

Anisotropic ion conduction in a unique smectic phase of self-assembled amphiphilic ionic liquids

Tomohiro Mukai,^a Masafumi Yoshio,^b Takashi Kato,^b Masahiro Yoshizawa^a and Hiroyuki Ohno*^a

Received (in Cambridge, UK) 23rd September 2004, Accepted 7th December 2004

First published as an Advance Article on the web 20th January 2005

DOI: 10.1039/b414631j

Two types of thermotropic smectic phase and of anisotropic ion conduction were observed in an amphiphilic ionic liquid, *N*-ethyl-*N'*-dodecylimidazolium dodecyl sulfonate/lithium tetrafluoroborate mixture.

Ionic liquids consist of charge-delocalized anions and organic cations such as imidazolium and pyridinium.¹ Ionic liquids provide advantages that include high ionic conductivity, non-volatility, non-flammability and catalytic properties. They are attracting keen attention as green solvents² or as an ion conductive matrix for electrochemical devices.³ Furthermore, the ready modification of ions is a great advantage in deploying organic ionic liquids. One way of giving the necessary functionality to ionic liquids is to introduce structures suited to self-assembly with a view to the construction of organized ion conduction pathways. Self-assembled ionic liquids are prepared by introducing long alkyl chains to the imidazolium ring⁴ or by mixing ionic liquids with calamitic molecules having polar groups at the alkyl chain ends.⁵ They show one-dimensional⁶ or two-dimensional⁵ ion conduction in a columnar or smectic phase.

In this work we have designed amphiphilic ionic liquids for target ion transport. Our previous studies have synthesized polymerizable ionic liquids⁷ and zwitterionic liquids⁸ as a new class of lithium ion conductive materials. To achieve a high lithium ion transport number, long-range ion migration was restricted in the design of these materials, except for Li⁺. Self-organized ionic liquids are unique materials, because they include a suitable space for a selective ion conduction path. In the phase-separated ionic liquid layer consisting of **1** (*N*-ethyl-*N'*-dodecylimidazolium dodecyl sulfonate; Chart 1), components of ionic liquids are fixed outside the hydrophobic alkyl layer.† In the liquid crystalline phase of the **1**/lithium salts mixture, both the Li cation and the anion were expected to migrate preferentially in the ionic layer. Below, we study the effect of adding lithium tetrafluoroborate (LiBF₄) on the phase transition behaviour, the self-assembled structure, and the ionic conductivity of assembled compound **1**.

Phase transition behaviour was studied by polarized optical microscopy and differential scanning calorimetry between –100

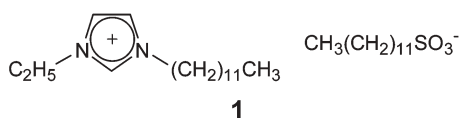


Chart 1 *N*-Ethyl-*N'*-dodecylimidazolium dodecyl sulfonate.

*ohnoh@cc.tuat.ac.jp

and 200 °C at a scanning rate of 10 °C min⁻¹. Dynamic and anisotropic ionic conductivities were measured by the complex impedance method over a frequency range running from 10 to 5 × 10⁶ Hz, using a comb-shaped gold electrode on a glass substrate (Au cell; as shown in Fig. 1) (σ_{\parallel} : ionic conductivity parallel to the ionic layer) or an ITO cell⁵ consisting of a pair of ITO glass electrodes and a Teflon spacer (σ_{\perp} : ionic conductivity perpendicular to the ionic layer) at temperatures from 150 to 30 °C at a cooling rate of –2 °C min⁻¹. The dynamic ionic conductivity measurement apparatus was developed in our laboratory.⁹ A voltage of 0.3 V was applied for measuring σ_{\parallel} and 0.01 V for measuring σ_{\perp} . The cell constant of these cells was calibrated with 0.01 M KCl aqueous solution. The cell constant of the Au cell was 80.5 and of the ITO cell was 0.16. Samples were charged on each electrode after they were heated to the isotropic temperature. After charging samples into the cells, homeotropic and mono-domain alignment at the liquid crystalline phase was confirmed by orthoscopic and conosopic observation.

