

One-Dimensional Ion Transport in Self-Organized Columnar Ionic Liquids

Masafumi Yoshio,[†] Tomohiro Mukai,[‡] Hiroyuki Ohno,[‡] and Takashi Kato^{*†}

Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Received September 1, 2003; E-mail: kato@chiral.t.u-tokyo.ac.jp

Columnar liquid crystals can be used for one-dimensional transportation of charge, ion, and energy.^{1–3} For such functionalization, it is important to control orientation, supramolecular association, and phase-segregation for the columnar assemblies ranging from molecular to macroscopic scales.^{1–6} In particular, the formation of self-organized monodomain in macroscopic scale plays key roles for the enhancement of properties. For example, fast charge (electron and hole) transports through columns were achieved for π -conjugated discotic molecules. As for ion-conductive liquid crystals, crown-ethers^{2a–c} and oligo(ethylene oxide)s (PEO)^{2d} were incorporated into mesogenic molecules to form columnar structures. However, to our knowledge, no one-dimensional ionic conductivities in a macroscopic monodomain had been measured for columnar liquid crystalline (LC) phases although two-dimensional macroscopic alignment of PEO-containing molecules leads to high two-dimensional ion conduction.⁷ Ionic liquids are functional isotropic liquids exhibiting high ionic conductivities.⁸ For example, *N,N'*-dialkylimidazolium salts containing perfluoro anions are one of common ionic liquids.⁹ Such materials have considerable potentials as electrolytes for batteries and capacitors. Recently, we have prepared two-dimensional ion-conductive materials formed by self-organization of dihydroxy-functional rodlike molecules and ionic liquids.¹⁰ Our design strategy here is to modify ionic liquids to prepare simpler columnar assemblies that exhibit fluid ordered states, maintaining both of high ionic conductivities and LC states at room-temperature ranges.

Here we report a new class of ionic liquids **1a,b** (Figure 1) exhibiting fluid self-organized structures. For the first time, one-dimensional ion conduction has been achieved for columnar LC materials, which are oriented uniaxially.

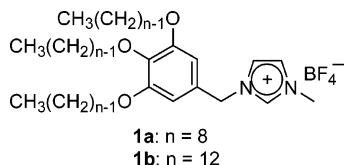


Figure 1. Chemical structure of self-organized columnar ionic liquids.

Liquid crystalline properties of compounds **1a,b** are shown in Table 1. These compounds exhibit hexagonal columnar phases over wide temperature ranges including room temperature, which is determined by DSC and X-ray measurements.¹¹ The X-ray patterns of **1a,b** at 25 °C show that the intercolumnar distances in the hexagonal columnar phases are 3.5 and 3.8 nm, respectively.

Macroscopically homogeneous alignment of the columnar structure is easily achieved by shearing these self-assembled materials. Figure 2 shows polarizing microscope images of **1b** in the columnar phases before and after shearing. The formation of monodomain

Table 1. Thermal Properties of Compounds **1a** and **1b**

compound	phase transition behavior ^a				
1a	G	−29	Col _h	133 (1.0)	I
1b	Cr	17 (29.3)	Col _h	183 (1.3)	I

^a Transition temperatures (°C) and enthalpies of transition (kJ mol^{−1}, in parentheses) determined by DSC (second heating scan, 10 °C min^{−1}). Col_h: hexagonal columnar; Cr: crystalline; G: glassy; I: isotropic.

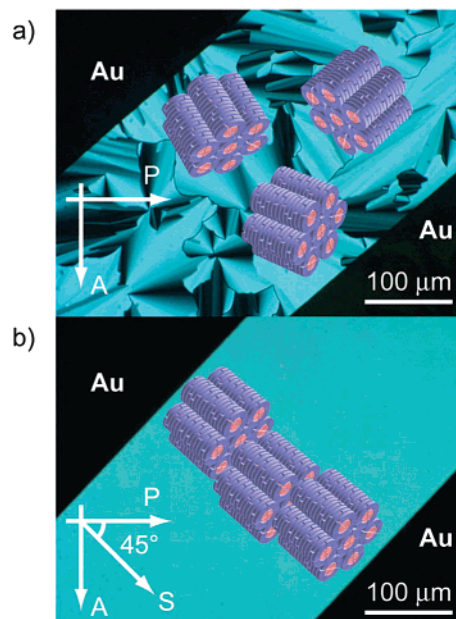


Figure 2. Polarizing optical microscopic images and schematic illustrations of the oriented and self-assembled structures of **1b** in the Col_h state at 25 °C: (a) before shearing; (b) after shearing the material along the direction perpendicular to the gold electrodes. Directions of A: analyzer; P: polarizer; S: shearing.

of the column is achieved after the polydomain of the columnar phase is sheared in the sandwiched glasses without rubbing treatment. The oriented structure is uniform over millimeters. The direction of the long axis of columns corresponds to the shearing direction, which is confirmed by the periodic change in the pattern with the sample's rotation for the polarizing microscopic observation. No birefringence is seen under the crossed Nicols condition when the shearing direction is along the polarizer or analyzer axis. The highest brightness is observed when the oriented sample is in a 45° angle.

