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3D Continuous Water Nanosheet as a Gyroid Minimal Surface Formed by Bicontinuous Cubic Liquid-Crystalline Zwitterions

Takahiro Ichikawa,[†] Takashi Kato,[‡] and Hiroyuki Ohno*[,†]

[†]Department of Biotechnology, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan

[‡]Department of Chemistry and Biotechnology, The University of Tokyo, Tokyo 113-8656, Japan

Ⓢ *Supporting Information*

ABSTRACT: Co-organization of amphiphilic zwitterions and bis(trifluoromethanesulfonyl)imide led to the formation of bicontinuous cubic liquid-crystalline structures having 3D continuous hydrophilic gyroid minimal surface. The gyroid surface, incorporating a small amount of water, provided extremely thin but macroscopically continuous water nanosheet with a thickness of approximately 5 Å. The water nanosheet functioned as alignment free proton conduction pathway.

Periodic minimal surfaces are a class of continuous surfaces that extend periodically in three independent directions in space, which can be described mathematically.[1] In particular, those formed by self-organization of bicontinuous cubic ($\mathrm{Cub_{bi}}$) liquid crystals[2] are of considerable interest because of their nano-ordered and well-defined periodical structures. $\mathrm{Cub_{bi}}$ phases are one of nanosegregated LC phases consisting of two incompatible domains: three-dimensionally (3D) interconnected channel networks and a 3D continuous sheath domain surrounding the channels. A periodic minimal surface is observed in the middle of the sheath domain as a continuous surface, on which ends of LC molecules sit.[3] It is noteworthy to mention here that the periodic minimal surface has potential to allow it to maintain a macroscopic continuity even without any orientation control of the surfaces due to their 3D periodical architectures. Our intention here is to construct a successive proton conduction pathway by aligning hydrated sulfonic acid groups on a gyroid minimal surface. More specifically, we envisioned that sandwiching the hydrated sulfonic acid layer by water-shedding hydrophobic layers would enable the construction of extremely thin but macroscopically continuous hydrogen-bonded water networks where proton can transport smoothly.

For this, we focused on the use of zwitterions.[4,5] Zwitterions are a kind of organic salts in which a pair of cation and anion is covalently tethered. We have previously found that the mixing of a series of imidazolium-, pyridinium-, or phosphonium-based zwitterions having sulfonate anions with bis(trifluoro methanesulfonyl)imide ($\mathrm{HTf_2N}$) provides a homogeneous liquid matrix while the pristine zwitterions are solids with high melting points over 100 °C.[4b] The decrease in crystallinity is attributed to a character of these zwitterions that their organic soft cations prefer to interact with the $\mathrm{Tf_2N}$ anion forming ion pairs similar to those of conventional hydrophobic ionic liquids with low glass transition temperatures.[4b] These preferential interactions are explained by the hard and soft, acids and bases principle.[6] We expected that the organization of these zwitterion/$\mathrm{HTf_2N}$ mixtures into ordered states at a molecular level, with maintaining the preferential ion pairs, leads to the formation of two adjacent incompatible layers, a hydrophilic sulfonic acid layer and a hydrophobic ionic liquid like layer.

Herein we demonstrate the construction of novel proton conductive materials having $\mathrm{Cub_{bi}}$ LC structures in which water molecules form a hydrogen-bonded water network on a gyroid minimal surface (Figure 1). Gyroid surface is a kind of periodic minimal surface discovered by Schoen in 1970.[8] To date, a number of nanostructured functional LC materials have been developed[9] and applied in a widespread area of research involving organic semiconductors,[10] ion conductors,[11] nanostructured catalysis,[12] and membranes for separation.[13] However, although several attempts have been made to develop new proton conductive materials by designing nanostructured liquid crystals,[4c,14] to the best of our knowledge, there has been no report until now on the use of the gyroid minimal surface in $\mathrm{Cub_{bi}}$ LC structures for proton conduction pathways.