Table 1 summarizes the phase transition behaviour for **1** and the **1**/LiBF₄ mixture in a heating and cooling cycle. During the cooling cycle, **1** displayed two types of liquid crystalline phase, smectic A and X (unidentified smectic). Addition of LiBF₄ raised the clearing point. The Li cation enhances intermolecular Coulombic interaction in the ionic layer because of the large surface charge density of Li⁺. The freezing point (and the enthalpy) fell drastically from 38 °C (–49.7 kJ mol⁻¹) to 20.2 °C (–9.09 kJ mol⁻¹). However, the phase transition point and enthalpy of smectic A to X were scarcely affected by adding LiBF₄. This suggests that the phase transition from smectic A to X is due entirely to crystallization of aggregated alkyl chain layers. Furthermore, this result indicates that LiBF₄ was introduced only into the ionic domain

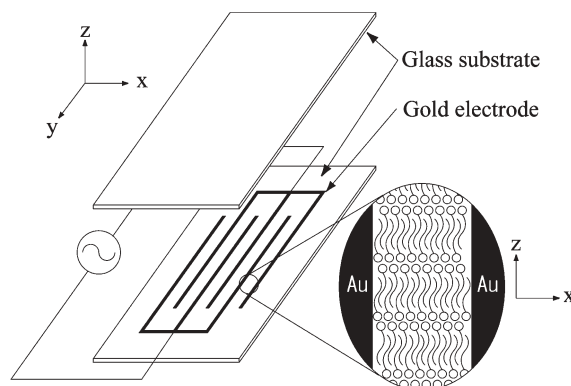


Fig. 1 Schematic illustration of Au cell and mono-domain alignment for liquid crystalline molecules **1** between gold electrodes.

Table 1 Phase transition temperature (°C) for **1** and **1**/LiBF₄ mixture (enthalpy/kJ mol⁻¹ in parentheses) detected by DSC from the second heating and cooling

Compound	Cycle	Phase transition temperatures
1	Heating	Cr 67.4 (70.1) S _A 121.3 (2.01) Iso
	Cooling	Cr 38.0 (-49.7) S _X 47.9 (-19.1)
		S _A 118.5 (-2.0) Iso
1 /LiBF ₄	Heating	Cr 30.4 (9.30) S _X 49.9 (-34.8)
		Cr' 65.1 (56.5) S _A 124.8 (2.18) Iso
	Cooling	Cr 20.2 (-9.09) S _X 48.8 (-19.6)
		S _A 121.3 (-2.3) Iso

^a Iso = Isotropic liquid, S_A = smectic A phase, S_X = unidentified smectic phase, Cr = Crystal

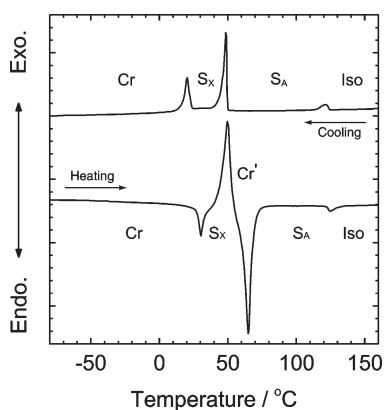


Fig. 2 DSC curves on second heating and cooling for **1**/LiBF₄.

of self-assembled **1**. Fig. 2 shows DSC curves of the second heating and cooling cycle for the **1**/LiBF₄ mixture. On heating, **1** displayed only the smectic A phase, whereas the **1**/LiBF₄ mixture displayed both smectic A and X phases. A recrystallization peak was observed in the smectic X phase during the heating cycle, suggesting that the smectic X phase is a supercooled metastable phase. The smectic X phase is therefore a unique phase in which only the alkyl chain layer is crystallized, while the ionic layer remains fused.

The temperature dependence of the ionic conductivity parallel to the ionic layer (σ_{\parallel}) upon cooling of **1** and the **1**/LiBF₄ mixture is shown in Fig. 3. The ionic conductivities of both systems increased after the phase transition from the isotropic to the smectic A phase. Fig. 4 shows typical Nyquist plots for **1** at 126 °C (in the isotropic phase) and 118 °C (in the smectic A phase). The frequency dependence of the impedance was a semicircle in the complex plane. These semicircles are equivalent to a resistor and a capacitor in parallel. The value extrapolated to the Z' axis corresponds to the sample resistance. Ionic conductivities were calculated as the reciprocal of the resistance (Ω^{-1}) multiplied by the cell constant (cm^{-1}). Figs. 3 and 4, show that the ionic conductivity in the smectic A phase is higher than that in the isotropic phase. In general, the viscosity of the liquid crystalline phase is higher than that of the isotropic phase, so that the ionic conductivity in the liquid crystals should be less than in the isotropic phase. However, the isotropic phase is a state of mixed polar ionic groups and nonpolar (insulator) alkyl chains. The results for σ_{\parallel} showed a high ionic conductivity in the aligned mono-domain ionic layer which was phase-separated

