

Induction of an Infinite Periodic Minimal Surface by Endowing An Amphiphilic Zwitterion with Halogen-Bond Ability

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We have designed an amphiphilic zwitterion with an iodine-substituted imidazolium cation. Although it forms a layered assembly with flat interfaces, the addition of an equimolar amount of bis(trifluoromethane)sulfonimide results in the formation of a bicontinuous cubic liquid-crystalline assembly with a primitive-type infinite periodic minimal surface, where its zwitterionic headgroup sits regularly. IR measurements revealed that halogen bond between the iodine atoms on the imidazolium cation and the anions is involved in its molecular-assembly behavior. The present results clearly indicate the potential utility of halogen bonding to control the dimensionality and continuity of the ionic/nonionic interface of amphiphiles in bulk and consequent mesophase patterns, which may be a significant new molecular technology for precisely arranging functional molecules on a 3D continuous interfaces.

An infinite periodic minimal surface (IPMS) is a unique interface that possesses incompatible characteristics, flatness on a minute scale and three-dimensional (3D) continuity on a large scale.^[1] These characteristics stimulated us to envision that the use of an IPMS could serve as the basis for an innovative strategy to develop alignment-free functional interfaces with macroscopic continuity. For the construction of such an interface, a promising approach is to use the self-organization of thermotropic bicontinuous cubic (Cub_{bi}) liquid crystals.^[2] Despite a growing interest in Cub_{bi} liquid-crystalline (LC) assemblies, the number of research studies that report on the appli-

cation of Cub_{bi} liquid crystals is very limited.^[3] This results from the difficulty in designing thermotropic LC molecules that exhibit Cub_{bi} phases. For the past decade, we have been engaged in overcoming the design difficulty of Cub_{bi} liquid crystals by employing the excellent designability of ionic liquids.^[4] For example, thermotropic Cub_{bi} liquid crystals have been successfully developed by introducing ionic-liquid structures into wedge-shaped molecules.^[4,5] They form three-dimensionally interconnected, periodic ionic nanochannels that function as alignment-free, ion-conducting pathways. Recently, we have focused on the design of Cub_{bi} liquid crystals based on zwitterions,^[6] because of their unique characteristic of forming ionic-liquid-like ion pairs in the co-existence of suitably selected acids or salts.^[7] To date, we have succeeded in the development of amphiphilic zwitterions that exhibit Cub_{bi} phases in the presence of some acids or lithium salts.^[6] It has been found that a gyroid minimal surface, a class of IPMS, is formed in the Cub_{bi} phases, which functions as a proton conduction pathway. This is a pioneering study that clearly shows the potential utility of IPMS as a transportation pathway. To make the strategy using IPMS more available, it is required to accumulate insight into the design of LC molecules that form Cub_{bi} phases. In the present study, we describe a novel strategy that causes ionic amphiphiles to form Cub_{bi} LC assemblies, which is inspired by the ion design developed in ionic-liquid chemistry.

During the decades of studies on ionic liquids, a number of cations and anions have been newly designed and combined to provide ionic liquids with desired functions and properties.^[8] Consequently, the relationships between the component ion structures and their physicochemical properties have been intensively studied. One often-used strategy is to introduce halogen atoms, such as fluorine, into the anion because the electro-drawing property of halogen atoms contributes to the delocalization of a negative charge over the anion that is effective in lowering the viscosity of ionic liquids. Contrary to the conventional strategy, the introduction of halogen atoms into cations has only been performed in a limited number of research studies,^[9] because the introduction of halogen atoms into cations enhances the positive charge, which leads to an enhancement of electrostatic interaction, which then increases the crystallinity of the resultant organic salts. Although halogen introduction has been avoided in the design of ionic liquids with low viscosity and/or low melting point, it gradually turns into an effective strategy for developing task-specific ionic liquids^[10] or organic salts.^[11] For example, recently, we have succeeded in increasing the refractive index of ionic liquids by attaching iodine atoms onto an imidazolium ring.^[9d]

