

One-Dimensional Ion-Conductive Polymer Films: Alignment and Fixation of Ionic Channels Formed by Self-Organization of Polymerizable Columnar Liquid Crystals

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Abstract: We have prepared two types of one-dimensional ion-conductive polymer films containing ion nanochannels that are both perpendicular and parallel to the film surface. These films have been obtained by photopolymerization of aligned columnar liquid crystals of a fan-shaped imidazolium salt having acrylate groups at the periphery. In the columnar structure, the ionic part self-assembles into the inner part of the column. The column is oriented macroscopically in two directions by different methods: orientation perpendicular to the modified surfaces of glass and indium tin oxide with 3-(aminopropyl)triethoxysilane and orientation parallel to a glass surface by mechanical shearing. Ionic conductivities have been measured for the films with columnar orientation vertical and parallel to the surface. Anisotropic ionic conductivities are observed for the oriented films fixed by photopolymerization. The ionic conductivities parallel to the columnar axis are higher than those perpendicular to the columnar axis because the lipophilic part functions as an ion-insulating part. The film with the columns oriented vertically to the surface shows an anisotropy of ionic conductivities higher than that of the film with the columns aligned parallel to the surface.

Introduction

The use of self-organized structures, such as liquid crystals, is a promising approach for the preparation of low-dimensional (anisotropic) functional materials.¹ For example, ion,^{2,3} electron,⁴ and hole⁴ transport materials have been prepared by using liquid crystalline (LC) molecular order. These materials have potential applications, such as electrolytes in lithium ion batteries and conducting paths in electronic devices. Control of intermolecular interactions and formation of phase-segregated structures are

key in the design and development of these materials.¹ Intermolecular interactions, such as hydrogen bonding,⁵ ionic interactions,⁶ ion–dipolar interactions,⁷ π – π interactions,⁸ and charge-transfer interactions,⁹ can be used for the construction of functional and ordered supramolecular structures. Block

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molecules consisting of immiscible parts^{1b,c,10} and molecular mixtures consisting of partially miscible components^{2b-e} can form phase-segregated structures from micro- to nanometer scale that induce function.

Recently, anisotropic ion conduction has been achieved in aligned LC materials based on imidazolium salts² and oligo-(ethylene oxide)s.^{3a-e} For example, aligned columnar LC phases of fan-shaped imidazolium tetrafluoroborate salts containing tris-(alkoxy)phenyl groups lead to the induction of one-dimensional (1D) ion conduction.^{2a} Imidazolium and pyridinium salts coordinating perfluorinated anions are representative ionic liquids showing nonvolatility and high ionic conductivity. Ionic liquids have received great interests as electrolytes for batteries¹¹ and reaction solvents for organic syntheses.¹² We designed ionic liquids having block molecular structures of ionic and nonionic moieties to exhibit LC properties.^{2a} The ionic moieties self-assembled into the inner part of columnar structures through nanosegregation and electrostatic interactions. These nanosegregated columnar structures were macroscopically oriented only in the direction in which columns are parallel to the surface. If we could also succeed in columnar orientation perpendicular to the film surface, the applicability of the anisotropically conductive materials will be increased. Moreover, these LC materials exhibit fluidity, which might decrease applicability as materials. If these LC nanostructures could be preserved in macroscopically ordered polymeric films, the materials can be more easily incorporated into solid devices.

We considered that if functional moieties capable of interacting with the ionic molecules are introduced into the surface of substrates vertical orientation of the 1D columns to the substrates could be induced spontaneously. We also expected that the

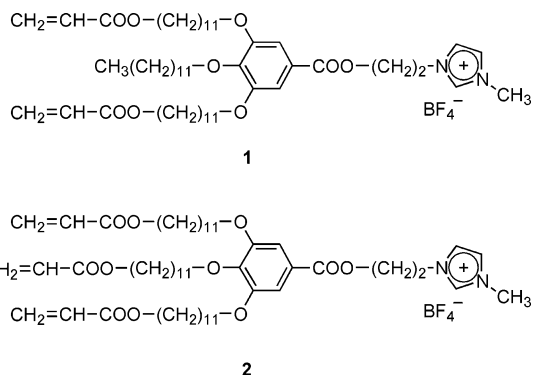


Figure 1. Polymerizable fan-shaped imidazolium salts **1** and **2**.

Table 1. Thermal Properties of Compounds **1** and **2**

compound	phase transition behavior ^a				
1	Cr	20 (44.2)	Col _h	50 (0.30)	I
2	Cr	13 (43.7)			I

^a Transition temperatures (°C) and enthalpies of transition (kJ mol⁻¹, in parentheses). Col_h: hexagonal columnar; Cr: crystalline; I: isotropic.

fixation of such oriented columns by polymerization could enhance the anisotropy due to the decrease of thermal fluctuation of the columns in solid polymer matrices. We previously prepared 2D ion-conductive films by photopolymerization of smectic LC methacrylate monomers containing imidazolium salts^{2f} and oligo(ethylene oxide)^{3d,e} moieties. These monomers that homeotropically aligned on the glass surface were polymerized in the smectic A phases. However, it is not easy to fix aligned 1D ionic channels because columnar orientation cannot be controlled easily.

Here we report on the development of anisotropically ion-conductive films that have ionic channels aligned vertical and parallel to the film surface. We have successfully designed and prepared 1D ion-conductive polymeric materials by orientation control of their self-assembled nanosegregated structures and subsequent photopolymerization of a columnar ionic liquid crystal based on an imidazolium salt.

Results and Discussion

Synthesis and Liquid Crystalline Properties. We have designed and synthesized molecules **1** and **2** shown in Figure 1. These compounds have imidazolium and tris(alkoxy)phenyl moieties containing acrylate polymerizable groups at their periphery. For these molecules, the nonionic (aliphatic and aromatic) and the imidazolium (ionic) moieties are connected through an ethyleneoxy carbonyl group. They were obtained by an esterification reaction of a hydroxy-functionalized imidazolium salt¹³ and etherified gallic acid derivatives having two or three acrylate polymerizable groups at their periphery.

