Communication

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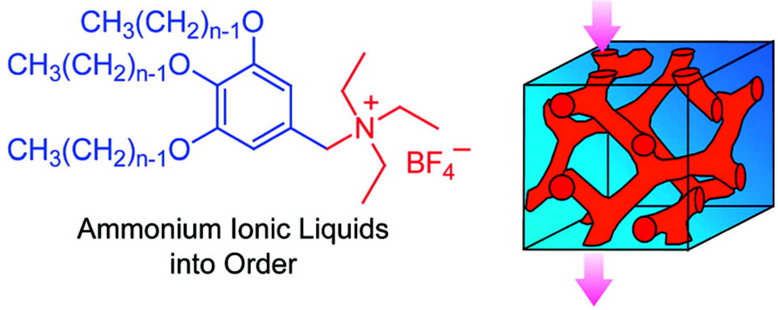

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Self-Organization of Room-Temperature Ionic Liquids Exhibiting Liquid-Crystalline Bicontinuous Cubic Phases: Formation of Nano-Ion Channel Networks

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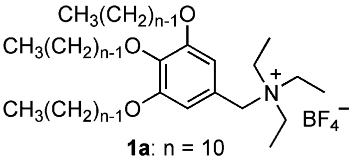
Ionic liquids have recently attracted a great deal of attention because they are expected to have potentials as materials in a variety of fields such as electrochemistry and organic synthesis.[1] A variety of room-temperature ionic liquids based on imidazolium, pyridinium, and ammonium cations have been prepared. They form disordered states. Our strategy has been to introduce liquid-crystalline (LC) order[2] into ionic liquids at ambient temperature because new function of these materials could be developed using self-organized anisotropic nanostructures.

Recently, we have prepared low-dimensional ion conductors based on LC ionic liquids which exhibit anisotropic fluidic states at ambient temperature.[3] In this molecular design, we intended self-assembly of ionic liquid crystals based on imidazolium salts.[3a−d] The nanosegregated structures of columnar (cylinder) and smectic (layer) liquid crystals consisting of ionic and non-ionic parts lead to the formation of one-dimensional and two-dimensional ion conductors.[4] In these materials, the control of macroscopic order of the nanosegregated LC structures is essential. For example, columnar order has been aligned in parallel direction to the surface of a glass substrate by mechanical shearing of the columnar ionic liquid crystals based on imidazolium salts.[3a,b] Moreover, the formation of monodomain and the vertical alignment of the columns have been achieved for these ionic LC materials.[3b]

If we could achieve continuous nanochannels of ions through the organic membranes based on ionic liquids, new ion-functional materials could be prepared. However, the fabrication of a large size of monodomains of the columnar structure is not easy, which limits wider applicability as functional materials. To overcome this problem in the columnar materials, we have focused on the use of LC bicontinuous cubic[5] ($\mathrm{Cub_{bi}}$) nanostructures as functional materials as ion conductors. Unlike the columnar phases, the LC $\mathrm{Cub_{bi}}$ phases would not require macroscopic channel alignment to facilitate ion transportation because of their three-dimensionally interconnected channel networks. However, to our knowledge, the advantage of the LC $\mathrm{Cub_{bi}}$ materials for ion transportation has not yet been explored, although cross-linked lyotropic LC $\mathrm{Cub_{bi}}$ assemblies[6,7] have been proposed for applications as catalysts,[7] selective separation membranes,[7] drug delivery,[8] and templates.[9]

Here we demonstrate that the thermotropic LC $\mathrm{Cub_{bi}}$ phases of ammonium salts **1a,b** (Figure 1) function as ion conductors by forming nano-ion channels (Figure 2). We show that the alignment free $\mathrm{Cub_{bi}}$ phases have higher ionic conductivities than the non-aligned columnar phases.



1a: n = 10
1b: n = 12
1c: n = 14

Figure 1. Molecular structure of self-organized ammonium salts.

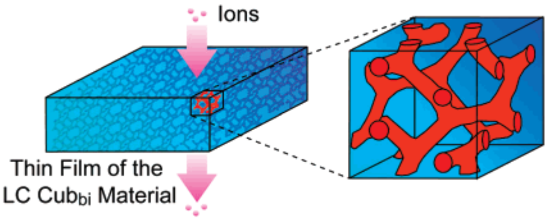


Figure 2. Nano-ion channel network based on a LC bicontinuous cubic structure with the *Ia*3*d* symmetry.

We have designed and prepared fan-shaped compounds **1a**−**c** that have block molecular structures composed of two immiscible molecular parts: the ammonium moiety at the focal point and the lipophilic alkylphenyl part. Compounds **1a**−**c** exhibit thermotropic LC $\mathrm{Cub_{bi}}$ and hexagonal columnar ($\mathrm{Col_h}$) phases as given in Table 1. In contrast, most of conventional thermotropic LC ammonium salts previously reported show smectic phases.[10] Few thermotropic materials exhibiting LC $\mathrm{Cub_{bi}}$ phases were reported.[4e,11] It was also difficult to obtain thermotropic LC $\mathrm{Cub_{bi}}$ materials based on imidazolium salts. It is considered that the balance of the size and shape of non-ionic and ionic parts is delicate for the induction of the $\mathrm{Cub_{bi}}$ phase.

