/BF$_4^-$) and **1**(n/PF$_6^-$) having octyl and dodecyl chains, and **2**(12/BF$_4^-$). The highest temperature of the columnar-isotropic transition is observed for **1**(12/BF$_4^-$) at 183 °C. For the series of **1**(n/(CF$_3$SO$_2$)$_2$N$^-$), the enantiotropic LC phases are induced by the introduction of the hexadecyl and octadecyl chains. The melting points show an increasing trend as the chain length increases. Figure 2 shows a polarizing microscopic image of **1**(16/

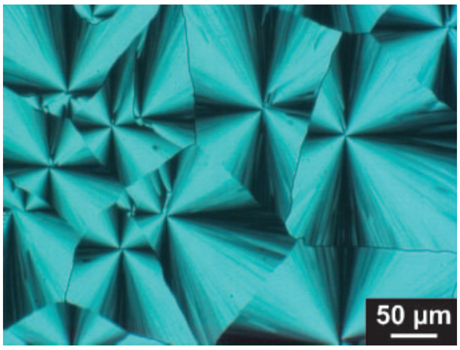

Fig. 2. Polarizing optical micrograph of **1**(16/$(CF_3SO_2)_2N^-$) in the Col_h phase at 57 °C.

$(CF_3SO_2)_2N^-$) in the Col_h phase at 57 °C. The clearing points show a decreasing trend with an increase in the size of anions. For example, the clearing points of **1**(16/X^-) with BF_4^-, PF_6^-, $CF_3SO_3^-$, and $(CF_3SO_2)_2N^-$ are 177, 167, 117, and 60 °C, respectively. This suggests that the order of the stabilization effects on the columnar LC structures is $BF_4^- > PF_6^- > CF_3SO_3^- > (CF_3SO_2)_2N^-$. The bulky anions may disturb their columnar packing. This trend in the fan-shaped imidazolium salts is similar to that of 1-alkyl-3-methylimidazolium salts[9h] showing smectic A phases, whereas no mesophases are formed for the salts with $(CF_3SO_2)_2N^-$. The volume fraction of ionic and non-ionic parts of the block molecules and the strength of electrostatic interactions and hydrogen bonding are important for the formation of the LC phases.

As for the **2**(12/X^-), except for **2**(12/$(CF_3SO_2)_2N^-$), the Col_h phase is formed despite the presence of a bulky methyl group on the imidazolium ring. Compound **2**(12/$CF_3SO_3^-$) shows an enantiotropic Col_h phase from 66 to 85 °C, whereas **1**(12/$CF_3SO_3^-$) shows only a monotropic Col_h phase from 73 to 10 °C. The electron-donating substituent at the second position of the imidazolium cation might stabilize the self-assembled structures.

X-ray Diffraction Study. X-ray diffraction patterns of compounds **1**(n/X^-) and **2**(12/X^-) forming a columnar LC phase show three reflections with the reciprocal spacing ratio of $1{:}\sqrt{3}{:}2$ in a small-angle region and a broad halo at $2\theta = 20°$ due to disordered aliphatic chains. For example, **1**(18/$(CF_3SO_2)_2N^-$) shows the reflections with d-spacing values of 37.7, 21.8, and 18.9 Å, as shown in Fig. 3. These results indicate that a hexagonal columnar structure is formed. The intercolumnar distances (a) of these salts were calculated with the equation of $a = 2d_{100}/\sqrt{3}$, where the values of d_{100} were obtained from the diffraction of the columnar phases at 10 degrees below the isotropization temperatures, except for **1**(n/$(CF_3SO_2)_2N^-$). The results for **1**(n/X^-) are summarized in Fig. 4. With an increase in the alkyl chain length, the distance between columns increases, except for **1**(18/X^-). A correlation between the anions and the intercolumnar distance is not clear, although the distance is expected to increase as the size of anions increases in the order of $BF_4^- < PF_6^- < CF_3SO_3^- < (CF_3SO_2)_2N^-$. The columnar distances for **1**(n/$CF_3SO_3^-$) are rather shorter than those for the salts with BF_4^- and PF_6^-. It can be attributed to the intrusion of $CF_3SO_3^-$ into the lipophilic alkyloxypheny region due to its weaker Coulombic interactions with the imidazolium cations. This position may not contribute to the increase of the size of columns. The $CF_3SO_3^-$ is relatively bulky, and its negative charge is stabilized by delocalization in the anion structure. Therefore, hydrogen bonding and Coulombic interactions with the imidazolium cations should be weaker. In contrast, the BF_4^- and PF_6^- are spherical and should form stronger interactions with the imidazolium cations in all directions in the center of the columns. Thus, the BF_4^- and PF_6^- may form inner ionic columnar structures with cations, resulting in larger intercolumnar distances than that of $CF_3SO_3^-$. As for the **2**(12/X^-), the intercolumnar distances is 38.3 Å. The introduction of the methyl group on the imidazolium ring does not disturb the hexagonal columnar packing.