The phase transition behavior of compounds **1** and **2** is summarized in Table 1. Compound **1** forms a hexagonal columnar LC (Col_h) phase between 20 and 50 °C on heating, while no mesomorphic behavior is observed for **2**. The three bulky acrylate groups of **2** may disturb its columnar packing. Analogous benzylimidazolium salts, which have no ester groups, having two and three acrylate groups exhibit no liquid crystal-

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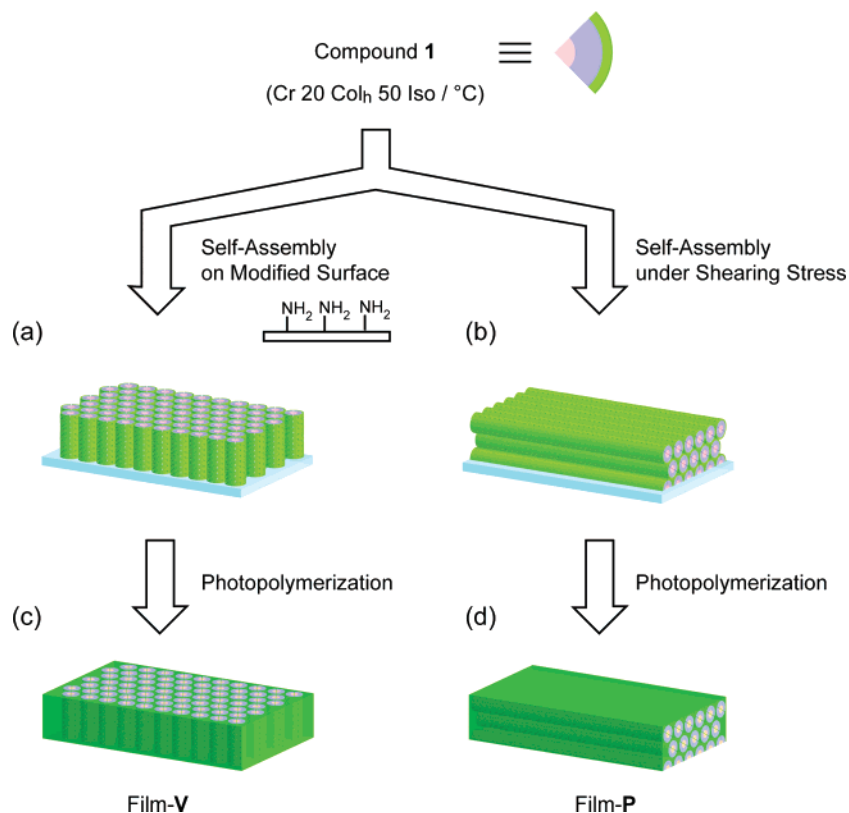


Figure 2. Schematic illustration of the strategy for preparation of one-dimensional ion-conductive polymeric films: self-assembly and subsequent photopolymerization of columnar liquid crystalline imidazolium salt **1** with two different columnar orientations. (a) Vertical orientation of unpolymerized columns on 3-(aminopropyl)triethoxysilane (APS)-modified surface of substrates; (b) parallel orientation of the unpolymerized columns by shearing; (c) polymer film with vertical columnar orientation to the film surface (Film-V); (d) polymer film with parallel columnar orientation to the film surface (Film-P).

linity (see Supporting Information). The dipole–dipole interactions between the ester groups for **1** should be important to stabilize the columnar packing.

X-ray Diffraction Study. The X-ray diffraction pattern of compound **1** at 25 °C presents three peaks with the ratio of 1:1/√3:1/2 ($d_{100} = 36.2 \text{ \AA}$ at $2\theta = 2.44^\circ$, $d_{110} = 20.8 \text{ \AA}$ at $2\theta = 4.24^\circ$, $d_{200} = 18.1 \text{ \AA}$ at $2\theta = 4.88^\circ$). This indicates the formation of a hexagonal columnar structure. The intercolumnar distance (a) is calculated to be 4.2 nm with the following equation: $a = 2 \langle d_{100} \rangle / \sqrt{3}$, $\langle d_{100} \rangle = (d_{100} + \sqrt{3}d_{110} + 2d_{200})/3$. The number (n) of molecules per unit cell in a hexagonal lattice is estimated to be 4.7 from $n = \sqrt{3}N_A a^2 h \rho / 2M$,¹⁴ where N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$), h is the layer thickness (4.4 Å), and M is molecular weight (983.07 g mol⁻¹). The density (ρ) of the material is 1.13 g cm⁻³, which has been determined by a flotation method in D-(+)-sucrose/H₂O at 20 °C. The value of h has been taken from the halo of X-ray at $2\theta = 20.3^\circ$ due to disordered aliphatic chains and benzene ring in the direction of the column axis.¹⁵

Alignment of a Monomer. Our approach to the preparation for macroscopically oriented 1D ion-conductive polymeric films is schematically shown in Figure 2. Molecular self-assembly, macroscopic orientation, and subsequent photopolymerization of columnar LC imidazolium salt **1** has given two types of

macroscopically oriented nanostructured films (Film-V (Vertical) and Film-P (Parallel)). Film-V and Film-P can transport ions in two directions: perpendicular and parallel to the film surface, respectively. These different structures of the Film-V and Film-P have been obtained by using different liquid crystal/surface interactions.