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These iodine-functionalized imidazolium salts show higher viscosities than that of conventional imidazolium salts. This behavior may be attributed to the formation of halogen-bond interactions between the iodine atoms and anions. This is a class of interaction between a electrophilic halogen atom and an electron donor, which is similar to hydrogen bonding in several respects, although far less familiar.^[12]

Inspired by the halogen-bond interaction between these imidazolium-based ionic liquids, we expected that the introduction of halogen-bond ability into the design of amphiphilic zwitterions will be an advantageous strategy for controlling the intermolecular distances between their ionic headgroups in the assembled state, which is greatly responsible for the dimensionality of the ionic/nonionic interface and resultant mesophase pattern. To test this hypothesis, we designed amphiphilic zwitterion **ImI₂ZI** with an iodine-functionalized imidazolium cation as an ionic headgroup (Figure 1a). For comparison, analogous amphiphilic zwitterion **ImH₂ZI** with no iodine atom has been also prepared.

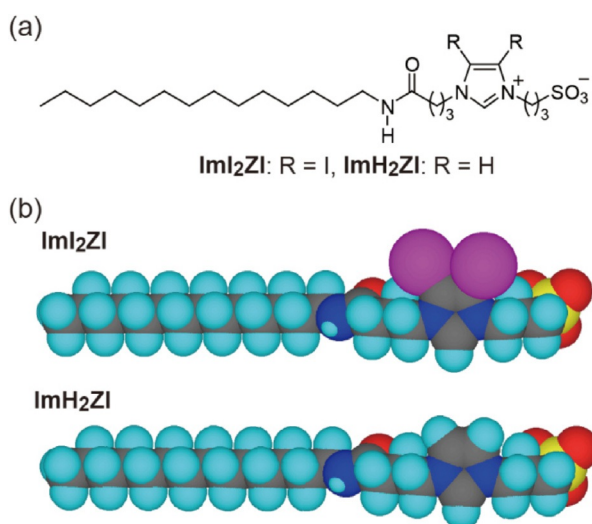


Figure 1. a) Molecular structures of **ImI₂ZI** and **ImH₂ZI**. b) 3D molecular modeling of **ImI₂ZI** and **ImH₂ZI**.

Compounds **ImI₂ZI** and **ImH₂ZI** exhibit thermotropic smectic (Sm) phases over wide temperature ranges (Figure 2). It is expected that electrostatic interactions between their zwitterionic parts, hydrogen bonds between their amide moieties, and ionophobic interactions play major roles in their self-organizing behavior. X-ray diffraction measurements for these compounds have revealed that they form bilayer structures, where their zwitterionic headgroups form flat interfaces with interdigitated states (see Figures S1–S3 in the Supporting Information).

To bend the flat interfaces in the Sm LC assemblies in order to induce the exhibition of Cub_{bi} phases with an IPMS, we adopted a previously developed strategy, in which some acids or lithium salts are added to form ionic complexes with their zwitterionic parts.^[6] Here, we report results obtained when using bis(trifluoromethane)sulfonimide (HTf₂N) as an additive. Equimolar mixtures of **ImR₂ZI** and HTf₂N were successfully pre-

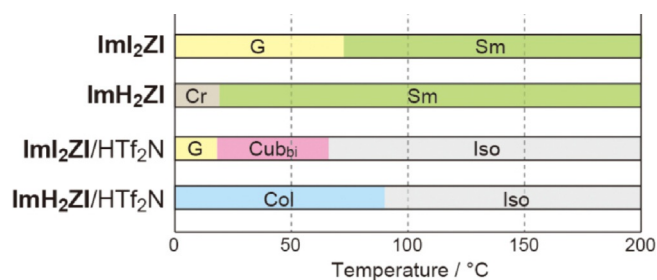


Figure 2. Thermotropic LC properties of **ImI₂ZI**, **ImH₂ZI**, and their mixtures with equimolar amounts of HTf₂N on heating. G, glass; Cr, crystalline; Sm, smectic; Cub_{bi}, bicontinuous cubic; Col, columnar; Iso, isotropic.

