

FOCUS REVIEW

Zwitterions as building blocks for functional liquid crystals and block copolymers

Takahiro Ichikawa^{1,2}

Zwitterions are a class of organic salts whose cation and anion are covalently tethered. This characteristic imparts unique physicochemical properties that differ from those of conventional organic salts. Recently, there has been increasing attention paid to the use of these zwitterions as building blocks for functional organic materials due to their unique properties. These materials have been applied to polymers, liquid crystals, dendrimers and nanoparticles. In this review, I focus on the development of nanostructured ionic materials through the organization of zwitterions. The strategies for such development can be roughly classified into two groups: the introduction of liquid-crystalline properties into zwitterions and the design of block copolymers with zwitterionic segments. These zwitterion derivatives show various organizational behaviors, such as self-organization, co-organization with acids or lithium salts and solvent-induced organizational behavior; they also function as unique ionic matrices. The potential applications of these ionic matrices are described.

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INTRODUCTION

Self-organization has been recognized as a significant strategy for creating nanostructured materials with well-ordered periodicity. A number of technologies that make use of self-organization have been developed in recent decades.¹ Liquid crystals,^{2,3} block copolymers,⁴ metal-organic-frameworks⁵ and supramolecules⁶ are representative self-organizing systems. By introducing functional groups into these self-organizing materials, it is possible to achieve novel functions and properties with these well-organized structures. For the development of new materials with innovative functions, it is important to select appropriate functional groups and align them in suitable structural geometries.

Zwitterions are a class of organic salts whose cation and anion are covalently tethered. This characteristic imparts these salts with higher crystallinity and higher melting temperature than conventional organic salts. Recently, there has been increasing attention paid to the use of zwitterions as alternatives to conventional ionic groups as building blocks for developing new functional materials; the tethered ion structures result in novel phenomena that are not produced in normal ionic groups. In the course of these studies, zwitterions have been organized via various materials design approaches, for example, using amphiphiles,⁷ polymeric betaines,⁸ polymer brushes,⁹ attachment on particles,¹⁰ introduction of liquid-crystalline (LC) properties¹¹ and block copolymerization.¹² In this review, I will focus on the design of liquid crystals and block copolymers containing zwitterions as molecular blocks and their potential as ionic matrices for various applications (Figure 1).

STUDIES ON ZWITTERIONIC LIQUID CRYSTALS

Corresponding to the development of synthetic technologies, a variety of LC molecules have been designed in recent decades.^{2,3} These liquid crystals can be classified from several viewpoints. For example, using dimensional geometry, they are classified into nematic, smectic (Sm), columnar (Col), bicontinuous cubic (Cub_{bi}) and micellar cubic (Cub_m) phases.¹³ In terms of molecular structures, rod-shaped,¹⁴

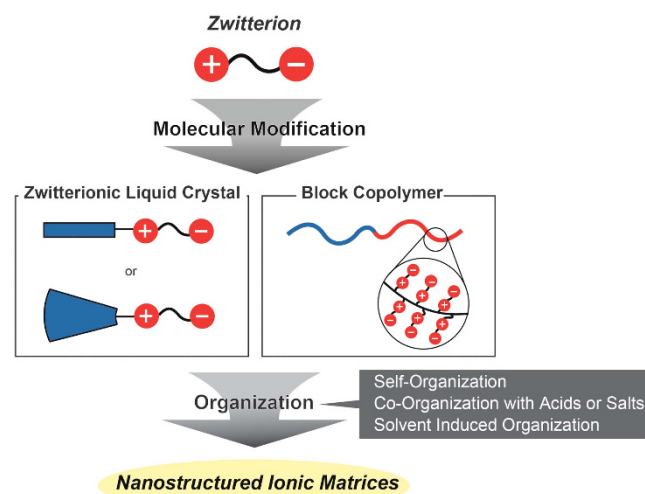


Figure 1 Design of nanostructured ionic matrices by introducing zwitterionic structures into liquid crystals and/or block copolymers.

¹Department of Biotechnology, Tokyo University of Agriculture and Technology, Tokyo, Japan and ²Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, Kawaguchi, Japan
Correspondence: Dr T Ichikawa, Department of Biotechnology, Tokyo University of Agriculture and Technology, Nakacho, Koganei, Tokyo 184-8588, Japan.
E-mail: t-ichi@cc.tuat.ac.jp