Compound **1** does not spontaneously form a single domain on glass and indium tin oxide (ITO) substrates. Polarizing optical micrographs shown in Figure 3a,b show that the polydomains of **1** are formed when its isotropic melt is cooled to the temperature range of the columnar phase on these substrates. For anisotropic 1D ion conduction in the direction perpendicular to the film surface, uniaxially vertical macroscopic orientation of the columns that function as ion-conductive paths is needed. We have used a modified surface for the alignment control of the columnar structure of **1**. Surface modification of the oxidized substrates such as silica and metal oxides with silane coupling agents is an effective approach for the orientation of LC materials.^{16,17} In the present study, we have achieved vertical alignment of the columns to the surface (homeotropic orientation) by using chemically modified glass and ITO substrates with 3-(aminopropyl)triethoxysilane¹⁸ (APS) as shown in Figure 3c and 3d. This alignment has been confirmed by the conoscopic

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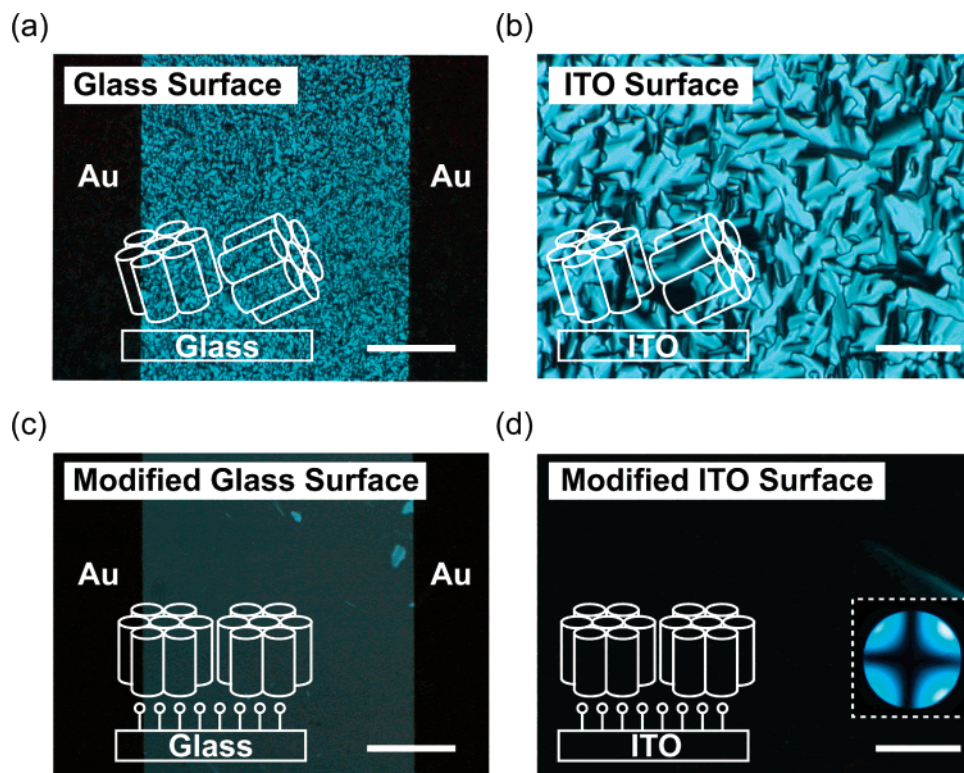


Figure 3. Polarizing optical micrographs of monomer **1** in the Col_h state at 25 °C: (a) on the nonmodified surface of a glass substrate with comb-shaped gold electrodes; (b) on the nonmodified surface of an ITO substrate; (c) on the surface of the 3-(aminopropyl)triethoxysilane (APS)-modified glass substrate; (d) on the surface of the APS-modified ITO substrate. The scale bar is 100 μm .

observation on a polarized microscope. A cross-shaped pattern is observed as shown in the inset of Figure 3d. This homeotropic alignment can be attributed to the interactions between the imidazolium moiety of **1** and the APS-modified surface. Self-assembly and orientation of columnar liquid crystals on a variety of substrates, including graphite, mica, and self-assembled monolayers, have been studied by several groups.^{19–24} The observed orientations of the columns have been interpreted in terms of interactions and affinity between the columnar liquid crystals and substrate surfaces and the flatness of substrates.

The macroscopic 1D orientation of the columns parallel to the surface has been induced by mechanical shearing of the polydomain sample of **1**. The columnar LC sample cooled from

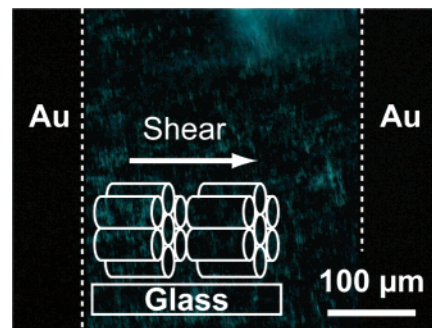


Figure 4. Polarizing optical micrograph of the monomer oriented by shearing in the Col_h state at 25 °C on the nonmodified surface of a glass substrate.

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the isotropic temperature range has been sheared with two glasses sandwiching the sample. Figure 4 shows a polarizing optical micrograph of **1** in the columnar phase after shearing. 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 observed when the shearing direction is along the polarizer or analyzer axis. The highest brightness is seen when the oriented material is at a 45° angle.

Fixation of Columnar Structures by Photopolymerization.

The macroscopic vertical and parallel alignment of the columns to the substrate surfaces has been successfully fixed by photopolymerization. These oriented columnar liquid crystals at 30 °C were irradiated by a UV lamp (365 nm, 30 mW cm⁻², for 1 h) in the presence of 1.0 wt % of 2,2-dimethoxy-2-phenylacetophenone as a photoinitiator. For example, after polymerization of **1** with vertical orientation of the columns on

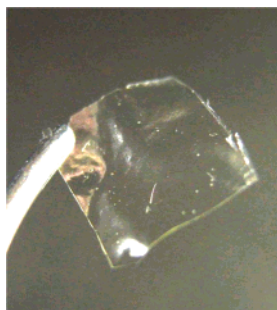


Figure 5. Photograph of a free-standing film (5 mm × 5 mm) obtained by photopolymerization of **1** with vertical orientation of the columns on the APS-modified glass substrate at 30 °C. The illustration of this film is shown as Film-V in Figure 2c.