pared by slow evaporation of methanol solutions of these compounds. Thermotropic LC behavior of these mixtures is also shown in Figure 2. It can be seen that the addition of HTf₂N greatly changes the thermotropic LC behavior of **ImR₂ZI**. Upon cooling from the isotropic (Iso) state of the **ImI₂ZI**/HTf₂N mixture at around 150 °C, it never shows birefringence until it turns into a glass state at around 10 °C, although a drastic increase in viscosity is observed at around 50 °C. This is a characteristic phase behavior of thermotropic liquid crystals exhibiting cubic phases. These phase transitions are confirmed by differential scanning calorimetry (DSC) measurements. DSC curves for the **ImI₂ZI**/HTf₂N mixture are shown in Figure 3a. Upon heating, this mixture shows a base-line shift correspond-

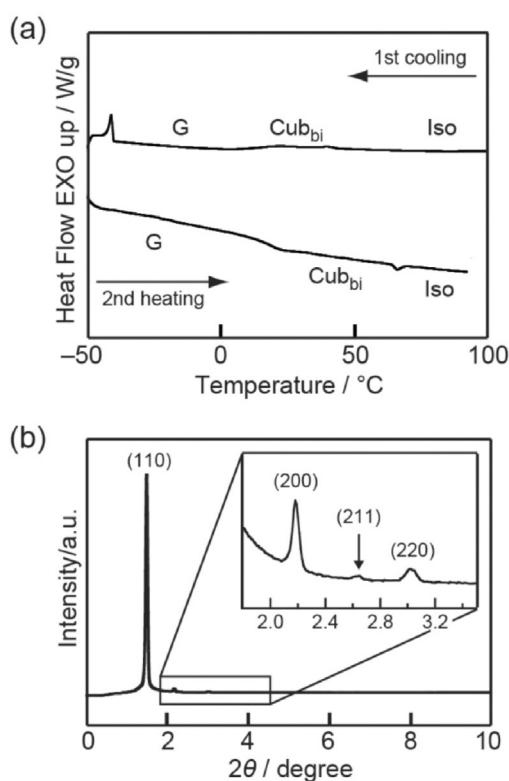


Figure 3. a) Differential scanning calorimetry curves of the **ImI₂ZI**/HTf₂N mixture. b) Synchrotron X-ray diffraction pattern of the **ImI₂ZI**/HTf₂N mixture at 40 °C.

ing to a glass–LC phase transition at 12 °C and a small endothermic peak at 62 °C, indicating a phase transition from LC to Iso phases. To characterize the cubic phase, synchrotron radiation X-ray diffraction measurements were performed for the **ImI₂ZI**/HTf₂N mixture at 40 °C, using a wavelength of 0.9993 Å. An intense diffraction peak and three weak peaks are observed at $2\theta = 1.51, 2.18, 2.65,$ and 3.02° (Figure 3b). By using the Bragg equation, *d*-spacing values were calculated to be 37.9, 26.3, 21.6, and 19.0 Å, respectively. The reciprocal ratio of these *d*-spacing values was $\sqrt{2}:\sqrt{4}:\sqrt{6}:\sqrt{8}$ and, therefore, they can be indexed to the reflection peaks of (110), (200), (211), and (220) of a cubic structure with a lattice parameter of 53 Å. The appearance of these peaks is a characteristic of a Cub_{bi} LC assembly with *Im3m* symmetry. For further confirmation of these LC phases, an effective approach is to examine amphotropic LC behavior.^[13] Addition of a small amount of water into the **ImI₂ZI**/HTf₂N mixture leads to the exhibition of Col phases showing a focal conic texture under the polarizing optical microscope (Figure 4a), which also supports that the **ImI₂ZI**/