One-dimensional ionic conductivities have been successfully measured with the complex impedance method by the cells having gold comblike electrodes.¹¹ The self-organized columns have been aligned in two directions by shearing perpendicular and parallel to

[†] The University of Tokyo.

[‡] Tokyo University of Agriculture and Technology.

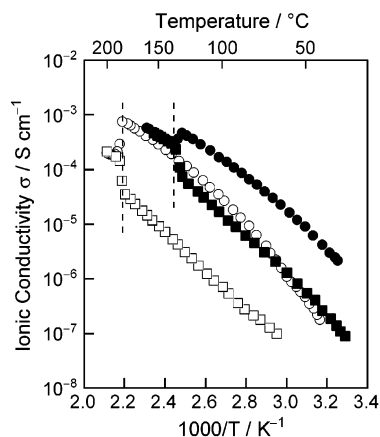


Figure 3. Anisotropic ionic conductivities of **1a** and **1b** as a function of temperature: (●) parallel and (■) perpendicular to the columnar axis for **1a**; (○) parallel and (□) perpendicular to the columnar axis for **1b**. The broken lines denote the $\text{Col}_h\text{-I}$ phase transition temperatures.

the electrodes. Figure 3 shows anisotropic ionic conductivities of the self-organized materials of **1a** and **1b** forming monodomains as a function of temperature. For the first time, anisotropic one-dimensional ionic conductivities have been measured for supra-molecular LC materials. The ionic conductivities parallel to the columnar axis (σ_{\parallel}) for **1a** and **1b** are higher than those perpendicular to the axis (σ_{\perp}) because the alkyloxyphenyl parts function as insulating parts. The σ_{\parallel} values for **1a** are higher than those of **1b** because the conductivities are calculated on the basis of the whole cross section area of the materials, and the area fraction of the insulating part of **1a** should be smaller than **1b**. The highest conductivity of $4.8 \times 10^{-4} \text{ S cm}^{-1}$ (σ_{\parallel}) is achieved for **1a** at 130 °C in the columnar phase. The anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) of ionic conductivities is observed to be a constant value of ca. 10 for **1a** in the columnar phase. No anisotropy is observed when the materials form isotropic liquid phases. The ionic conductivities of polydomain samples as a function of temperature are also measured for **1b**.¹¹ The values of 2.5×10^{-6} and $3.1 \times 10^{-5} \text{ S cm}^{-1}$ obtained in the polydomain at 100 and 150 °C, respectively, are between the values of σ_{\parallel} and σ_{\perp} of the oriented samples at the same temperatures.

These self-organized columnar ionic liquids can also function as self-organized electrolytes, which dissolve a variety of ionic species. The incorporation of the lithium salts in these columnar materials leads to the enhancement of the ionic conductivities and their anisotropy. For example, columnar material **1b** containing LiBF_4 (molar ratio of LiBF_4 to **1b**: 0.25) shows the conductivities of $7.5 \times 10^{-5} \text{ S cm}^{-1}$ (σ_{\parallel}), $8.0 \times 10^{-7} \text{ S cm}^{-1}$ (σ_{\perp}), and $\sigma_{\parallel}/\sigma_{\perp}$ of 94 at 100 °C respectively, while those of **1b** alone are $3.1 \times 10^{-5} \text{ S cm}^{-1}$ (σ_{\parallel}), $7.5 \times 10^{-7} \text{ S cm}^{-1}$ (σ_{\perp}), and $\sigma_{\parallel}/\sigma_{\perp}$ of 41 at 100 °C, respectively. The existence of the lithium salts increases only the conductivity along the columnar axis (σ_{\parallel}), which leads to the enhancement of anisotropy. These results suggest that the ions are incorporated in the central ionic part of the column. This approach would enable us to make a variety of ion conductors based on these materials. It should be noted that the addition of the lithium salt enhances the liquid crystallinity. For example, **1b** incorporating LiBF_4 (molar ratio of LiBF_4 to **1b**: 0.25) shows the columnar phase from 17 to 193 °C, while for the single component of **1b**, the columnar phase is observed from 17 to 183 °C. The ionic columnar core in the LC phase is stabilized by the existence of the metal salt.

In summary, a new class of materials, anisotropic ion-conductive ionic liquid crystals have been obtained. These materials would be useful for transportation of ion, energy, and information at the nanometer level. We have succeeded in measuring one-dimensional anisotropic ionic conductivities for the macroscopically ordered columnar assemblies.

Acknowledgment. Partial financial support of Grant-in-Aid for Scientific Research on Priority Areas, Scientific Research B, Encouragement of Young Scientists B, and The 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology is gratefully acknowledged.

Supporting Information Available: Synthesis, experimental details, and characterization of compounds **1a,b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0382516