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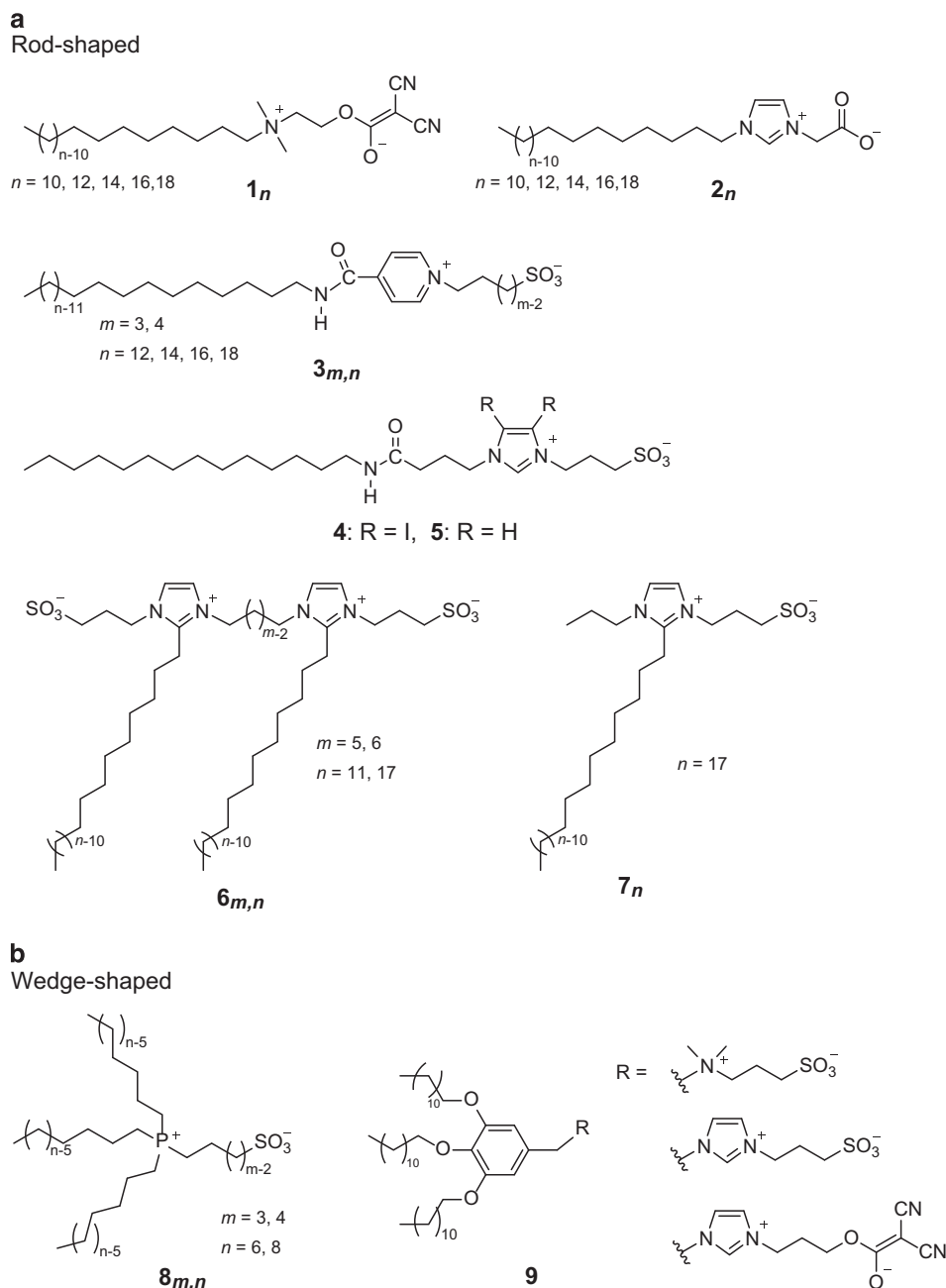


Figure 2 Molecular structures of amphiphilic zwitterions showing thermotropic and/or lyotropic liquid-crystalline behavior. (a) Rod-shaped molecules **1**,¹¹ **2_n**,³⁰ **3_{m,n}**,³¹ **4**,³² **6_{m,n}** and **7_n**.³³ (b) Wedge-shaped molecules **8_{m,n}** (ref. 34) and **9**.^{35,36}

disc-shaped,^{15,16} and wedge-shaped-structures^{16,17} are representative. The liquid crystals may or may not contain ionic structures in their molecular structures and can be accordingly divided into two groups: ionic liquid crystals and others. A significant characteristic of ionic liquid crystals is that electrostatic interactions between the ionic parts have a major role in determining their self-organization behavior due to differences in strength between electrostatic interactions and other intermolecular interactions. Comprehensive reviews on ionic liquid crystals have been published.^{18–21} In the present review, a class of ionic liquid crystals with zwitterionic moieties is highlighted, and their unique characteristics, which differ from normal ionic liquid crystals, are described.

Phospholipid is a representative amphiphilic biomolecule with a zwitterionic part, namely an ammonium betaine. It is well known that this molecule exhibits self-organization behavior in water and shows lyotropic LC behavior. Apart from this most well-known example, there have been artificial zwitterionic amphiphiles showing lyotropic and/or thermotropic LC behavior. Representative molecular structures are shown in Figure 2. An early report on amphiphilic zwitterions showing thermotropic LC behavior was published by Galin and colleagues in the 1990s.¹¹ The authors reported that amphiphilic ammonium betaine **1_n** exhibits thermotropic LC behavior, which varies with alkyl chain length. For example, **1₁₄** exhibits the Cub_{b1} phase from 78 to 114 °C, while **1₁₆** exhibits