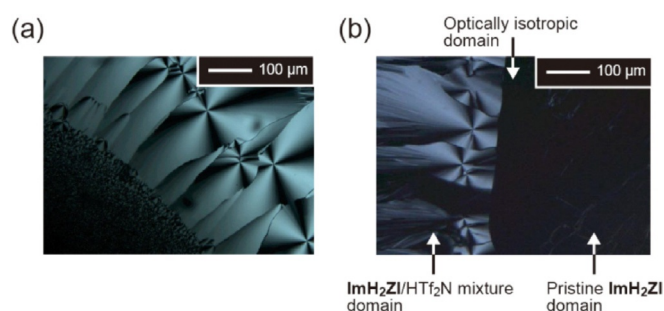


Figure 4. Polarizing optical microscope textures of: a) **ImI₂ZI**/HTf₂N mixture with a small amount of water; b) the contact test sample of the **ImH₂ZI**/HTf₂N mixture and **ImH₂ZI** at 70 °C.

HTf₂N mixture forms a Cub_{bi} phase under the water-poor conditions. In contrast to the **ImI₂ZI**/HTf₂N mixture, the **ImH₂ZI**/HTf₂N mixture exhibits a Col phase without addition of water (Figure S9). To examine if **ImH₂ZI** has the potential to exhibit Cub_{bi} phases, depending on the molar ratio of HTf₂N per **ImH₂ZI**, we tried a contact test for the **ImH₂ZI**/HTf₂N mixture and pristine **ImH₂ZI**. Here, we note that pristine **ImH₂ZI** exhibits only a Sm phase. From this contact test, we observed a band-shaped optically isotropic LC domain between the domain of the **ImH₂ZI**/HTf₂N mixture and that of pristine **ImH₂ZI** (Figure 4b). It is most plausible to assume that the appearance of the non-birefringent domain is indicative of the formation of a Cub_{bi} phase as a mesophase between Sm and Col phases.

In our previous study on the thermotropic LC behavior of a series of amphiphilic zwitterions with a pyridinium cation structure, we reported that the addition of HTf₂N into the amphiphilic zwitterions results in the induction of Col and Cub_{bi} phases, where hydrophobic alkyl-chain domains are surrounded by an ionic-liquid-like domain.^[6] This phenomenon was explained by ion exchange between the zwitterion part and HTf₂N through the hard and soft acids and bases principle.

Taking into account the previous results, we inferred that the molecular-assembly structures of the **ImI₂ZI**/HTf₂N mixture in the Cub_{bi} phase adopted *Im3m* symmetry. A schematic illustration is described in Figure 5. In the Cub_{bi} assembly, it is expect-

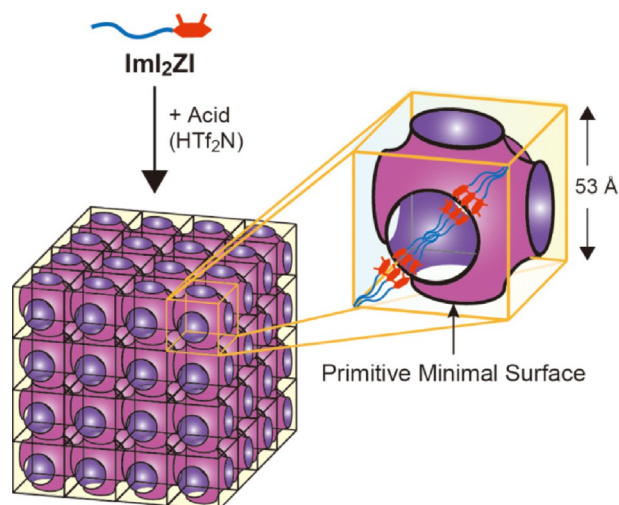


Figure 5. Schematic illustration of the proposed molecularly assembled structure of the **ImI₂ZI**/HTf₂N mixture in the Cub_{bi} phase with *Im3m* symmetry.

ed that the ionic headgroup of **ImI₂ZI** sits on a primitive minimal surface, a class of IPMS, and the periphery of its alkyl chain locates in the center of 3D interwoven nanochannel domains.