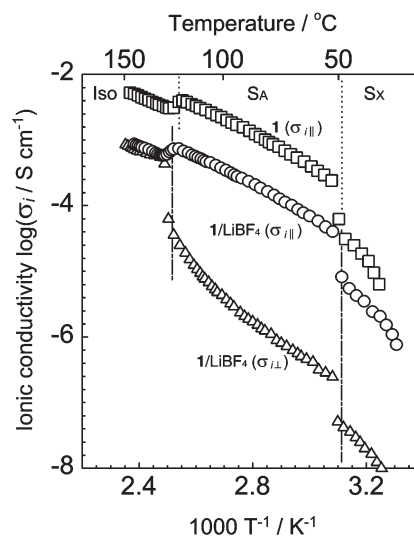


Fig. 3 Temperature dependence of ionic conductivity for **1** and **1**/LiBF₄ on cooling; σ_{\parallel} and σ_{\perp} are the ionic conductivities along the direction perpendicular and parallel to the aligned monodomain smectic layer.

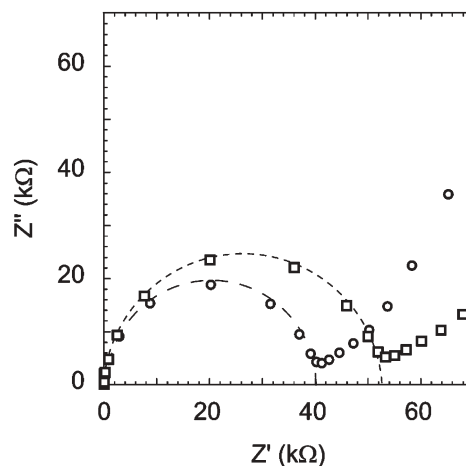


Fig. 4 Nyquist plots for **1** at 126 °C in the isotropic phase (\square), and 118 °C in the smectic A phase (\circ).

from the nonpolar alkyl chains. It becomes clear that an aggregated ionic domain formed in the smectic A phase contained effective ion conductive pathways. The ionic conductivity fell upon adding LiBF₄. This reduction is presumably due to the increased Coulomb interaction and restricted mobility of ions.

We measured the ionic conductivity of **1**/LiBF₄ perpendicular to the smectic layer (σ_{\perp}). Fig. 3 shows the temperature dependence of the ionic conductivity [**1**/LiBF₄ (σ_{\perp})]. In the isotropic liquid phase, the both ionic conductivities were almost the same whether using the Au or ITO cell, reflecting the state of disordered molecular alignment. On the other hand, the ionic conductivities σ_{\parallel} and σ_{\perp} at 51.5 °C in ordered smectic A phase were 4.1×10^{-5} and $2.6 \times 10^{-7} \text{ S cm}^{-1}$, respectively. The value of σ_{\parallel} was 150 times greater than σ_{\perp} as a result of the assembled two-dimensional ionic liquid domain in the smectic A phase of **1**/LiBF₄. Furthermore, these results indicate that mono-domain molecular alignment was formed spontaneously by the phase transition from isotropic to

smectic A phase. These ionic liquid crystalline molecules should be useful for reusable materials. Because, reproduction of mono-domain orientation is easy simply by allowing the temperature go up to the isotropic phase and down to the smectic phase, even if the mono-domain structure collapses.¹⁰

At the phase transition from smectic A to X, the ionic conductivity ($\sigma_{||}$) did not fall drastically. This should be the result of crystallization of alkyl chains alone, with the ionic layer remaining in the liquid state. The crystallization generally froze the motion of charged sites, causing a considerable reduction in the conductivity. In the present system, motion which should be effective for ion transport was possible. This is an important characteristic of this smectic X phase.

In summary, an ionic layer formed in a liquid crystalline smectic phase and was found to display a higher ionic conductivity than the isotropic phase. Anisotropic ion conduction was clearly observed. The amphiphilic liquid-crystalline ionic liquid **1** having long alkyl chains, showed both a smectic A phase and a smectic X phase, which gave rise to phase separation of the fused ionic layer and the crystallized alkyl chain layer. A mixture of amphiphilic ionic liquid **1** and LiBF₄ displayed a spread temperature range of the liquid crystalline phase. The amphiphilic ionic liquids formed a two-dimensional and temperature-controllable ion conductive pathway.