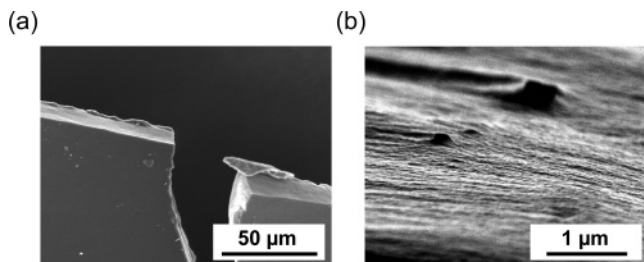


Figure 6. FE-SEM images of the macroscopically oriented polymer Film-P: (a) over view; (b) high magnified view of the image in (a).

the APS-modified glass substrate, a transparent free-standing film has been obtained (Figure 5). In the infrared spectrum of the photopolymerized sample, the acrylate bands at 1637 and 811 cm^{-1} disappear, although all reacted polymerizable groups might not be completely consumed during polymerization. This resultant film is thermally stable, and no peaks of phase transitions are detected up to 250 °C in DSC measurements. The film is also mechanically stable and insoluble in water and conventional organic solvents, such as methanol and chloroform. The density of the polymer film (Film-V) has been determined to be 1.11 g cm^{-3} by the same flotation method as that for the monomer. This value is smaller than that of the monomer. These results suggest that cross-linked network structures are formed in the films. Before and after polymerization, no changes of the optical properties have been observed under the polarized microscope.

The X-ray diffraction patterns of the polymer films (Film-V and Film-P in Figure 2) exhibit the fixation of the hexagonal columnar structures in the film, and the size of the polymerized columns slightly increases upon polymerization (see Supporting Information). The intercolumnar distance is 4.3 nm.

The Film-P obtained by polymerization of **1** has been observed by scanning electron microscopy, as shown in Figure 6. Oriented grooves along the direction of shearing are formed in the photopolymerized film. This observation also supports the macroscopic alignment of the columnar nanostructures.

Functional nanostructured polymeric materials were prepared by photopolymerization of LC monomers.^{1f,2f,3d,e,25–31} For example, Gin and co-workers developed nanoporous polymer materials exhibiting catalytic properties^{1f,30} and molecular-size-

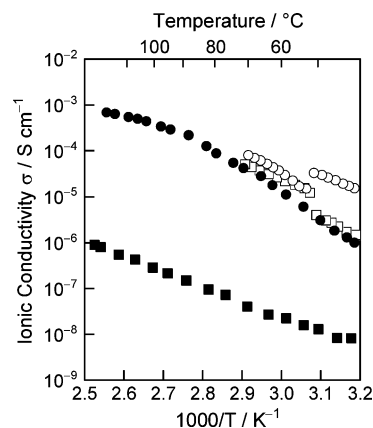


Figure 7. Anisotropic ionic conductivities of Film-V and the corresponding monomer whose columnar axes are aligned perpendicular to the surface of the APS-modified glass and ITO substrates: (●) parallel and (■) perpendicular to the columnar axis for the Film-V; (○) parallel and (□) perpendicular to the columnar axis for the monomer.

selective filtration properties³¹ by using polymerizable lyotropic columnar liquid crystals in the presence of water. By using a thermotropic columnar liquid crystal with polymerizable groups, our present study is the first example of 1D ion-conductive polymer films consisting of anisotropic ionic channels with controlled directions.

Anisotropic Ionic Conductivities. Anisotropic ionic conductivities of the Film-V comprised of polymer **1** as well as those of an unpolymerized sample of monomer **1** with columnar orientation vertical to the surface of substrates have been successfully measured using two different types of electrodes, APS-modified ITO and comb-shaped gold electrodes with APS-modified glass substrates (see Supporting Information). To measure the ionic conductivities along the direction parallel to the columns (σ_{\parallel}), a pair of APS-modified ITO electrodes filled with the Film-V or corresponding monomer **1** was used. The distance between the two electrodes was fixed by a Teflon spacer of thickness 10 μm . The ionic conductivities perpendicular to the columnar axis (σ_{\perp}) were measured using an APS-modified glass cell with comb-shaped gold electrodes. The Film-V or monomer **1** was filled between the gold electrodes for σ_{\perp} .

Figure 7 shows the anisotropic ionic conductivities of the Film-V and its monomer as a function of temperature. The ionic conductivities parallel to the columnar axis (σ_{\parallel}) are higher than those perpendicular to the columnar axis (σ_{\perp}). The magnitude of anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) for the Film-V is 2.6×10^2 at 50 °C and 1.4×10^3 at 150 °C. These values are 10–100 times higher than those obtained for the unpolymerized sample of **1**. These results show that the fixation of the oriented nanostructure for the monomer by in situ photopolymerization enhances the

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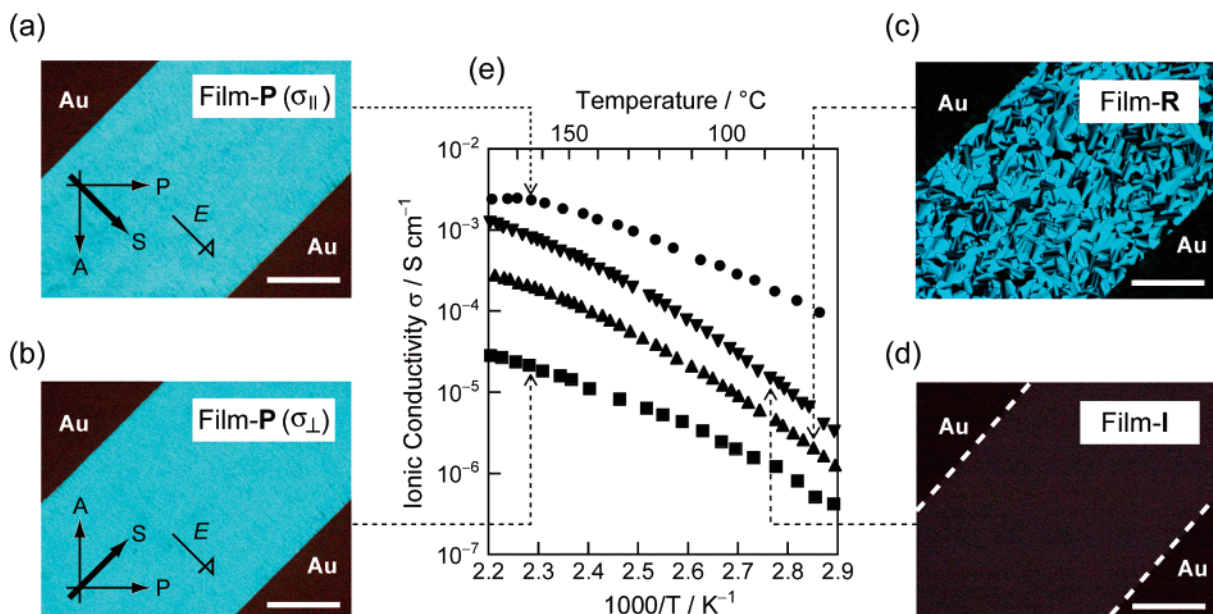