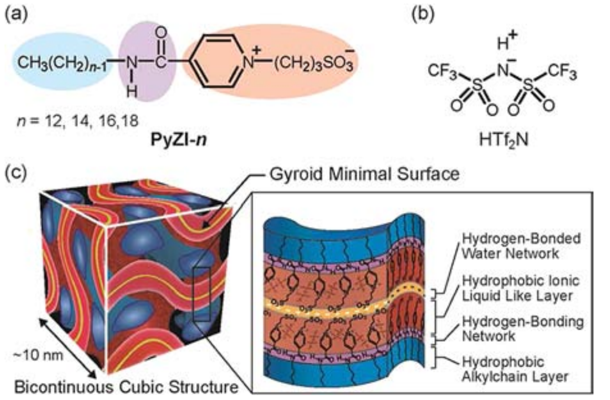

Figure 1. (a) Molecular structure of amphiphilic zwitterions **PyZI-*n***. (b) Ion structure of bis(trifluoromethanesulfonyl)imide ($\mathrm{HTf_2N}$). (c) Schematic illustration of bicontinuous cubic structure formed by the co-organization of **PyZI-*n*** and $\mathrm{HTf_2N}$.

We prepared a series of pyridinium-based zwitterions **PyZI-*n*** (*n*: number of carbon atoms in the alkyl chain) (Figure 1a).

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These amphiphilic zwitterions consist of two incompatible parts: a pyridinium zwitterionic part and a long alkyl chain part. Amide bond has been employed to connect these incompatible parts, because the amide group forms hydrogen bonding networks that are effective to control the order and position of the zwitterionic parts in the assembled states. **PyZI-*n*** are white solids with high isotropization temperatures of over 200 °C. Equimolar mixtures of **PyZI-*n*** and HTf$_2$N (**PyZI-*n***/HTf$_2$N mixture) were prepared by slow evaporation of the tetrahydrofuran/methanol solution of both components. The resultant mixtures form homogeneous complexes with lower isotropization temperatures than those of **PyZI-*n*** alone. The decrease in the isotropization temperatures is explained by the formation of preferential interactions between the soft pyridinium cation with the soft Tf$_2$N anion.[4] Karl Fischer titration revealed that these mixtures contain a small amount of water, approximately 2−3 wt %, due to their hygroscopic nature and strong hydration ability. We will discuss their LC properties and ion conduction behavior with respect to the water content in them.

Mixtures of **PyZI-*n*** and HTf$_2$N exhibit columnar (Col), Cub$_{bi}$, and smectic (Sm) phases. The phase transition behavior of the mixtures is summarized in Figure 2. Although their phase transition temperatures vary by the absorption of moisture with a variation range of about 5 °C, the observed LC phases are consistent with the bar graph shown in Figure 2. It is noteworthy that the induction of the objective Cub$_{bi}$ phases is observed for **PyZI-*n***/HTf$_2$N mixtures with the alkyl chain length *n* from 12 to 16. Especially, **PyZI-14**/HTf$_2$N mixture shows only a Cub$_{bi}$ phase. It is also of interest that the shortening of the alkyl chain length *n* from 14 to 12 leads to the exhibition of not only a Cub$_{bi}$ phase but also a Col phase. In contrast, extension of the alkyl chain length *n* from 14 to 16 induces the formation of Cub$_{bi}$ and Sm phases. Moreover, further elongation of the alkyl chain results in the induction of a Sm phase excluding the Cub$_{bi}$ phases. The characterization of these LC phases is described below and the Supporting Information. Considering the results that the alkyl chain length *n* of zwitterions **PyZI-*n*** greatly influences the phase transition behavior of their mixtures with HTf$_2$N, it is assumed that the segregation between the ionophilic zwitterion/HTf$_2$N part and the ionophobic alkyl chain part in a nanometer scale plays an important role for the formation of these mesophases.

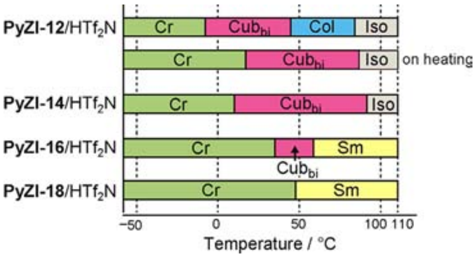

Figure 2. Thermotropic liquid-crystalline properties of **PyZI-*n***/HTf$_2$N mixtures on cooling. Those of **PyZI-12**/HTf$_2$N mixture on heating are also described. Cr, crystalline; Cub$_{bi}$, bicontinuous cubic; Col, columnar; Sm, smectic; Iso, isotropic.