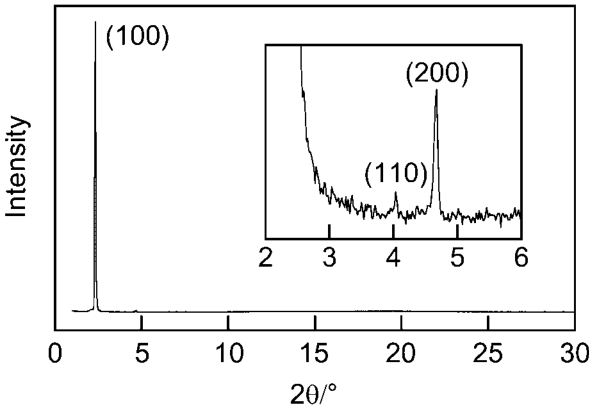

Fig. 3. X-ray diffraction pattern of **1**(18/$(CF_3SO_2)_2N^-$) in the Col_h phase at 74 °C.

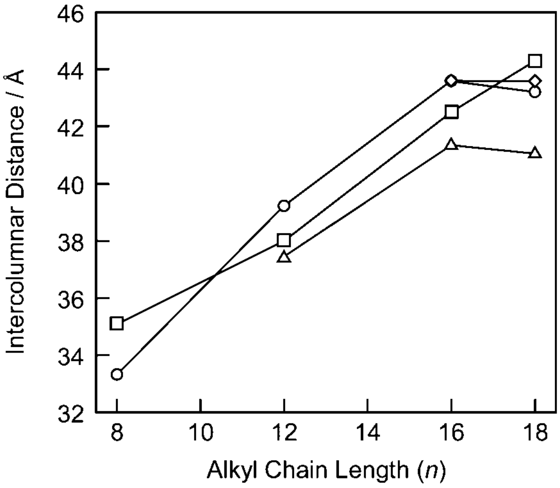

Fig. 4. Intercolumnar distances of the salts **1**(n/X^-) containing BF_4^- (□), PF_6^- (○), $CF_3SO_3^-$ (△), and $(CF_3SO_2)_2N^-$ (◇) in the Col_h phases as a function of the alkyl chain length of the imidazolium cation.

Alignment of Columns and Ion-Conductive Properties. The LC columns of **1**(16/X^-) containing BF_4^-, PF_6^-, and $CF_3SO_3^-$ were aligned macroscopically perpendicular and parallel to the comb-shaped gold electrodes by mechanical shearing (Fig. 5). This alignment technique for columnar LC imidazolium salts were described in previous papers.[5] The formation of columnar monodomains for **1**(16/X^-) has been confirmed with polarizing optical microscope observation.