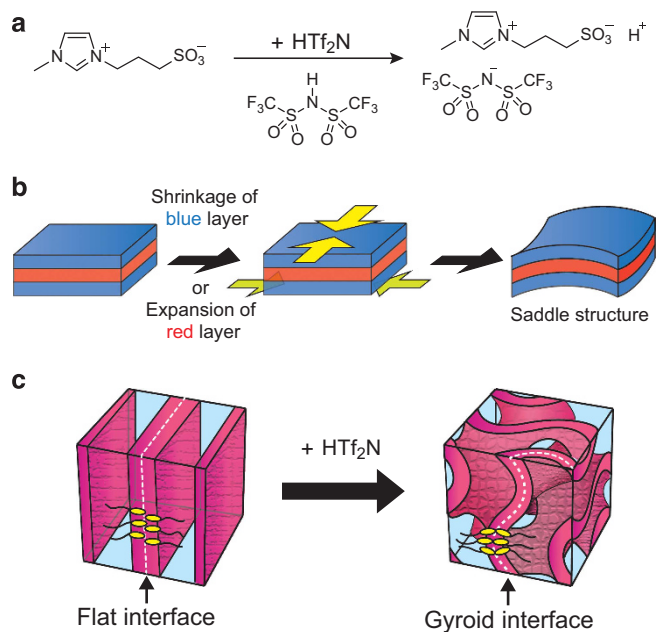


Figure 3 (a) Unique characteristic of zwitterion-forming ionic liquid-like ion pair through ion exchange with acids and/or lithium salts. (b) Formation mechanism of a saddle structure from a layered structure. (c) Phase change from a layered smectic phase to a bicontinuous cubic phase with a three-dimensional (3D) continuous gyroid minimal surface.

the Sm phase from 84 to 199 °C. Strong dipolar interactions between the zwitterionic moieties are an important driving force for self-organization.

In three decades of studies on ionic materials, an important turning point has been the growing interest in organic salts that exist in the liquid state at ambient temperature, that is, 'ionic liquids'.²² The unique properties of ionic liquids, such as their negligible vapor pressure,²³ flame retardancy²⁴ and high ionic conductivity,²⁵ have motivated applications as liquid electrolytes in batteries. A variety of ion designs have been exploited to develop functional ionic liquids.²⁶ To increase the transference number of target ions, such as protons and lithium ions, zwitterions consisting of imidazolium-, pyridinium- and ammonium-betaines were prepared.²⁷ These molecules form homogeneous mixtures with specific acids and/or lithium salts (Figure 3a) to provide ionic liquid-like media that selectively transport target ions such as protons and lithium ions.^{28,29} Taking into account their drastically altered physicochemical properties on incorporation of these particular acids and lithium salts, it is expected that this ability can be used for morphological control of amphiphilic zwitterions and zwitterionic polymers. Compounds 2–9 are representative examples of zwitterionic liquid crystals whose phase behaviors are controlled by the addition of acids or lithium salts.^{30–36} For these zwitterionic liquid crystals, ion conduction behavior with ion-selectivity and anisotropy is expected. It is thus of interest whether they exhibit unique functions and properties that are more than a combination of the intrinsic properties of zwitterions and ionic liquid crystals. Lin *et al.*³⁰ reported an early example of zwitterionic liquid crystals. They designed amphiphilic zwitterion 2 and examined the thermotropic LC behavior of their mixtures with certain lithium salts.³⁰ In the following sections, I will describe in detail the phase behavior and function of compounds 3–9.^{31–36}