PyZI-12/HTf$_2$N exhibits a Col phase approximately ranging from 80 to 45 °C and a Cub$_{bi}$ phase ranging from 45 to −5 °C on cooling. The phase transition from Col to Cub$_{bi}$ phases was visually observed through a polarizing optical microscope (Figure 3). These LC phases were characterized by X-ray measurements. The small-angle X-ray scattering pattern for **PyZI-12**/HTf$_2$N mixture at 25 °C shows two intensive reflection peaks at 38.0 and 32.7 Å with the reciprocal *d*-spacing ratio of $\sqrt{6}:\sqrt{8}$ (Figure S9), which can be indexed as (211) and (220) reflections of a cubic structure with *Ia*3*d* symmetry. There have been some reports on the induction of thermotropic Cub$_{bi}$ phases in ionic compounds having a single long alkyl chain,[15] while the number of reports is very limited. On the other hand, the wide-angle X-ray diffraction pattern for **PyZI-12**/HTf$_2$N mixture at 60 °C shows one strong and two weak reflections (Figure S10). The reciprocal *d*-spacing ratio of the three peaks is 1:2:3, which can be indexed as (10), (20), and (30) reflections of a columnar structure.

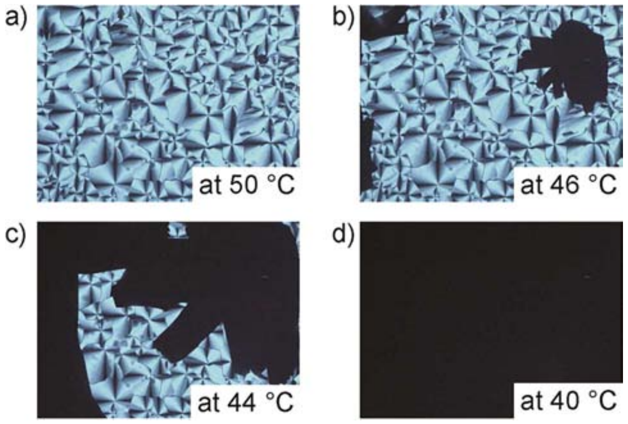

Figure 3. Polarizing optical microscopy images of **PyZI-12**/HTf$_2$N (a) in the Col phase at 50 °C; (b and c) on the phase transition from the Col to Cub$_{bi}$ phases; (d) in the Cub$_{bi}$ phase at 40 °C.

PyZI-14/HTf$_2$N showed no birefringence under crossed Nicols. Moreover, the dark image was maintained even after shearing at every temperature ranging from 30 to 90 °C. Upon shearing, form changes of air bubbles in the LC sample were observed (Figure S21). This observation significantly indicates the formation of an optically isotropic cubic LC phase possessing a high viscosity. On the other hand, **PyZI-16**/HTf$_2$N and **PyZI-18**/HTf$_2$N showed oily streak textures, indicative of the formation of Sm phases (Figures S26 and S30). The Cub$_{bi}$ and Sm phases formed by mixture of **PyZI-14, 16**, or **18** and HTf$_2$N were also characterized in the same procedure. Considering the results that the Col, Cub$_{bi}$, and Sm phases appear in this order as the elongation of the alkyl chain of zwitterions **PyZI-*n***, it is most likely that mixtures **PyZI-*n***/HTf$_2$N (*n* = 12−16) form normal-types of nanosegregated Cub$_{bi}$ and Col phases consisting of ionophobic channels surrounded by ionophilic sheath domains. In the Cub$_{bi}$ phase, the ionophobic alkyl chains form 3D interconnected channel networks separated by a 3D continuous ionophilic sheath domain occupied by the zwitterionic part and HTf$_2$N. A periodic minimal surface is formed in the middle of the ionophilic sheath domain, on which the end of **PyZI-*n***, the sulfonic acid group, sits.

To evaluate these LC mixtures as proton conductive materials, we performed ion conduction measurements by the alternating current impedance method. Figure 4a shows the ionic conductivity of **PyZI-12**/HTf$_2$N and **PyZI-14**/HTf$_2$N containing 2.7 and 2.6 wt % of water, respectively. For comparison, the ionic conductivity of an equimolar mixture of 3-sulphopropyl pyridinium betaine and HTf$_2$N, which forms an isotropic liquid, is also plotted. It is of interest that, although