Comparison of the LC behavior between **ImI₂ZI**, **ImH₂ZI**, and their mixtures with HTf₂N leads us to conclude that the attachment of iodine atoms onto the imidazolium cation of the amphiphilic zwitterions has significant effects on their self-organization behavior. To elucidate the effects of this halogen substitution on intermolecular interactions, we have carried out IR measurements for the LC samples. Before discussing the IR spectra of these LC samples, here we note the results obtained for an ionic liquid, 1-butyl-4,5-diiodo-3-methylimidazolium bis(trifluoromethane)sulfonimide, [BmimI₂][Tf₂N]. Compared to the IR spectrum of 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([Bmim][Tf₂N]), it has been found that iodine introduction into the imidazolium cation gives rise to a peak shift of the stretching vibration of the C–H bond at the C₂ position of the imidazolium ring (C₂–H) from 3156 to 3139 cm⁻¹ (Figure 6a). Based on these results, we discuss the IR spectra obtained for the LC samples. The IR spectra of **ImI₂ZI**, **ImH₂ZI**, and their mixtures with HTf₂N in the LC phases are compared in Figures 6b–e. Focusing on the symmetric stretching vibration of the S=O group (S=O_s) of **ImI₂ZI**, it has been found that the position of the S=O_s band shifts from 1173 to 1140 cm⁻¹ upon the addition of HTf₂N (Figure 6d). This shift indicates that the sulfonate anion of **ImI₂ZI** is protonated by HTf₂N through ion exchange between the two compounds (Scheme 1). The change of the IR band peak position of C₂–H upon the addition of HTf₂N also supports the ion exchange. Although the IR absorbance peak of C₂–H is observed at 3108 cm⁻¹ for pristine **ImI₂ZI**, that of **ImI₂ZI** in the presence of

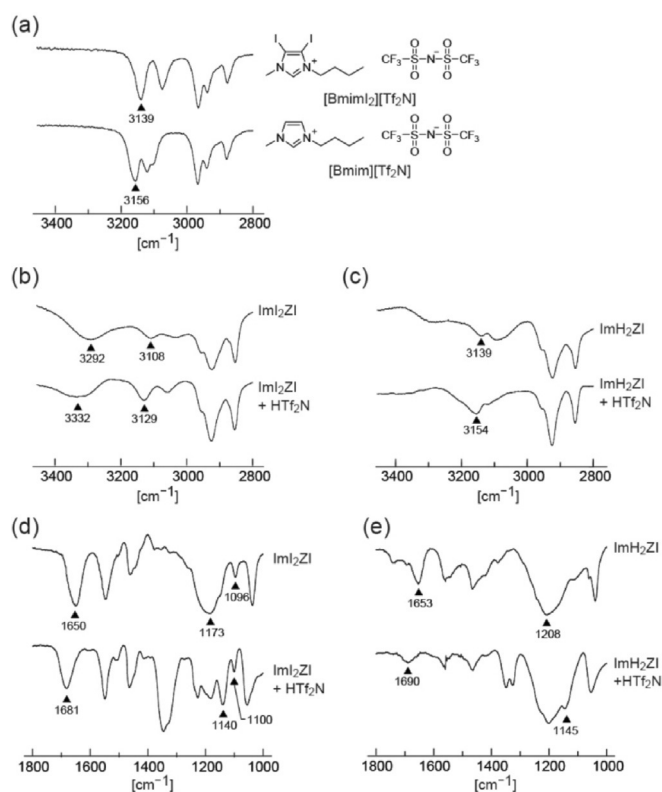
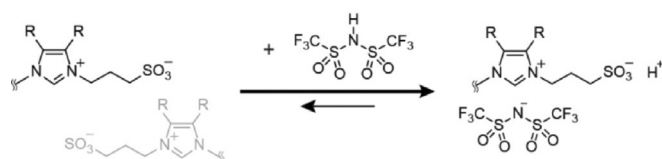


Figure 6. IR spectra of: a) $[Bmim]_2[TF_2N]$ and $[Bmim][TF_2N]$; b–e) ImI_2ZI , c) ImH_2ZI , and their respective mixtures with equimolar amounts of HTf_2N , respectively.