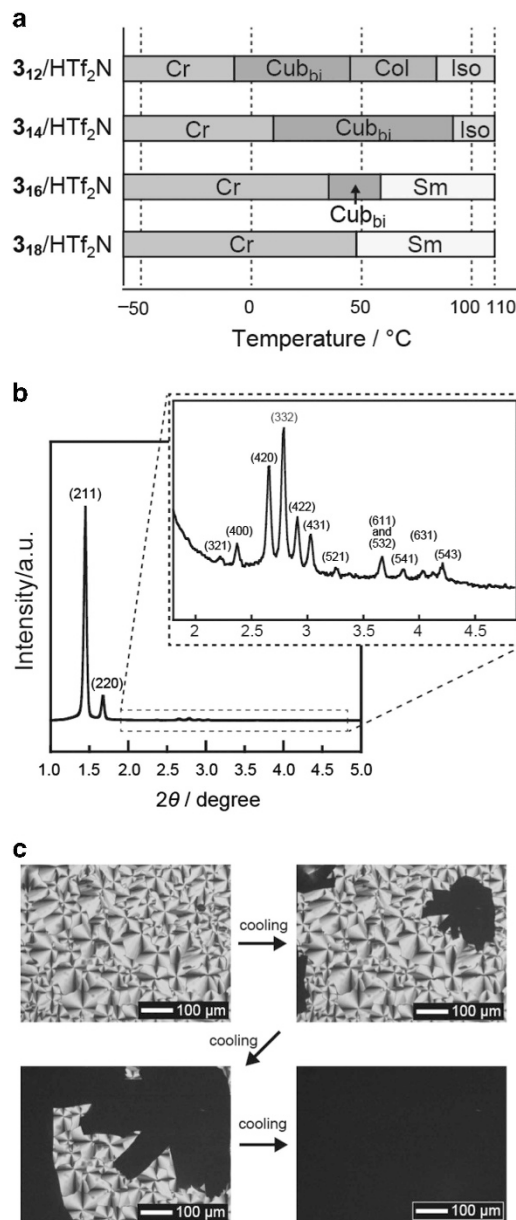


Figure 4 (a) Thermotropic liquid-crystalline behavior of 3_n/HTf₂N mixtures.³¹ Cr, crystalline; Cub_{bi}, bicontinuous cubic; Col, columnar; Sm, smectic; Iso, isotropic. (b) Synchrotron X-ray diffraction pattern of 3₁₄/HTf₂N mixture in the Cub_{bi} phase. (c) Polarizing optical microscopy of 3₁₂/HTf₂N mixture upon phase transition from Col to Cub_{bi} phases.³¹ Reproduced with permission from the reference. A full colour version of this figure is available at the *Polymer Journal* journal online.

MOLECULAR DESIGNS FOR THREE-DIMENSIONAL GYROID STRUCTURES

Nanosegregated phases formed by liquid crystals are classified into Sm, Col, Cub_{bi} and Cub_m depending on their structural geometry. Among these, our recent target is the Cub_{bi} phase, which forms gyroid structures due to their unique three-dimensional structures.^{37–40} In the Cub_{bi} LC assembly, the end of an LC molecule is located in the center of the nanochannel, and the other end sits on an infinite periodic minimal surface that appears as a set of middle points between the two interwoven nanochannels. There are three types

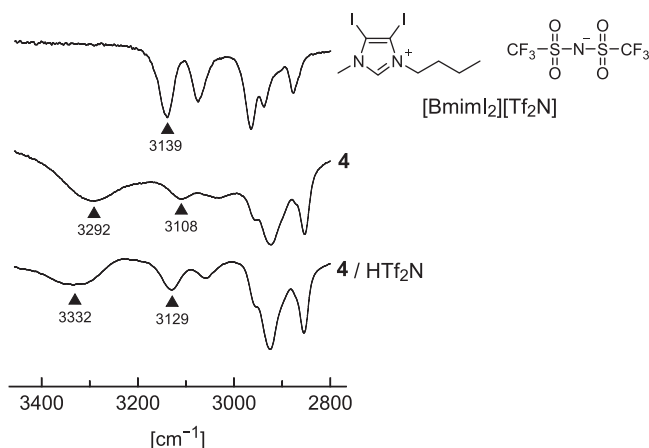


Figure 5 IR spectra of **4**, **4**/HTf₂N mixture and [Bmim]₂[Trf₂N].³² Reproduced with permission from the reference.

of infinite periodic minimal surface: gyroid, primitive and diamond. Among these, gyroid is observed most often. A variety of gyroid-structured materials have been produced, and various unique functions and properties derived from gyroid structures have been explored.⁴¹ For example, the three-dimensional nanochannels in Cub_{bi} liquid crystals have been studied intensively for transport pathways because these nanochannels enable maintenance of macroscopic continuity without special alignment control of the liquid crystal domains.^{42–46}

It has been mathematically revealed that a gyroid minimal surface is formed by the connection of saddle-like surfaces in three-dimension. Therefore, it is important to induce saddle structures to construct gyroid structures. When one imagines a red flat layer sandwiched by blue layers, a saddle structure is created by shrinking the blue layers in the cross direction or by expanding the red layer (Figure 3b). This model enables us to envision that the formation of a saddle structure at a molecular level leads to the creation of Cub_{bi} LC assemblies. With this idea in mind, we have designed amphiphilic compound **3_n**, consisting of a pyridinium-based zwitterionic head group, an amide group and a long alkyl chain.³¹ This compound exhibits Sm phases consisting of alternate layers of ionic and non-ionic layers. To control the organizational behavior of **3_n**, bis(trifluoromethanesulfonyl)imide (HTf₂N) was selected as an additive. An equimolar mixture of **3_n** and HTf₂N was successfully prepared by slow evaporation of a solution of the two components in methanol. As expected, Cub_{bi} phases are observed in the obtained mixtures. For example, the **3₁₄**/HTf₂N mixture shows a Cub_{bi} phase from 10 to 91 °C (Figure 4a). The Cub_{bi} phases were characterized by synchrotron X-ray diffraction measurements (Figure 4b). Interestingly, the induced LC phases show a clear dependence on alkyl chain length. Elongation of the alkyl chain leads to the induction of Sm phases, and their shortening results in the induction of Col phases. Polarizing optical microscopy images of the mixture upon phase transition from the Col to Cub_{bi} phase are shown in Figure 4c. The alkyl chain dependence of the LC phases indicates that the volume balance between ionophilic and ionophobic domains is a significant factor governing the mesophase patterns. The change in thermotropic LC phases from Sm to Cub_{bi} on the addition of HTf₂N can be attributed to swelling of the ionic domains on the formation of ionic liquid-like ion pairs between the pyridinium-betaine moiety of **3_n** and HTf₂N (Figure 3c). Ion exchange between the two components has been successfully revealed by Raman spectroscopy.⁴⁷

