

Ionic Liquid Crystals: Self-assembly of Imidazolium Salts Containing an L-Glutamic Acid Moiety

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Liquid-crystalline (LC) behavior and ionic conductivities of imidazolium salts containing an L-glutamic acid moiety have been studied. The ionic conductivities of the $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ salt forming the columnar LC phase are higher than those of the Br^- salt in the columnar LC state. The ionic conductivity shows a sudden decrease at the columnar–micellar cubic LC transition of the Br^- salt.

Self-assembly of liquid-crystalline (LC) molecules with functional moieties is one of the versatile approaches to the preparation of functional soft materials with dynamic and anisotropic nature.^{1–4} Ionic liquid crystals^{5–8} have attracted attention because they have potentials for applications as ion conductors,⁶ redox-active materials,⁷ and ordered solvents.⁸ They form a variety of LC nanostructures^{1,2,9} such as micelles, cylinders, layers, and bicontinuous cubic structures through ionic interactions and nanosegregation between ionic and non-ionic moieties.

Recently, we have reported on one-dimensional ion conduction in ionic columnar liquid crystals,^{6a–6d} 1-methyl-3-[3,4,5-tris(alkyloxy)benzyl]imidazolium salts containing BF_4^- , PF_6^- , CF_3SO_3^- , and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (TFSI[−]). The LC properties and ionic conductivities were strongly dependent on the properties of counter anions. To obtain highly ion-conductive materials, the use of TFSI[−] is considered to be desirable because of its negative charge delocalization and weak electrostatic interactions with cations.¹⁰ However, the preparation of LC imidazolium TFSI[−] salts that form columnar phases in wide temperature ranges has not yet been achieved.^{6a–6c} For the preparation of self-assembled materials that exhibit stable mesophases, it should be important to control intermolecular interactions and the balance of volume fraction of ionic and non-ionic parts of the molecules.^{2,9,11}

Our molecular design here is to attach a fan-shaped L-glutamic acid derivative bearing bis(alkyloxy)phenyl moieties¹² to imidazolium salts (Figure 1). The glutamic acid derivative can be used as a molecular building block to produce stable columnar and micellar cubic LC materials upon hydrogen bonding.¹² In addition, the incorporation of a more bulky lipophilic part than those of previously reported ionic

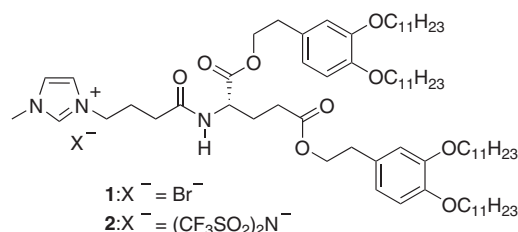


Figure 1. Imidazolium salts having an L-glutamic acid moiety.

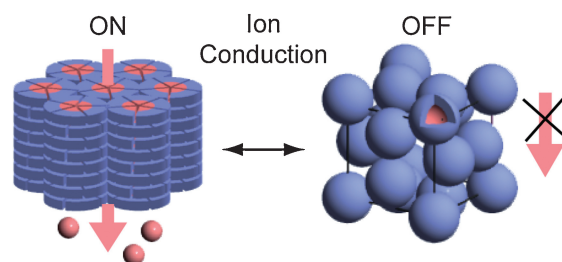


Figure 2. Schematic illustration of an ideal on–off switch of ion conduction using the structural change from columnar to micellar cubic LC structures.

Table 1. Thermal properties of **1** and **2**

Compound	Phase-transition behavior ^a				
1	Cr	51 (48)	Col _h	136 (1.0)	Cub ^b
2	Cr	64 (60)	Col _h	99 (1.2)	Iso

^aTransition temperatures (°C) and enthalpies (kJ mol^{−1}, in parentheses) were determined by DSC on the second heating at 2 °C min^{−1}. The transition temperatures were taken at the onset points of transition peaks. ^bThe isotropization temperature could not be determined because thermal degradation occurred above 180 °C before reaching the isotropic liquid state. Cr: crystalline, Col_h: hexagonal columnar, Cub: cubic, Iso: isotropic liquid.

molecules^{6a–6c} into imidazolium salts may induce a structural change from columnar to micellar cubic phases, leading to the on–off switch^{3d} of ion conduction (Figure 2). Herein, we report on self-assembly of imidazolium-based ionic liquid crystals **1** and **2** exhibiting stable columnar and cubic LC phases and their ionic conductivities.