One of the authors (T. M.) acknowledges financial support from the Japan Society for the Promotion of Science (Research Fellowships for Young Scientists). This study was carried out under the 21st Century COE program for "Future Nanomaterials" at Tokyo University of Agriculture and Technology. The study was also supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (No. 14205136).

Tomohiro Mukai,^a Masafumi Yoshio,^b Takashi Kato,^b Masahiro Yoshizawa^a and Hiroyuki Ohno^{*a}

^aDepartment of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184-8588, Japan.

E-mail: ohnoh@cc.tuat.ac.jp; Fax: +81-42-388-7024;

Tel: +81-42-388-7024

^bDepartment of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

E-mail: kato@chiral.t.u-tokyo.ac.jp; Fax: +81-3-5841-8661;

Tel: +81-3-5841-7440

Notes and references

† *N*-Ethyl-*N'*-dodecylimidazolium bromide was obtained by reacting *N*-ethylimidazole with 1-dodecyl bromide in toluene for 24 h at 80 °C. The resulting crude product was purified by recrystallization from a mixed ethyl acetate–acetonitrile system at least three times, giving the desired product as a white powder in 86.0% yield. *N*-Ethyl-*N'*-dodecylimidazolium bromide was dissolved in distilled water, and the resulting solution was added to a solution of sodium dodecyl sulfonate in water at 80 °C. The solution was stirred for 24 h at 80 °C and the precipitate was then extracted with chloroform. The organic phase was washed with water and dried over MgSO₄. After filtration, the chloroform was removed under reduced pressure. The resulting white powder was recrystallized from acetonitrile three times. After drying under 1 Torr at 150 °C for 4 h, amphiphilic imidazolium salt **1** was obtained as a white solid with a yield of 92.3%. The water content after drying, measured by Karl–Fisher titration, was 488 ppm. The structure of the target salt was confirmed by ¹H NMR spectroscopy and elemental analysis. A mixture of **1** and LiBF₄ was prepared by direct and careful mixing of **1** with 5 mol% of LiBF₄. The mixture was heated to a temperature above the clearing points and was stirred under reduced pressure for 2 h. ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 0.81 (t, CH₃, 6H), 1.19 (m, CH₂, 36H), 1.52 (t, CH₃, 3H), 1.80 (m, CH₂, 4H), 2.81 (m, CH₂, 2H), 4.24 (m, CH₂N, 2H), 4.34 (q, NCH₂CH₃, 2H), 7.07 (d, CH, 1H), 7.10 (d, CH, 1H), 10.23 (s, H, 1H). Elemental analysis: calc. for C₂₉H₅₈N₂O₃S: C, 67.65; H, 11.35; N, 5.44. Found: C, 67.59, H, 11.25, N, 5.41%.

- 1 J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965; T. Welton, *Chem. Rev.*, 1999, **99**, 2071; P. Bonhôte, A.-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.
- 2 J. D. Holbrey and K. R. Seddon, *Clean Prod. Process.*, 1999, **1**, 223; *Ionic Liquids: Industrial Applications to Green Chemistry*, ed. R. D. Rogers and K. R. Seddon, American Chemical Society, Washington, DC, 2002.
- 3 J. Fuller, A. C. Breda and R. T. Carlin, *J. Electroanal. Chem.*, 1998, **459**, 29; A. B. McEwen, H. L. Ngo, K. LeCompte and J. L. Goldman, *J. Electrochem. Soc.*, 1999, **146**, 5, 1687; Md. A. B. H. Susan, A. Noda, S. Mitsushima and M. Watanabe, *Chem. Commun.*, 2003, 938.
- 4 C. J. Bowlas, D. W. Bruce and K. R. Seddon, *Chem. Commun.*, 1996, 1625; C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 1998, **8**, 2627; K. M. Lee, C. K. Lee and I. J. B. Lin, *Chem. Commun.*, 1997, 899.
- 5 M. Yoshio, T. Mukai, K. Kanie, M. Yoshizawa, H. Ohno and T. Kato, *Adv. Mater.*, 2002, **14**, 351.
- 6 M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994.
- 7 M. Hirao, K. Ito and H. Ohno, *Electrochim. Acta*, 2000, **45**, 1291.
- 8 M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057.
- 9 H. Ohno, Y. Inoue and P. Wang, *Solid State Ionics*, 1993, **62**, 257.
- 10 S. Ujiie and K. Iimura, *Macromolecules*, 1992, **25**, 3174.