A halogen bond is an interaction between an electron-rich group and an electron poor group. This interaction has been used to design LC materials.^{48,49} For example, Bruce *et al.*⁴⁸ designed complexes of alkoxy stilbazoles and an iodopentafluorobenzene exhibiting LC behavior through the formation of supramolecular mesogens via halogen bonds. Apart from previous examples of halogen bond interaction for liquid crystal design, this interaction has been used for ionic liquid design.^{50,51} In this context, I expect that the introduction of halogen bonds into zwitterionic amphiphiles can be used to control the interface curvature of molecular assemblies. Accordingly, amphiphilic zwitterion **4** with an iodine-substituted imidazolium cation has been designed.³² For comparison, an analogous compound **5** was also prepared. Although **4** and **5** exhibit only Sm phases, Cub_{bi} and Col phases have been observed for a **4**/HTf₂N mixture and a **5**/HTf₂N mixture, respectively. To examine the interionic interactions between these mixtures, infrared (IR) spectroscopy has been performed. The C₂H of the imidazolium ring of **4** was observed at 3108 cm⁻¹, which shifts to 3129 cm⁻¹ on the addition of HTf₂N (Figure 5). Because the C₂H of the imidazolium ring of 1-butyl-4,5-diiodo-3-methylimidazolium bis(trifluoromethane)sulfonimide, [Bmim]₂[Trf₂N] is observed at 3139 cm⁻¹, it is assumed that the Trf₂N anion in a **4**/HTf₂N mixture is located near the imidazolium cation of **4**. Although definitive evidence for the formation of a halogen bond between the ions has not been obtained, it is assumed that the iodine-substituted imidazolium cation can form halogen bonds with the electron-rich Trf₂N anion present near the cation.

The use of a gemini structure is an effective strategy for controlling the self-organization behavior of amphiphilic molecules.⁵² In particular, this strategy has been effective for decreasing the critical micellar concentration and lowering the Krafft temperature of amphiphiles in solvents. In the course of studies on gemini-amphiphiles for lyotropic liquid crystals, it was gradually found that gemini-amphiphiles are predisposed to form lyotropic Cub_{bi} phases compared with monomeric-type ones.^{53–55} This insight leads us to hypothesize that the gemini design should also be effective for designing thermotropic Cub_{bi} liquid crystals. To verify this hypothesis, gemini-type amphiphilic zwitterions **6_{m,n}** have been designed and synthesized.³³ Notably, these zwitterions exhibit Cub_{bi} phases over a wide temperature range. For example, **6_{6,17}** shows a Cub_{bi} phase from 51 to 207 °C on heating. In contrast, **7_{3,17}**, a monomeric-type compound, shows no mesomorphic behavior. It is also noteworthy that **6_{6,17}** shows a glass transition on cooling from the Cub_{bi} LC state, whereas **7_{3,17}** shows crystallization at 191 °C on cooling from the isotropic state. The significant difference in crystallinity results from covalently tethered structures that prevent each long alkyl chain from aligning in a suitable position for crystallization. We assume that the strong incompatibility between the zwitterionic portion and the alkyl chain portion leads to minimization of the interface area, leading to Cub_{bi} phases with a gyroid-structured interface. These results suggest that a combination of gemini amphiphile design and zwitterionic amphiphile design is a promising molecular strategy for developing thermotropic Cub_{bi} liquid crystals.

MOLECULAR DESIGNS FOR ONE-DIMENSIONAL ION-CONDUCTIVE MATERIALS

Phosphonium-based zwitterions **8_n** have been designed and mixed with HTf₂N to form ionic nanochannels surrounded by ionophobic sheath domains.³⁴ Although the **8_n**/HTf₂N mixtures show no mesomorphic behavior, the addition of water to the mixtures induces the formation of hexagonal columnar (Col_h) phases with