Compound **1a** shows a crystalline (Cr)−$\mathrm{Cub_{bi}}$ transition at 42 °C on heating. After the melting transition, the sample forms a viscous fluid and no birefringence is observed between crossed polarizers even after shearing. Upon further heating, **1a** becomes an isotropic liquid (Iso) at 82 °C. The X-ray pattern of **1a** at 50 °C shows two intense peaks at 31.8 and 27.4 Å and five weak peaks at 20.7, 17.5, 16.7, 15.9, and 15.3 Å in a small-angle region and a broad halo at 4.5 Å in a wide-angle region (see Supporting Information). The reciprocal spacing ratio of seven peaks in the small-angle region are $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{20}:\sqrt{22}:\sqrt{24}:\sqrt{26}$, which can be assigned to the (211), (220), (321), (420), (332), (422), and (510) reflections of the gyroid $\mathrm{Cub_{bi}}$ phase with the *Ia*3*d* symmetry as illustrated in Figure 2.[12]

The increase of the alkyl chain length induces LC columnar phases (Table 1). Under observation with a polarized optical microscope, compound **1b** shows no birefringence at 46 °C and a fan texture typical for a $\mathrm{Col_h}$ phase at 110 °C (see Supporting Information). Compound **1b** exhibits the LC $\mathrm{Col_h}$ phase at higher

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Table 1. Phase Transition Behavior[a] of Compounds **1a**−**c**

compound	Cr		Cub$_{bi}$		Col$_{h}$		Iso
1a	•	42 (0.5)	•			82 (0.8)	•
1b	•	32 (30.3)	•	49 (1.0)	•	126 (0.7)	•
1c	•	53 (63.9)			•	142 (1.0)	•

[a] Cr: crystal, Cub$_{bi}$: bicontinuous cubic, Col$_{h}$: hexagonal columnar, Iso: isotropic liquid. Temperatures in °C are given as the onset of the peak observed during second heating run at a scanning rate of 10 °C min^{-1} from differential scanning calorimetry traces. The enthalpy changes (kJ mol^{-1}) are in parentheses.

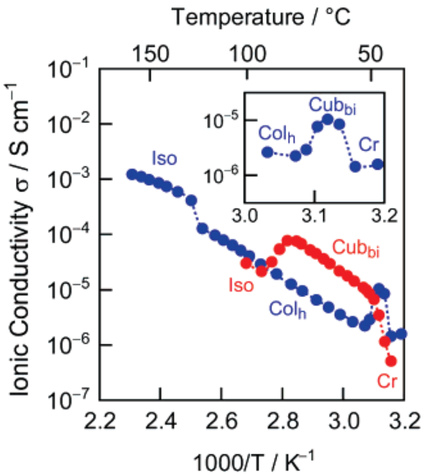

Figure 3. Ionic conductivities of **1a** (red) and **1b** (blue) as a function of temperature.

temperature forming the LC Cub$_{bi}$ phase. For **1c** having the alkyl chain that is longer than that of **1b**, only a LC Col$_{h}$ phase is seen in the range of 53−142 °C. The X-ray patterns of **1b** and **1c** at 110 °C show three peaks corresponding to the (100), (110), and (200) reflections, which are characteristic of a hexagonal columnar structure (see Supporting Information). The intercolumnar distances of **1b** and **1c** at 110 °C are 3.6 and 3.9 nm, respectively.

The ionic conductivities of **1a** and **1b** (Figure 3) have been measured with an alternating current impedance method.[3a,b] The ionic conductivities for **1a**, which only exhibits the LC Cub$_{bi}$ phase, increase up to 82 °C at which the Cub$_{bi}$−Iso transition starts. It is noteworthy that the ionic conductivities for **1a** decrease at the Cub$_{bi}$−Iso transition on further heating. These results suggest that the nanochannels that transport ions collapse after the Cub$_{bi}$−Iso transition on heating and the formation of nanochannel networks is more effective than the disordered isotropic phase that is more mobile. For **1b**, the ionic conductivities increase at the Cr−Cub$_{bi}$ transition at 32 °C and decrease at the Cub$_{bi}$−Col$_{h}$ transition at 49 °C, followed by the increase of the conductivities at the Col$_{h}$−Iso transition at 126 °C. It should be noted that the ionic conductivities in the Cub$_{bi}$ phase are higher than those in the Col$_{h}$ phase, where the columns form randomly oriented polydomains between electrodes. It is an advantage of the LC Cub$_{bi}$ assemblies forming interconnected ion channels where relatively higher ionic conductivities are achieved without a macroscopic orientation of the assemblies.

The self-organized ionic materials reported here are a novel system that exhibits the thermotropic LC Cub$_{bi}$ phase forming continuous ionic nanochannels. Such nanostructures can transport ions more efficiently than the non-oriented LC columnar materials. These materials can provide new transporting materials that form efficient networks of nanochannels.

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Supporting Information Available: Syntheses, polarized optical microscopic images, DSC charts, and X-ray diffraction patterns of compounds **1a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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