Figure 8. Molecular alignment and ionic conductivities of polymer films prepared by photopolymerization of monomer **1**. Polarizing optical microscopic images of polymer films with four different molecular orientations: (a) Film-P with parallel orientation of the columnar axis (\parallel) to the direction of electric field; (b) Film-P with perpendicular orientation of the columnar axis (\perp) to the direction of electric field; (c) Film-R comprised of randomly oriented columns; (d) Film-I of the disordered amorphous (isotropic) state. Directions of A: analyzer; P: polarizer; S: shearing of unpolymerized columns of monomer; E: electric field. The scale bar is 100 μm . Ionic conductivities of polymer films as a function of temperature (e): (●) parallel and (■) perpendicular to the columnar axis for Film-P; (▲) for Film-R; (▼) for Film-I.

anisotropy of the conductivities. It seems that ion conduction perpendicular to the columnar axis may be effectively disturbed in the solid polymer film due to the low mobility of the cross-linked alkyl chains. It is an advantage of the polymer film that anisotropy of the ionic conductivities is maintained for the Film-V up to 200 $^{\circ}\text{C}$, while no anisotropy of the conductivities is observed for the monomer above the isotropization temperature.

We have also measured the anisotropic ionic conductivities of the Film-P with columnar orientation parallel to the surface of the glass substrate using nontreated comb-shaped gold electrodes (see Supporting Information). To measure anisotropic conductivities, the columns have been aligned in two directions by shearing parallel (Figure 8a, Film-P (σ_{\parallel})) and perpendicular (Figure 8b, Film-P (σ_{\perp})) to the direction of the electric field between Au electrodes, and their alignments have been fixed by photoirradiation. To examine the effects of molecular alignment on the ionic conductivities, nonaligned films have been obtained: the polymer film consisting of a nonoriented columnar polydomain (Figure 8c, Film-R (Random)) and the polymer film of a disordered amorphous state (Figure 8d, Film-I (Isotropic)). Film-R was prepared by photopolymerization of monomer **1** in the nonoriented columnar phase at 30 $^{\circ}\text{C}$. Film-I was obtained by photopolymerization of **1** in the isotropic phase at 70 $^{\circ}\text{C}$.

Figure 8e shows the ionic conductivities for these polymer films. The ionic conductivities parallel (σ_{\parallel}) to the columnar axis are higher than those perpendicular (σ_{\perp}) to the columnar axis. For example, the Film-P exhibits conductivities of 1.6×10^{-3} S cm^{-1} (σ_{\parallel}), 1.4×10^{-5} S cm^{-1} (σ_{\perp}), and a $\sigma_{\parallel}/\sigma_{\perp}$ of 1.2×10^2 at 150 $^{\circ}\text{C}$. The magnitude of anisotropy of Film-P is lower than that of Film-V with columnar orientation perpendicular to the film surface. For the polydomain columnar film (Film-R) (▲), the value of 1.1×10^{-5} S cm^{-1} at 100 $^{\circ}\text{C}$ is between the values of σ_{\parallel} (3.1×10^{-4} S cm^{-1}) and σ_{\perp} (2.2×10^{-6} S cm^{-1}) for the

homogeneously oriented films (Film-P). These results are attributable to the random formation of ion-conduction paths in the polydomain film. As for the isotropic film (Film-I) (▼), the value of 3.7×10^{-5} S cm^{-1} at 100 $^{\circ}\text{C}$ is lower than that of σ_{\parallel} for the oriented film (Film-P) at the same temperature. Furthermore, the ionic conductivities of the amorphous film (Film-I) is higher than those of the polydomain film (Film-R). The results obtained for Films-V, P, R, and I indicate that the introduction of only oriented nanostructures can enhance the conductivity of the polymer film. The highest ion conduction for the polymer **1** has been achieved by the formation of the anisotropic nanosegregated structure and the macroscopic orientation.

Conclusion

Two types of 1D ion-conductive polymeric films that transport ions both perpendicular and parallel to the film surface have been prepared by using liquid crystal self-assembly of a polymerizable fan-shaped imidazolium salt and that have been aligned by different techniques. We have demonstrated that macroscopic alignment of the nanostructures of the columnar liquid crystals in the polymeric films enhances the ion-conductive properties. Ionic channels shielded by the ion-insulating alkyloxyphenyl part are spontaneously formed through nanophase segregation of nonionic and ionic parts. They have been fixed by photopolymerization. The anisotropically oriented nanochannels can transport ions most effectively. Furthermore, the films show distinct anisotropy of ionic conductivities. These results show the approach presented here is useful for the preparation of new low-dimensionally functional solid materials.