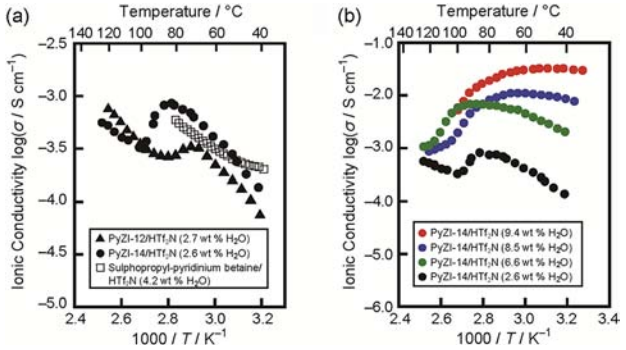

Figure 4. (a) Ionic conductivity of **PyZI-12**/HTf_2N and **PyZI-14**/HTf_2N containing 2.7 and 2.6 wt % of water on heating. For comparison, ionic conductivity of an equimolar mixture of 3-sulphopropyl pyridinium betaine and HTf_2N containing 4.2 wt % of water is also plotted. (b) Ionic conductivity of four samples of **PyZI-14**/HTf_2N mixtures containing 2.6, 6.6, 8.5, and 9.4 wt % water on heating.

the ionic conductivity of 3-sulphopropyl pyridinium betaine/HTf_2N mixture simply increases with the increase of temperature, LC mixtures such as **PyZI-12**/HTf_2N (2.7 wt % water) and **PyZI-14**/HTf_2N (2.6 wt % water) exhibit assembled-structure dependent ion conduction behavior. For example, **PyZI-14**/HTf_2N mixture (2.6 wt % water) shows an ionic conductivity of 1.4×10^{-4} S cm^{-1} at 40 °C and the conductivity increases upon heating until it reaches around 80 °C. The highest ionic conductivity is observed for 8.5×10^{-4} S cm^{-1} at 82 °C. Then, the conductivity abruptly decreases at the temperature, following the phase transition to the isotropic liquid. Similar ion conduction behavior is observed for **PyZI-12**/HTf_2N mixture (2.7 wt % water) that shows only a Cub_{bi} phase on heating. A plausible explanation for the efficient ion conduction behavior in the Cub_{bi} phases is that the 3D continuous ionophilic sheath domain provides a macroscopically continuous ionic liquid like layer without any orientation control of the LC domains where ions can migrate smoothly. Since the cation and anion are covalently bound in zwitterions, they never migrate under external gradient electric fields and therefore never function as career ions. Thus, the career ions in the presented system should be both proton and the Tf_2N anion. The activation energy of **PyZI-14**/HTf_2N mixture (2.6 wt % water) in the Cub_{bi} phase is estimated to be 41 kJ mol^{-1} from the Arrhenius plots of the conductivity. This value is comparable to those of conventional ionic liquids transporting ions by vehicular mechanisms. It is assumed that, in the water-poor condition, **PyZI-12**/HTf_2N and **PyZI-14**/HTf_2N transport ions based on the vehicular diffusion mechanism by using the 3D continuous ionophilic layers as pathways.

The presence of enough water to form a successive hydrogen-bonded networks is necessary for inducing the hopping conduction of protons.[16] For example, Nafion membranes,[16,17] one of the most representative proton conductive organic materials, show proton hopping conduction when they contain more than six or seven water molecules per sulfonic acid group.[16] It should be pointed out that the proton conduction based on the hopping mechanism is much faster than that based on the vehicular mechanism.[18] We expected that the hydrophilic gyroid minimal surfaces formed by **PyZI-*n***/HTf_2N mixtures can be applied to the construction of successive hydrogen-bonded water networks. Along with the idea, some samples of **PyZI-14**/HTf_2N mixture with varying water content ratios were prepared. The water content ratios in the resultant samples were calculated to be 3−10 wt %. These water rich samples also show Cub_{bi} phases while those containing over 10 wt % water exhibit Col phases as a result of the increase of the volume of the ionophilic domain (Figures S22−S24). The change of mesophase pattern with the addition of solvents indicates that these materials show not only thermotropic LC behavior, but also lyotropic LC behavior. LC materials showing both thermotropic and lyotropic LC behavior can be classified into amphotropic liquid crystals.[19]