Scheme 1. Schematic presentation of ion exchange between ImR_2ZI and HTf_2N .

HTf_2N is observed at 3129 cm^{-1} (Figure 6b), which is approximately the same position as that observed for $[Bmim]_2[TF_2N]$. Similarly, a high-frequency shift of C_2-H upon the addition of HTf_2N is also observed for ImH_2ZI systems (Figure 6c). The high-frequency shift can be understood as follows. In the assemblies of pristine ImR_2ZI , a hydrogen bond is formed between C_2-H and the sulfonate anion with strong hydrogen-bond-acceptor ability. Upon the addition of HTf_2N , the probability that the sulfonate anion locates near C_2-H drastically decreases, owing to the presence of the TF_2N anion near the imidazolium cation. It is well known that the hydrogen-bond-acceptor ability of the TF_2N anion is weaker than that of the sulfonate anion. As a result, the hydrogen bond between C_2-H and the anion weakens, and the peak position then shifts to the high-frequency region. These results strongly suggest that the mixture of ImR_2ZI and HTf_2N co-organizes into LC assemblies, forming a preferable ion pair between the imidazolium cation and the TF_2N anion. This conclusion is consistent with

a result that has been inferred from Raman measurements for our previously reported LC materials composed of pyridinium-based amphiphilic zwitterions and HTf_2N .^[6b]

It is expected that the amide group of ImR_2ZI is also involved in their self-organization behavior in the presence or absence of HTf_2N . To evaluate the contribution of the amide group, we discuss the stretching vibration band of $C=O$ and $N-H$. The $C=O$ stretching band of the amide group of ImI_2ZI is observed at 1650 cm^{-1} , whereas that of the ImI_2ZI/HTf_2N mixture is observed at 1681 cm^{-1} (Figure 6d). A similar shift is also found for the ImH_2ZI system (Figure 6e). The high-frequency shifts of the $C=O$ stretching vibration upon the addition of HTf_2N indicate that the intermolecular hydrogen bonding between the amide group of ImR_2ZI weakens upon the formation of the preferential ion pair between the imidazolium cation and the TF_2N anion. The weakening of hydrogen bonding is also confirmed by the peak shift of the $N-H$ stretching band. Although the $N-H$ stretching band is observed for pristine ImI_2ZI at 3292 cm^{-1} , it shifts to 3332 cm^{-1} upon the addition of HTf_2N (Figure 6b). The most plausible explanation is that the penetration of the TF_2N anion between the imidazolium cations of ImI_2ZI expands the distance between the ionic headgroups, consequently increasing the distance between the amide groups (Figure S12). This explanation is consistent with the results that ImR_2ZI/HTf_2N mixtures exhibit nano-segregated LC phases, in which the ionic/nonionic interface is curved toward the alkyl-chain regions and the zwitterionic parts form a continuous layer around a primitive IPMS.

Comparing the IR spectra between the ImI_2ZI system and the ImH_2ZI system, we found some differences that provide significant insights concerning intermolecular interactions in the present LC systems. A notable difference is that $S=O_2$ of ImI_2ZI is observed at 1173 cm^{-1} , whereas that of ImH_2ZI is observed at 1208 cm^{-1} (Figures 6d and 6e). The peak shift toward lower wavenumbers upon the introduction of iodine atoms can be explained by assuming that the substitution of the hydrogen atoms on the imidazolium cation of ImR_2ZI for iodine atoms endows the imidazolium cation with an ability to form a halogen bond with its sulfonate anion as well as a hydrogen bond. It has been reported that halogen atoms on the imidazolium cation form halogen bonds with an electron donor site, owing to their electrophilic properties.^[9a-c] A pioneering study on ionic liquids with halogen-bond ability was reported by Mukai and Nishikawa.^[9a] They designed imidazolium salts with halogen atoms on the imidazolium rings and showed the formation of halogen bonds between the halogen atoms and some anions, including the TF_2N anion, through analysis of the crystal structures of these compounds.^[9b] In parallel with the experimental proof, the formation of halogen bonding between imidazolium cations and TF_2N anions was also indicated by simulation studies.^[14] Considering these studies, it is reasonable to assume that, in the presence of HTf_2N , C_4-I and C_5-I of ImI_2ZI form halogen bonds with the neighboring TF_2N anions that are located close to the imidazolium cation through ion exchange (Scheme 1).