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-LA400 at 400 and 100 MHz in CDCl_3 , respectively. Chemical shifts of ^1H and ^{13}C NMR signals were quoted to $(\text{CH}_3)_4\text{Si}$

($\delta = 0.00$) and CDCl_3 ($\delta = 77.0$) as internal standards, respectively, and expressed by chemical shifts in parts per million (δ), multiplicity, coupling constant (hertz), and relative intensity. Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. Matrix-associated laser desorption/ionization-time-of-flight mass spectra (MALDI-TOF MS) were taken on a PerSeptive Biosystems Voyager-DE STR spectrometer using dithranol as the matrix. Elemental analyses were carried out on a Perkin-Elmer CHNS/O 2400 apparatus. IR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. Phase transition behavior of the materials was examined by a differential scanning calorimetry (DSC) using a Netzsch DSC204 Phoenix. The heating and cooling rates were 5°C min^{-1} . Transition temperatures were taken at the maximum 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 monochromated $\text{Cu K}\alpha$ radiation. UV irradiation was carried out using a high-pressure mercury lamp (Ushio, 500 W) with appropriate glass filter (Asahi Technoglass UV-35 and UVD-36C) as an irradiation source. FE-SEM measurements were performed on a HITACHI S-900 at an accelerating voltage of 10 kV for the free-standing oriented polymer films, whose cross-section was shaded with platinum.

Materials. All chemical reagents and solvents were obtained from commercial sources and used without purification. All reactions were carried out under an argon atmosphere in anhydrous solvents.

Synthesis of Ethyl 3,5-Bis(*tert*-butyldimethylsilyloxy)-4-hydroxybenzoate (3). A solution of *tert*-butyldimethylsilyl chloride (TBSCl) (15.4 g, 102.2 mmol) in *N,N*-dimethylformamide (DMF) (20 mL) was added dropwise to a solution of ethyl gallate (ethyl 3,4,5-trihydroxybenzoate) (10.1 g, 50.1 mmol) and imidazole (10.5 g, 154.4 mmol) in DMF (50 mL) at 0°C . The reaction mixture was warmed to room temperature and stirred for a further 12 h. Then water and ethyl acetate (EtOAc) were added, and the organic layer was separated and washed with a saturated NH_4Cl aqueous solution. The resulting organic phase was dried over anhydrous MgSO_4 , filtered through a pad of Celite, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: hexane/chloroform = 2/1) to give **3** (14.9 g, 34.9 mmol, 70%) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.22$ (s, 2H), 5.65 (s, 1H), 4.31 (q, $J = 6.8$ Hz, 2H), 1.36 (t, $J = 7.0$ Hz, 3H), 1.00 (s, 18H), 0.24 (s, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 166.29$, 143.46, 142.77, 120.98, 114.68, 60.71, 25.67, 18.25, 14.29, -4.37. IR (KBr): $\nu = 3422$, 2956, 2931, 2860, 1717, 1603, 1506, 1472, 1435, 1394, 1372, 1338, 1260, 1224, 1073, 1029, 841, 785 cm^{-1} . MS (MALDI-TOF): calcd for $[\text{M} + \text{H}]^+$, 427.23; found, 427.28.

Synthesis of Ethyl 3,5-Bis(*tert*-butyldimethylsilyloxy)-4-dodecyloxybenzoate (4). To a solution of triphenylphosphine (6.11 g, 23.3 mmol), 1-dodecanol (6.12 g, 32.9 mmol), and **3** (10.0 g, 23.5 mmol) in toluene (50 mL) was added dropwise diethyl azodicarboxylate (DEAD) (3.8 mL, 24.1 mmol) with stirring at room temperature. After stirring for 10 h at room temperature, the resulting mixture was poured into a mixture of water and EtOAc. The organic phase was separated and washed with a saturated aqueous NaCl solution. The resulting organic phase was dried over anhydrous MgSO_4 , filtered through a pad of Celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: hexane/chloroform = 2/1) to give **4** (13.2 g, 22.2 mmol, 94%) as a viscous liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.19$ (s, 2H), 4.32 (q, $J = 6.8$ Hz, 2H), 3.94 (t, $J = 6.8$ Hz, 2H), 1.73 (t, $J = 7.2$ Hz, 3H), 1.26 (s, 20H), 1.00 (s, 18H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.20 (s, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 166.20$, 149.59, 146.57, 124.84, 115.82, 72.92, 60.78, 31.91, 30.11, 29.64, 29.63, 29.57, 29.54, 29.35, 26.06, 25.87, 25.76, 22.68, 18.32, 14.29, 14.13, -4.48. IR (KBr): $\nu = 2956$, 2929, 2857, 1721, 1577, 1490, 1472, 1428, 1391, 1369, 1346, 1254, 1215, 1094, 1032, 1006,

980, 831, 784 cm^{-1} . MS (MALDI-TOF): calcd for $[\text{M} + \text{H}]^+$, 595.21; found, 595.56.

Synthesis of Ethyl 3,5-Dihydroxy-4-dodecyloxybenzoate (5). A 1.0 M solution of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (50 mL, 50 mmol) was added dropwise to a solution of **4** (13.2 g, 22.2 mmol) in dichloromethane (40 mL) at 0°C . The mixture was stirred for 10 h at room temperature. The solution was poured into water and extracted with chloroform three times. The combined organic phase was washed with brine, dried over anhydrous MgSO_4 , filtered through a pad of Celite, and concentrated with a rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluent: chloroform) to afford **5** (8.12 g, 22.1 mmol, 100%) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.30$ (s, 2H), 6.29 (s, 2H), 4.34 (q, $J = 6.8$ Hz, 2H), 4.16 (t, $J = 6.8$ Hz, 2H), 1.77 (t, $J = 7.6$ Hz, 3H), 1.26 (s, 20H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 166.85$, 148.87, 137.75, 125.57, 109.64, 73.80, 61.33, 31.87, 30.10, 29.60, 29.59, 29.53, 29.49, 29.34, 29.31, 25.81, 22.65, 14.15, 14.08. IR (KBr): $\nu = 3403$, 2917, 2850, 1696, 1601, 1520, 1471, 1448, 1397, 1350, 1240, 1190, 1099, 1054, 1029, 877, 768 cm^{-1} . MS (MALDI-TOF): calcd for $[\text{M} + \text{Na}]^+$, 389.23; found, 389.33.