Figure 4b shows the ionic conductivity of four samples of **PyZI-14**/HTf_2N mixture containing 2.6, 6.6, 8.5, and 9.4 wt % water. It is notable that the addition of water remarkably enhances the ionic conductivity. For example, the ionic conductivity of **PyZI-14**/HTf_2N mixture with 6.6 wt % water is 2.0×10^{-3} S cm^{-1} at 40 °C, which is 15 times higher than that of **PyZI-14**/HTf_2N mixture with 2.6 wt % water. This sample also shows a drastic decrease in ionic conductivity at around the Cub_{bi}-isotropic phase transition. The further addition of water increases the ionic conductivity over the order of 10^{-2} S cm^{-1} at room temperature. For example, **PyZI-14**/HTf_2N mixture with 9.4 wt % water shows an ionic conductivity of 3.1×10^{-2} S cm^{-1} at 35 °C. It is also noteworthy that the addition of water significantly lowers the activation energies. For example, the activation energy of **PyZI-14**/HTf_2N mixture with 8.5 wt % water in the temperature region ranging from 40 to 60 °C is 14 kJ mol^{-1}, which is 3 times lower than that of **PyZI-14**/HTf_2N mixture with 2.6 wt % water in the Cub_{bi} LC state. The drastic enhancement of ionic conductivity and the decrease in activation energy upon the addition of water can be attributed to the change of the conduction mechanism from vehicular to hopping mechanisms. Namely, the higher conductivity should be induced by the hopping conduction of protons via hydrogen-bonded water networks on the gyroid minimal surface. The numbers of water molecules per sulfonic acid group for **PyZI-14**/HTf_2N mixtures with 8.5 and 9.4 wt % water are estimated to be 2.5 and 2.8, respectively. These values are comparable to or smaller than the number of water molecules required for inducing hopping conduction in conventional proton conductive organic materials in the literature.[16] This comparison leads us to assume that two important effects are involved in the formation of macroscopically successive hydrogen-bonded water networks by a limited amount of water. One is the strong hydration force of the sulfonic acid group. The other is that the preferential interaction between the pyridinium cation of **PyZI-*n*** and the Tf_2N anion forming water-shedding hydrophobic ionic liquid like layers on the neighbor to the hydrophilic gyroid minimal surface. It is a well-known fact that conventional pyridinium salts having Tf_2N anion form hydrophobic ionic liquids.[7] The cooperation of these two effects should promote the location of the water molecules exclusively on the 3D periodic gyroid minimal surface. Furthermore, in addition to the character of the gyroid minimal surface that maintains continuity even on the interfaces between the liquid crystal domains, the incorporated water molecules lead to the formation of extremely thin but macroscopically continuous hydrogen-bonded water networks, so-called water nanosheets. Such water nanosheet should function as efficient matrices for proton hopping conduction, for example. The thickness of the water nanosheet can be roughly calculated to be 3−5 Å. These water nanosheets confined in hydrophobic ionic liquid like domains have potential to exhibit different properties from those of bulk water. Finally, it should be pointed out that the ionic conductivity of the water rich samples starts to decrease upon heating before they undergo the phase transition to isotropic liquids. We suppose two reasons account for the decrease in ionic conductivity. One is a gradual evaporation of water and/or $\mathrm{HTf_2N}$. The other is a structural fluctuation of the hydrogen-bonded water networks upon increasing the thermal motion of zwitterions. For overcoming the problem, we are currently exploring a way to fix the $\mathrm{Cub_{bi}}$ LC structures into solid polymer states by in situ polymerization.

In conclusion, we have succeeded in constructing $\mathrm{Cub_{bi}}$ LC materials having a gyroid minimal surface on which water molecules form extremely thin but macroscopically continuous hydrogen-bonded networks. The $\mathrm{Cub_{bi}}$ structures have been induced by co-organization of amphiphilic pyridinium-based zwitterions and $\mathrm{HTf_2N}$ in the presence of a small amount of water. The hydrogen-bonded water networks function as efficient matrices for proton hopping conduction. Although there have been several reports that focus on the application of 3D interconnected channel networks or sheath domains surrounding the channels in $\mathrm{Cub_{bi}}$ structures,[20] no research taking advantages of the gyroid minimal surface in $\mathrm{Cub_{bi}}$ structures has been achieved. The present work may shed light on the potential application of gyroid minimal surfaces in $\mathrm{Cub_{bi}}$ structures for development of 3D continuous functional surface.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and results of characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

ohnoh@cc.tuat.ac.jp

Notes

The authors declare no competing financial interest.

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