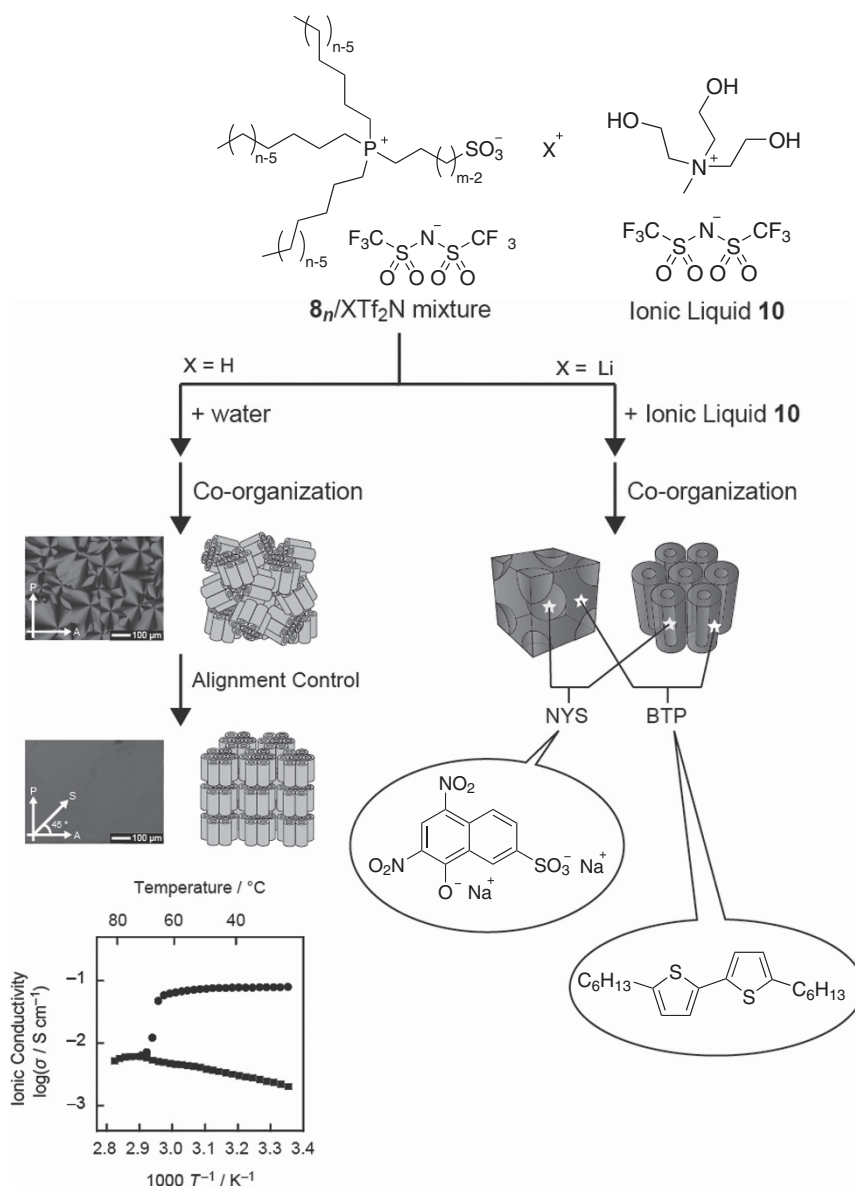


Figure 6 Lyotropic liquid-crystalline behavior of $8_n/HTf_2N$ mixtures using water and ionic liquid **10** as solvent. Using water leads to a columnar phase with effective ion conduction behavior in the aligned state.³⁴ The use of ionic liquid **10** provides a nanobiphasic ionic liquid system dissolving various solvatochromic dyes into nanosegregated domains.^{58,59} A full colour version of this figure is available at the *Polymer Journal* journal online.

one-dimensional hydrophilic nanochannels. For example, an $8_6/HTf_2N$ mixture with 20 wt% H_2O exhibits a Col_h phase from room temperature to 65 °C that can be identified by polarizing optical microscopy and X-ray diffraction measurements. The Col_h liquid crystals have been successfully aligned using mechanical shearing (Figure 6, left), a technique to measure anisotropic ion conductivity in columnar liquid crystals.^{56,57} Ionic conductivities of the $8_6/HTf_2N$ mixture with 20 wt% H_2O in the aligned Col_h and polydomain states have been successfully measured using a cell equipped with comb-shaped gold electrodes. Notable improvements in conductivities have been observed on control of the alignment of the liquid crystal domain, while the conductivities converge after the phase transition to the isotropic phase (Figure 6, left). Similar ion conduction behavior has also been observed for other zwitterionic liquid crystals. For example, Soberats *et al.*^{35,36} designed a series of wedge-shaped zwitterionic salts **9** and examined their applications

to proton- and lithium ion-conductive materials. These results indicate that macroscopic alignment of one-dimensional nanochannels is required to obtain the maximum potential properties of these zwitterions to form anisotropic structures.

The self-organization behavior of 8_6 can be controlled by the addition of certain ionic liquids as well as that of water.^{58,59} For example, the addition of ionic liquid **10** to the $8_6/LiTF_2N$ mixture leads to the formation of Col and Cub_m phases, depending on the molar ratio of **10** in the mixture (Figure 6, right). As the obtained LC matrices are composed of high-polarity (**10**) and low-polarity ($8_6/LiTF_2N$) ionic liquids, it is expected that these nanostructured matrices may function as nanobiphasic ionic liquids, where two ionic liquids co-exist on a macroscopic scale but exist separately on a nanometer scale. To prove the formation of the two incompatible ionic liquid-like domains, the solvatochromism of some dye molecules has been used. Certain dyes, such as naphthol yellow S (NYS) and