The LC properties of **1** and **2** are summarized in Table 1. Compound **1** exhibits columnar and cubic phases, while compound **2** shows only a columnar phase in the temperature range that is wider than those of previously reported imidazolium-based LC salts with TFSI[−].^{6b} The X-ray diffraction (XRD) patterns confirm that the LC phases of **1** and **2** at 80 °C are hexagonal columnar phases. The intercolumnar distances for both of **1** and **2** are 50 Å. The XRD pattern of **1** shows three peaks at 45.5, 26.0, and 22.4 Å with a reciprocal *d*-spacing ratio of 1:√3:2. These peaks correspond to the (100), (110), and (200) reflections, respectively. The cubic LC phase of **1** has been determined as a micellar cubic phase with *Pm3n* symmetry from the XRD pattern taken at 150 °C.¹³

The macroscopic orientation of the LC columns parallel to the surface of a glass substrate having comb-shaped gold electrodes was achieved by mechanical shearing of the polydomain samples of **1** and **2**.^{6a–6c} Anisotropic ionic conductivities of the aligned columnar liquid crystals on heating were measured by

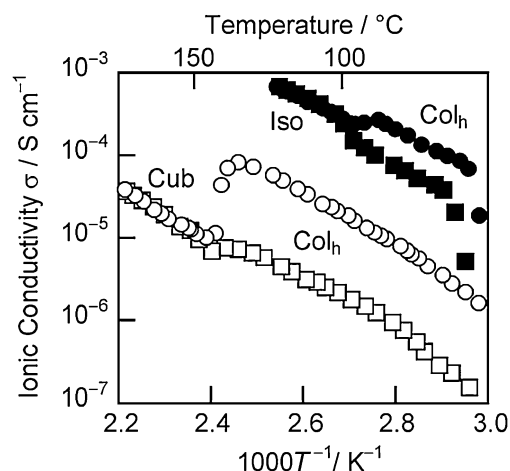


Figure 3. Ionic conductivities of **1** and **2** as a function of temperature: for **1**, (○) parallel and (□) perpendicular to the columnar axis; for **2**, (●) parallel and (■) perpendicular to the columnar axis. Frequency range: 10 Hz to 5 MHz.

using an alternating current impedance method^{6a,13} (Figure 3). The ionic conductivities parallel to the columnar axis ($\sigma_{||}$) are higher than those perpendicular to the columnar axis ($\sigma_{\perp}$). The $\sigma_{||}$ values of **2** are about 10 times higher than those of **1** at the same temperature. The highest value of $\sigma_{||}$ for **2** in the columnar phase is $2.9 \times 10^{-4} \text{ S cm}^{-1}$ at 91°C .

As for **1**, the conductivity suddenly decreases from 8.4×10^{-5} to $9.6 \times 10^{-6} \text{ S cm}^{-1}$ at the columnar–micellar cubic LC transition around 136°C . In the micellar cubic phase, ionic moieties are confined in the micelles insulated by the lipophilic alkyloxyphenyl parts, preventing the ion conduction over long distance. The decrease in ionic conductivity at the phase transition can potentially be used as an on–off switch.

Infrared measurements were performed for **1** and **2** in the LC phases¹³ to examine the relationship between the ionic conductivities and molecular interactions involving the hydrogen bonds at the glutamic acid moiety. The spectra of **1** show the N–H stretching band of the amide group involved in hydrogen bonding at 3220 cm^{-1} . In contrast, for the spectra of **2**, the N–H stretching band appears at 3381 cm^{-1} , suggesting that hydrogen bonds are only weakly formed. The C=O stretching band of the amide group is observed at 1670 cm^{-1} for **1** and **2** in the LC phases, showing that the C=O group of the amide group does not form strong hydrogen bonds in the LC phases. These results suggest that Br^- of **1** forms a hydrogen bond with the proton of the amide group and may thus disturb the formation of intermolecular hydrogen bonding between amide groups, and that the TFSI^- is not involved in hydrogen bonding, possibly leading to the higher ionic conductivities for **2**.

In conclusion, we have prepared new imidazolium-based ion-conductive columnar and cubic liquid crystals containing an L-glutamic acid moiety.

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