Synthesis of 3,5-Bis(11-hydroxyundecyloxy)-4-dodecyloxybenzoic acid (6). A DMF (50 mL) suspension of **5** (1.44 g, 3.92 mmol), 11-bromoundecane-1-ol (2.36 g, 9.41 mmol), and K_2CO_3 (1.38 g, 10.0 mmol) was vigorously stirred for 6 h at 70°C . After the resulting brown mixture was cooled to room temperature, the mixture was poured into a saturated NH_4Cl aqueous solution and extracted with EtOAc three times. The combined organic extracts were washed with brine. The resulting organic phase was dried over anhydrous MgSO_4 , filtered through a pad of Celite, and concentrated under reduced pressure. The residue was dissolved in a mixture of ethanol/water (99:1 v/v, 100 mL) containing KOH (1.0 g, 18 mmol). After stirring for 3 h under a refluxed condition, the solution was neutralized with a 1.0 M HCl aqueous solution and extracted with EtOAc twice. The combined organic phase was dried over anhydrous MgSO_4 , filtered, and concentrated. The residue was recrystallized from ethanol to yield **6** (1.86 g, 2.74 mmol, 70%) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.31$ (s, 2H), 4.03 (t, $J = 6.8$ Hz, 6H), 3.66 (t, $J = 6.8$ Hz, 2H), 1.84–1.70 (m, 4H), 1.70–1.63 (m, 4H), 1.51–1.44 (m, 6H), 1.44–1.20 (m, 42H), 0.88 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 170.83$, 152.75, 142.92, 123.94, 108.50, 73.51, 69.10, 63.02, 32.66, 31.92, 30.28, 29.72, 29.69, 29.67, 29.61, 29.56, 29.54, 29.49, 29.44, 29.38, 29.23, 29.16, 26.01, 25.93, 25.70, 22.68, 14.12. IR (KBr): $\nu = 3349$, 2920, 2850, 1687, 1588, 1506, 1468, 1433, 1386, 1335, 1278, 1227, 1129, 1058, 993, 862, 768 cm^{-1} . MS (MALDI-TOF): calcd for $[\text{M} + \text{Na}]^+$, 701.53; found, 701.90.

Synthesis of 3,5-Bis(11-acryloyloxyundecyloxy)-4-dodecyloxybenzoic acid (7). To a solution of **6** (1.84 g, 2.71 mmol) and *N,N*-diethylaniline (1.21 g, 8.13 mmol) in 1,4-dioxane (100 mL) was added dropwise acryloyl chloride (0.74 g, 8.13 mmol) at 70°C in a light resistant container, and the reaction mixture was stirred for 3 h at 60°C . After an excess amount of acryloyl chloride was inactivated by the addition of methanol (10 mL), the mixture was concentrated by using a rotary evaporator. The residue as a viscous liquid was dissolved in a mixture of pyridine (5 mL) and water (5 mL). The mixture was stirred for 1 h at 80°C to cleave the benzoic acryloyl anhydride. Then, the mixture was acidified with a HCl aqueous solution (5%) and extracted with EtOAc. The organic phase was washed with a NaHCO_3 aqueous solution (5%) and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: chloroform/methanol = 10/1) and then recrystallized from EtOAc to give **7** (1.52 g, 1.93 mmol, 71%) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.32$ (s, 2H), 6.40 (dd, $J = 17$, 1.4 Hz, 2H), 6.12 (dd, $J = 17$, 10 Hz, 2H), 5.82 (dd, $J = 11$, 1.4 Hz, 2H), 4.15 (t, $J = 6.8$ Hz, 4H), 4.04 (t, $J = 6.8$ Hz, 6H), 1.84–1.70 (m, 4H), 1.70–1.63 (m, 4H), 1.51–

1.44 (m, 6H), 1.44–1.20 (m, 42H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.54, 166.37, 152.80, 143.02, 130.46, 128.59, 123.61, 108.45, 73.50, 69.11, 64.71, 38.17, 31.91, 30.28, 29.72, 29.70, 29.68, 29.66, 29.55, 29.52, 29.49, 29.36, 29.34, 29.25, 29.22, 28.57, 26.02, 26.00, 25.90, 22.67, 14.11$. IR (KBr): $\nu = 2920, 2851, 1726, 1683, 1635, 1586, 1505, 1472, 1432, 1410, 1386, 1335, 1295, 1275, 1228, 1200, 1122, 1058, 987, 966, 811, 723\text{ cm}^{-1}$. MS (MALDI-TOF): calcd for $[\text{M} + \text{Na}]^+$, 809.55; found, 810.07. Elemental analysis calcd (%) for $\text{C}_{47}\text{H}_{78}\text{O}_9$: C, 71.72; H, 9.99. Found: C, 71.40; H, 10.15.