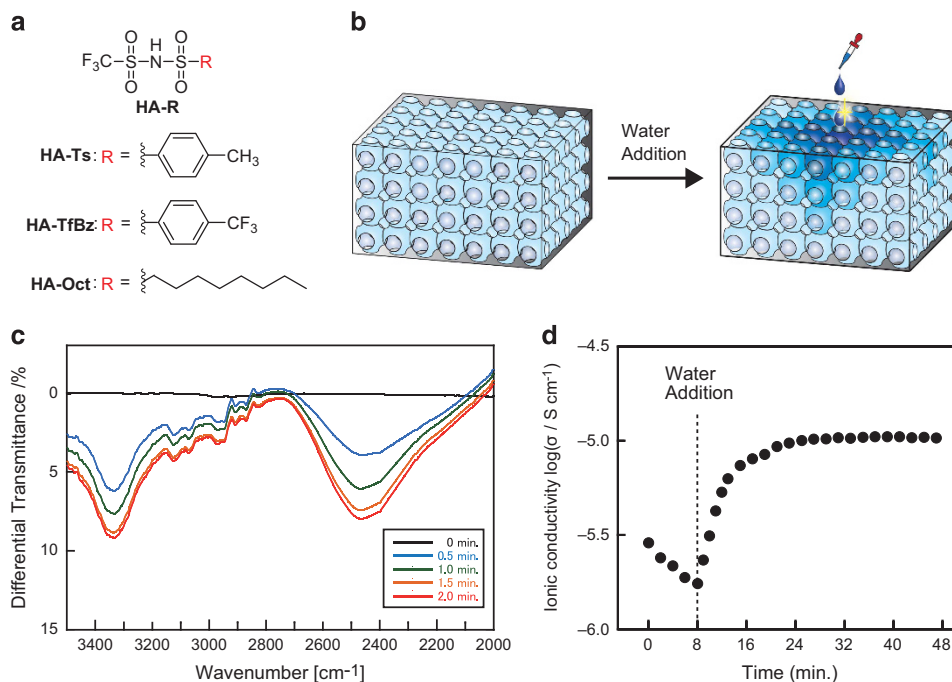


Figure 7 (a) Design of imide-type acids **HA-TS**, **HA-TfBz** and **HA-Oct** with aromatic or aliphatic groups.⁷³ (b) Absorption of water into glassy Cub_{bi} LC materials. (c) Change in differential transmittance of IR spectra of $\mathbf{3}_{12}/\text{HA-TfBz}$ mixture before and after addition of D_2O at -15°C . (d) Change in ionic conductivities of $\mathbf{3}_{12}/\text{HA-TfBz}$ mixture on addition of H_2O in the glassy Cub_{bi} state at -15°C .⁷³ Reproduced with permission from the reference.

3,4'-dihexyl-2,2'-bithiophene (BTP), partition into one of the two domains (Figure 6, right). By examining the solvatochromic behavior of these dyes in the LC samples, we succeeded in clarifying the formation of high-polarity and low-polarity ionic liquid domains in the matrices. Recently, there has been increasing attention paid to the combination of ionic liquids and zwitterions.^{60–62} As the cation and anion of zwitterions are covalently tethered, they maintain ion pair topology even in the presence of other ions, such as ionic liquids, enabling the formation of novel ionic matrices that cannot be constructed using a combination of conventional organic salts.

DEVELOPMENT OF GLASSY BICONTINUOUS CUBIC LIQUID CRYSTALS

Some liquid crystals are known to show glass transitions (instead of crystallization) on cooling.^{63–67} These liquid crystals are called glassy liquid crystals, and several examples of glassy liquid crystals among ionic liquid crystals have been reported.^{68–70} In the design of functional LC materials, the importance of molecular dynamics changes is dependent on their applications. For example, liquid crystals for displays should have high molecular dynamics to enable high response to external stimuli. In contrast, in the case of organic semiconductors, the presence of molecular dynamics impairs function; therefore, glassification is used to improve function.^{66,67} Therefore, it is expected that there are various potential applications where glassy liquid crystals are more suitable than normal liquid crystals. In this context, I expect that glassy liquid crystals can be exploited to develop nanostructured scaffolds whose structures do not change on the ingress of guest molecules. To construct glassy ionic liquid crystals, it is important to understand why some ionic liquid crystals adopt glassy states while others undergo crystallization upon cooling.^{68–70} Our understanding is that when alkyl chains begin ordering before freezing of the ionic domains, they crystallize. In contrast, when ionic domains freeze before the ordering of the alkyl chains starts, the

alkyl chains do not form well-aligned states, resulting in glassification. Taking this idea into account, ion design that increases the glass transition temperature of ionic domains is expected to be important for the development of glassy ionic liquid crystals. In the course of studies of the physicochemical properties of ionic liquids, the relationships between the ion structures and the glass transition temperature of ionic liquids have gradually been revealed. It has been reported that the introduction of aromatic rings into ion structures leads to an increase in the glass transition temperature of ionic liquids.^{71,72} This insight led us to design the imide-type acids, **HA-Ts**, **HA-TfBz**, and **HA-Oct**, as additives for zwitterionic liquid crystals (Figure 7a).⁷³ Compound $\mathbf{3}_{12}$ was selected as the amphiphilic zwitterion, and homogeneous mixtures of $\mathbf{3}_{14}$ and the designed acids were prepared. As expected, the mixtures were LC materials showing glass transition behavior. For example, $\mathbf{3}_{12}/\text{HA-TfBz}$ exhibits a Cub_{bi} phase that forms a glassy state near 0°C while maintaining the Cub_{bi} structure. Interestingly, these vitrified Cub_{bi} LC materials absorb water while preserving their molecular assembled structures (Figure 7b). The absorption of water can be confirmed by IR spectroscopy and ion conduction measurement (Figures 7c and d). In contrast, the absorption of water in the LC state induces a change in mesophase pattern from the Cub_{bi} to the Col phase. These results clearly suggest that glassification prevents a change in molecular arrangement upon water absorption. We are now exploring a way to use glassified Cub_{bi} liquid crystals as scaffolds for various functional guest molecules.