A noteworthy point is that the ImI_2ZI/HTf_2N mixture exhibits the Cub_{bi} phase, whereas the ImH_2ZI/HTf_2N mixture exhibits

the Col phase. Generally, it is known that the increase in size of the headgroup of amphiphiles results in increasing curvature of the interface of assembled molecules. The molecular weight of **ImI₂ZI** is 723.49, which is 251.79 larger than that of **ImH₂ZI**. This difference directly signifies an increase in the size of the ionic headgroup, which is depicted with a 3D molecular model in Figure 1b. According to the general insight, it seems to be reasonable to expect that the **ImI₂ZI**/HTf₂N mixture should form a nano-segregated structure with a curvature that is larger than the Col structure of **ImH₂ZI**/HTf₂N. However, in fact, it exhibits a Cub_{bi} phase. These results suggest that the type of thermotropic mesophase pattern formed by amphiphilic compounds is governed not only by the size of their headgroups, but also by the cooperation of various intermolecular and intramolecular interactions, such as electrostatic, hydrogen-bond, and halogen-bond interactions. Throughout the course of studies on molecular architectures, halogen bonding has been employed for the development of diverse molecular assemblies, such as supramolecular systems,^[15] metal-organic frameworks,^[16] and so on.^[17] Needless to say, during the course of research on functional nano-segregated liquid crystals,^[18] it has been integrated into liquid-crystal chemistry.^[19] One pioneering study was achieved by Bruce and co-workers.^[19e] They reported that the complex of alkoxystilbazole and iodopentafluorobenzene exhibits LC behavior through the formation of supramolecular mesogens. In most studies on halogen-bonded liquid crystals, halogen bonding has been introduced for the expansion of mesogen parts and is usually formed parallel to the molecular axis.^[19b,c,20] In contrast, the present study is unique in that halogen bonding is used to control the intermolecular distance and intermolecular interactions perpendicular to the molecular axis.

One of our aims throughout the course of these studies on Cub_{bi} LC materials is to clarify the potential utility of IPMSs for preparing organic materials with ordered transport pathways. Especially considering the unique characteristics of the amphiphilic zwitterion LC systems that provide a hydrophilic interface sandwiched by hydrophobic ionic-liquid-like layers, it is expected to be a peerless situation for creating an extremely thin, but macroscopically continuous, hydrogen-bond network of water molecules where protons can migrate through a Grotthuss hopping mechanism.^[6a] As well as our previous materials, the ionic conductivities of the present materials have been measured (Figure S13). Recently, there has been increasing attention on the development of proton-conductive materials based on liquid crystals.^[21] In the future, we will follow up on the present work with some sophisticated molecular design, selection of more suitable ion structures, and fixation of the formed Cub_{bi} structures to construct an ideal situation for proton transport through a hopping mechanism along an IPMS.

In summary, we have succeeded in inducing a zwitterionic amphiphile to self-organize into a Cub_{bi} thermotropic LC phase by attaching iodine atoms onto its ionic headgroup. Considering the fact that induction of Cub_{bi} phase behavior is inextricably associated with the formation of an IPMS, it can be concluded that the zwitterionic headgroup aligns on a periodic

minimal surface. IR measurements have revealed that halogen bonding between the iodine-substituted imidazolium cation and anions plays an important role in the self-organization behavior. The use of IPMSs is a promising approach for constructing functional interfaces with 3D continuity; however, further improvement of the methods in order to program molecules to form these surfaces is still required. We expect that the present study will be an important step towards the design and application of nanostructured materials with IPMSs.

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