Synthesis of 3-{3,5-Bis(11-acryloyloxyundecyloxy)-4-dodecyloxy-benzoyloxyethyl}-1-methylimidazolium tetrafluoroborate (1). To a mixture of **7** (1.00 g, 1.27 mmol), 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate¹³ (0.278 g, 1.30 mmol), and 4-(*N,N*-dimethylamino)pyridine (DMAP) (1.6 mg, 0.012 mmol) in a mixture of dichloromethane/acetonitrile (1:1, v/v, 30 mL) was added *N,N*-dicyclohexylcarbodiimide (DCC) (0.262 g, 1.27 mmol). The reaction mixture was stirred for 13 h at room temperature. After filtration of insoluble materials, the organic phase was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: $\text{CHCl}_3/\text{MeOH} = 10/1$) followed by GPC to yield **1** (0.691 g, 0.703 mmol, 55%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.90$ (s, 1H), 7.35 (s, 1H), 7.26 (s, 1H), 7.19 (s, 2H), 6.39 (dd, $J = 17, 1.8$ Hz, 2H), 6.12 (dd, $J = 18, 10$ Hz, 2H), 5.82 (dd, $J = 10, 1.4$ Hz, 2H), 4.67–4.64 (m, 4H), 4.14 (t, $J = 7.0$ Hz, 4H), 4.03–3.98 (m, 6H), 3.95 (s, 3H), 1.84–1.70 (m, 4H), 1.70–1.63 (m, 4H), 1.51–1.44 (m, 6H), 1.44–1.20 (m, 42H), 0.88 (t, $J = 6.8$, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 166.32, 165.77, 152.96, 142.94, 137.34, 130.43, 128.58, 123.27, 123.23, 122.66, 107.99, 73.52, 69.26, 64.66, 62.73, 49.00, 36.44, 31.89, 30.30, 29.71, 29.68, 29.65, 29.56, 29.53, 29.50, 29.49, 29.39, 29.35, 29.28, 29.23, 28.56, 26.08, 26.01, 25.89, 22.66, 14.09$. IR (KBr): $\nu = 3155, 3091, 2921, 2851, 1726, 1699, 1635, 1587, 1505, 1469, 1432, 1410, 1387, 1338, 1298, 1271, 1200, 1130, 1063, 984, 855, 810, 723\text{ cm}^{-1}$. MS (MALDI-TOF): calcd for $[\text{M} - \text{BF}_4]^+$, 895.64; found, 895.76. Elemental analysis calcd (%) for $\text{C}_{53}\text{H}_{87}\text{BF}_4\text{N}_2\text{O}_9$: C, 64.75; H, 8.92; N, 2.85. Found: C, 64.15; H, 8.92; N, 2.85.

3-{3,4,5-Tris(11-acryloyloxyundecyloxy)benzoyloxyethyl}-1-methylimidazolium tetrafluoroborate (2). To a mixture of 3,4,5-tris(11-acryloyloxyundecyloxy benzoic acid^{4d}) (1.00 g, 1.19 mmol), 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate¹³ (0.278 g, 1.30 mmol), and DMAP (1.6 mg, 0.012 mmol) in a mixture of dry $\text{CH}_2\text{-Cl}_2/\text{acetonitrile}$ (1:1, v/v, 30 mL) was added DCC (0.268 g, 1.30 mmol). The reaction mixture was stirred for 13 h at room temperature. After filtration of insoluble materials, the organic phase was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: $\text{CHCl}_3/\text{MeOH} = 10/1$) followed by GPC to give **2** (0.473 g, 0.455 mmol, 38%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.90$ (s, 1H), 7.35 (s, 1H), 7.26 (s, 1H), 7.19 (s, 2H), 6.39 (dd, $J = 17, 1.8$ Hz, 2H), 6.12 (dd, $J = 18, 10$ Hz, 2H), 5.82 (dd, $J = 10, 1.4$ Hz, 2H), 4.67–4.64 (m, 4H), 4.14 (t, $J = 7.0$ Hz, 4H), 4.03–3.98 (m, 6H), 3.95 (s, 3H), 1.84–1.70 (m, 4H), 1.70–1.63 (m, 4H), 1.51–1.44 (m, 6H), 1.44–1.20 (m, 42H), 0.88 (t, $J = 6.8$, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 166.32, 165.77, 152.96, 142.94, 137.34, 130.43, 128.58, 123.27, 123.23, 122.66, 107.99, 73.52, 69.26, 64.66, 62.73, 49.00, 36.44, 31.89, 30.30, 29.71, 29.68, 29.65, 29.56, 29.53, 29.50, 29.49, 29.39, 29.35, 29.28, 29.23, 28.56, 26.08, 26.01, 25.89, 22.66, 14.09$. IR (KBr): $\nu = 2920, 2851, 1726, 1683, 1620, 1586, 1505, 1472,$

1432, 1410, 1386, 1335, 1295, 1275, 1228, 1200, 1122, 1058, 987, 966, 811, 723 cm^{-1} . MS (MALDI-TOF): calcd for $[\text{M} - \text{BF}_4]^+$, 951.63; found, 952.20. Elemental analysis calcd (%) for $\text{C}_{55}\text{H}_{87}\text{BF}_4\text{N}_2\text{O}_{11}$: C, 63.57; H, 8.44; N, 2.70. Found: C, 63.05; H, 8.71; N, 2.79.

Preparation of APS-Modified Glass and ITO Substrates. Glass substrates with comb-shaped gold electrodes (25×10 mm) and ITO-coated glass substrates (15×10 mm) were immersed in piranha solution (3:7 by volume of 30% H_2O_2 and H_2SO_4) for 5 min at room temperature to generate hydroxyl groups as well as to clean the surfaces. These substrates were washed with H_2O , acetone, and MeOH, and dried. The cleaned substrates were immersed in a 5% toluene solution of 3-(aminopropyl)triethoxysilane (APS) for 1 h at 25 °C. Then, the APS-modified substrates were rinsed with toluene and MeOH and dried at 120 °C for 30 min under an argon atmosphere.

Sample Preparation for Photopolymerization. The photopolymerizable sample was prepared by mixing monomer **1** and 2,2-dimethoxy-2-phenylacetophenone (5 wt % to the monomer) as the photoinitiator. The mixture was sandwiched between two glass substrates, two ITO substrates, or the APS-modified substrates, heated to an isotropic state at 70 °C, and then cooled to room temperature at a cooling rate of 1 °C min^{-1} . Photopolymerization of columnar liquid crystals was carried out at 30 °C for 60 min under the exposure to UV light (365 nm, 22 mW/cm^2).

Measurements of Ionic Conductivities. Ionic conductivities were measured by the 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.^{2a,3a,32} The heating rate of the measurements was fixed to 3 °C min^{-1} from 30 to 200 °C. Ionic conductivities were calibrated with aqueous KCl solution (1.00 mmol L^{-1}) as a standard conductive solution.

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Supporting Information Available: X-ray diffraction spectra of **1** in the columnar LC phase before and after photopolymerization, illustrations of the cells for anisotropic ionic conductivity measurements, and synthesis and phase transition behavior of non-LC benzylimidazolium salts having two and three acrylate groups. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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