DESIGN OF BLOCK COPOLYMERS WITH ZWITTERIONIC SEGMENTS

Block copolymers are also organized structural materials that can potentially be formed through the segregation of incompatible segments.⁴ There is some commonality in the structural geometry between nanostructures formed by liquid crystals and those formed

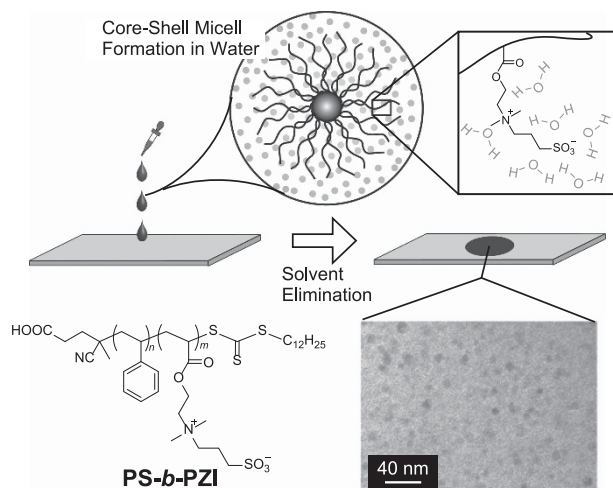


Figure 8 Molecular structure of block copolymer **PS-*b*-PZI**,⁷⁷ which forms core-shell micelles in water. Casting of the colloidal solution on a substrate and elimination of water results in the formation of a nanostructured film sample. A full colour version of this figure is available at the *Polymer Journal* journal online.

by block copolymers, although there is a definite difference in the lattice length between these two materials. A variety of zwitterionic block copolymers have recently been designed. Yoshida and co-worker reported the thermoresponsivity and pH sensitivity of zwitterionic block copolymers.⁷⁴ Erel-Goktepe and colleagues reported micelle formation of poly[3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate]-block-poly[2-(diisopropylamino)ethyl methacrylate] and its application to pH-responsive layer-by-layer films.⁷⁵ In these studies, the ability of zwitterions to recognize acids has been successfully introduced into block copolymer systems. Employment of bio-compatible zwitterions, such as phosphorylcholine derivatives, enable the use of zwitterionic block copolymers for biotechnologies and biofriendly materials.⁷⁶

To construct solid electrolytes having mechanical stability and high ionic conductivity, we designed block copolymers, **PS-*b*-PZI**, composed of polystyrene and polyzwitterionic segments (Figure 8).⁷⁷ These molecules form micellar assemblies comprising polystyrene cores and polyzwitterion shells in polar solvents such as water. Slow evaporation of the solvent at 70 °C followed by vacuum drying results in the formation of a thin-film sample. The morphology of this film has been investigated using transmission electron microscopy, which reveals that these **PS-*b*-PZI** form aggregated micelles in the films. When forming the film in the presence of specific acids or lithium salts, nanosegregated electrolytes can be successfully prepared. For example, a mixture of **PS-*b*-PZI** and phosphoric acid formed a solid electrolyte with an ionic conductivity of 10^{-5} S cm⁻¹ at 40 °C. We believe that further control of the morphology of these block copolymers can be achieved by the suitable selection of the two incompatible segments and control of the component ratio between these segments.

Interest in zwitterions has not been limited to their availability as bulk materials. For example, there is increasing interest in the use of zwitterions as surface-coating materials⁷⁸ and interface-stabilizers,⁷⁹ among other uses. In the course of these studies, a variety of novel functions and properties unique to zwitterions have gradually been found. I believe the accumulation of insight into these zwitterions will pave the way to develop next-generation technologies.

CONCLUSIONS

In this review, the potential utility of zwitterions as building blocks for functional soft materials such as liquid crystals and block copolymers has been described. These zwitterion-derived materials show diverse organizational behaviors, including self-organization, co-organization with acids and/or lithium salts and solvent-induced organization. In particular, co-organization with some acids and/or lithium salts is unique, as it varies significantly with the selected additives. This is attributed to the tendency of these zwitterions to form ionic liquid-like ion pairs with the acids and lithium salts. The selection of additives is important for obtaining the desired functions for the resultant materials. In particular, the application of these materials as ion transport materials has been the main focus. However, as some recent papers have reported the availability of zwitterions for the design of bio-compatible matrices,⁸⁰ it is expected that the ionic materials described in this review will be used in a wide variety of fields ranging from materials chemistry to biotechnology.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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Takahiro Ichikawa is an Associate Professor at the Department of Biotechnology and Life Science at Tokyo University of Agriculture and Technology. He received his PhD from The University of Tokyo in 2013 under the supervision of Professor Takashi Kato. Before his PhD, he joined Ohno-Nakamura laboratory at Tokyo University of Agriculture and Technology as an Assistant Professor (2010–2015). He has focused on the functionalization of bicontinuous cubic liquid crystals based on ionic materials, such as ionic liquids and zwitterions. He received an Award for Encouragement of Research in Polymer Science from the Society of Polymer Science, Japan (2016).