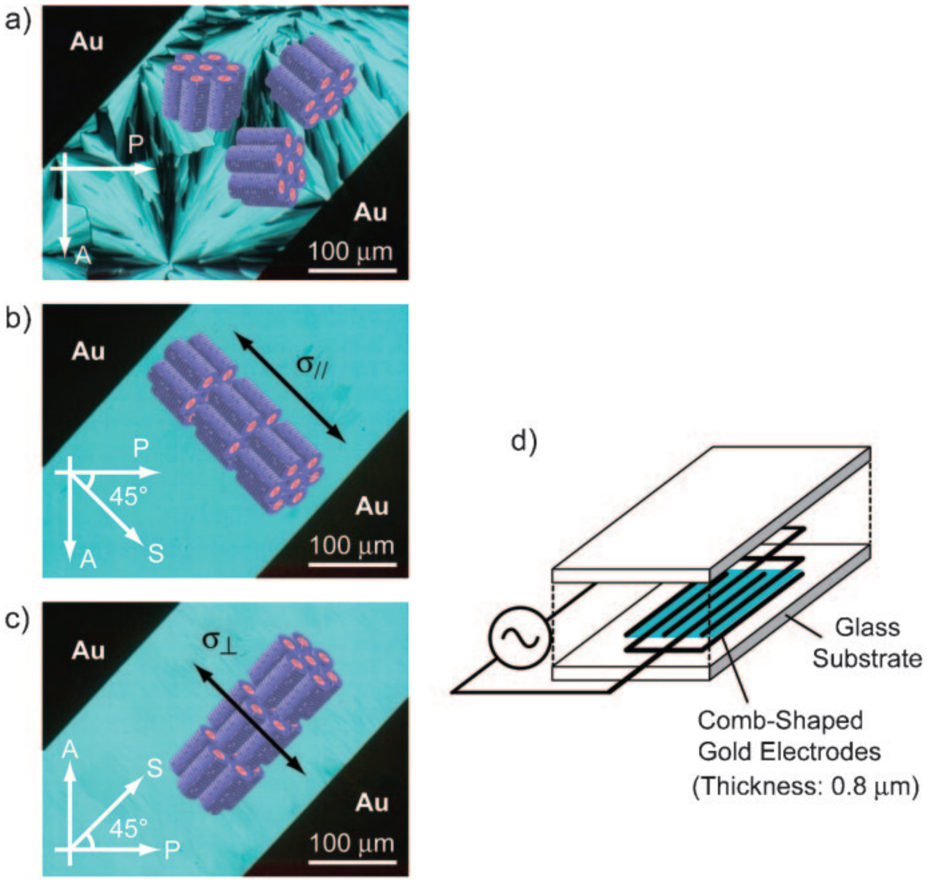

Fig. 5. Polarizing optical microscopic images and schematic illustration of the self-assembled structures of **1**(16/$CF_3SO_3^-$) in the Col_h phase at 100 °C: (a) before shearing; after shearing the material along the direction, (b) parallel, and (c) perpendicular to the electric field. Directions of A: analyzer; P: polarizer; S: shearing. (d) Illustration of a glass cell with comb-shaped gold electrodes for the anisotropic ion conduction measurements. Sample thickness: 0.8 μm.

The ionic conductivities were measured for **1**(16/X^-) with columnar orientation parallel to the surface of the glass substrate. Figure 6 shows the ionic conductivities parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the columnar axis for these **1**(16/X^-) as a function of temperature. Anisotropic conductivities are observed for **1**(16/X^-) in the columnar phases. The values of $\sigma_{\parallel}$ are higher than those of $\sigma_{\perp}$. For example, **1**(16/$CF_3SO_3^-$) shows the conductivities of 1.3×10^{-5} S cm^{-1} ($\sigma_{\parallel}$) and 6.5×10^{-7} S cm^{-1} ($\sigma_{\perp}$) at 100 °C. No anisotropy is observed when the materials form isotropic liquid phases. For example, the anisotropy for **1**(16/$CF_3SO_3^-$) disappears at 117 °C. These results indicate that ion-conducting paths are formed along the columnar axis in the Col_h phases and the alkyloxyphenyl part functions as an ion-insulating part.

As for **1**(16/BF_4^-) and **1**(16/PF_6^-), anisotropy is observed until temperatures that are 10–15 degrees above the onset points of the columnar-isotropic transitions because these compounds show broader isotropization temperature ranges.

The $\sigma_{\parallel}$ values for **1**(16/PF_6^-) are higher than those for **1**(16/BF_4^-) from 85 to 150 °C. The ionic conductivities ($\sigma_{\parallel}$) for **1**(16/$CF_3SO_3^-$) are almost the same as those of **1**(16/BF_4^-) below 100 °C, while the $\sigma_{\parallel}$ values for **1**(16/$CF_3SO_3^-$) are lower than those for **1**(16/BF_4^-) above 100 °C. The $\sigma_{\parallel}$ values for **1**(16/X^-) in the Col_h phases at 110 °C increase in the order of $PF_6^- > BF_4^- > CF_3SO_3^-$. The anisotropy of

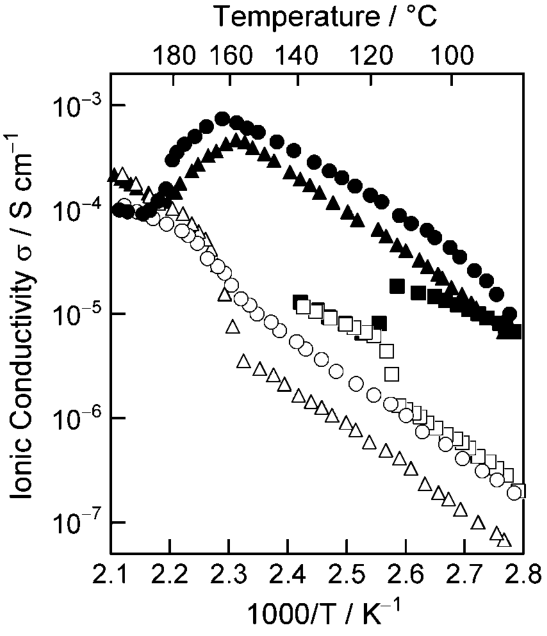

Fig. 6. Anisotropic ionic conductivities of **1**(16/BF_4^-) ($\sigma_{\parallel}$: ▲, $\sigma_{\perp}$: △), **1**(16/PF_6^-) ($\sigma_{\parallel}$: ●, $\sigma_{\perp}$: ○), and **1**(16/$CF_3SO_3^-$) ($\sigma_{\parallel}$: ■, $\sigma_{\perp}$: □) as a function of temperature.

ionic conductivities ($\sigma_{\parallel}/\sigma_{\perp}$) decreases with an increase in the size of the anions. For example, the values of anisotropy obtained for **1**(16/BF_4^-), **1**(16/PF_6^-), and **1**(16/$CF_3SO_3^-$) in the Col$_h$ phases at 110 °C are 1.1×10^2, 8.1×10, and 1.5×10, respectively. For **1**(16/$(CF_3SO_2)_2N^-$), only ionic conductivities of the polydomain sample were measured because the formation of a columnar monodomain was difficult due to the narrow temperature range of the Col$_h$ phase (from 55 to 60 °C). Compound **1**(16/$(CF_3SO_2)_2N^-$) shows the conductivities of 4.7×10^{-6} S cm^{-1} in the Col$_h$ phase, forming polydomain at 59 °C, and 3.6×10^{-5} S cm^{-1} in the isotropic phase at 110 °C.

As for **1**(16/X^-), the cationic imidazolium moiety is considered to be less mobile than the anions in the columnar structure. The observed ionic conductivities may be mostly due to the diffusion and/or hopping of the anions inside the columns because the conductivities strongly depend on the anions. In future, we will examine the mechanism of ion conduction in the columnar LC phases using NMR measurements.[11]

Conclusion

The anions of columnar LC 1-methyl-3-[3,4,5-tris(alkyloxy)benzyl]imidazolium salts (**1**(n/X^-)) exert significant effects on the mesomorphic properties and ionic conductivities. The salts of BF_4^- and PF_6^- having octyl and dodecyl chains exhibit room-temperature columnar LC phases, while no LC behavior is observed for the corresponding salts containing $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$. It is noteworthy that the mesophases displayed by the salts **1**(12/X^-) containing BF_4^- and PF_6^- are stable over 150 °C. Columnar LC phases are observed for the salts **1**(16/X^-) and **1**(18/X^-) containing $CF_3SO_3^-$ and $(CF_3SO_2)_2N^-$. As for 1,2-dimethyl-3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium salts (**2**(12/X^-)) containing BF_4^-, PF_6^-, and $CF_3SO_3^-$, columnar LC phases are formed despite the presence of a bulky methyl group on the imidazolium ring. Anisotropic ionic conductivities are observed for the **1**(16/X^-) containing BF_4^-, PF_6^-, and $CF_3SO_3^-$ in the Col$_h$ phases, in which the columns of these salts are macroscopically aligned by mechanical shearing. The ionic conductivities parallel to the columnar axis are higher than those perpendicular to the columnar axis.

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Supporting Information

Synthesis of **1**(18/X^-) and **2**(12/X^-). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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