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3D Anhydrous Proton-Transporting Nanochannels Formed by Self-Assembly of Liquid Crystals Composed of a Sulfobetaine and a Sulfonic Acid

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Supporting Information

ABSTRACT: Herein we describe anhydrous proton transportation through 3D interconnected pathways formed by self-assembled molecular complexes. A thermotropic bicontinuous cubic ($\mathrm{Cub_{bi}}$) phase has been successfully obtained by mixing a wedge-shaped sulfobetaine with benzenesulfonic acid in different ratios. These ionic complexes exhibit the $\mathrm{Cub_{bi}}$ phase in a wide range of temperatures, while the single zwitterionic compound shows only a columnar hexagonal phase, and benzenesulfonic acid is nonmesomorphic. Anhydrous proton conduction on the order of 10^{-4} S cm^{-1} has been achieved for the mixture in the $\mathrm{Cub_{bi}}$ phase over 100 °C, which can be useful for the development of new electrolytes for the next generation of fuel cells.

Use of molecular self-assembly to create nanostructures for the transportation of ionic species such as lithium ions and protons has attracted attention because of the potential applications in lithium ion batteries and fuel cells, respectively.[1] In particular, ionic liquid-crystalline (LC) materials have been shown to be good candidates for efficient ion conduction because they form well-organized channels for the transportation of ions in their LC phases.[2] If proton conduction in thermotropic LC states is achieved, new efficient anhydrous proton conductors could be developed. Here we report on anhydrous proton-conductive LC materials exhibiting bicontinuous cubic ($\mathrm{Cub_{bi}}$) phases by self-assembly of an ammonium-based zwitterionic molecule having a sulfonate anion **1** and nonvolatile benzenesulfonic acid **2** (Figure 1).

Organic proton conductors[3] have gained remarkable interest as the electrolytes in fuel cells.[4] Perfluorinated sulfonic acid-based polymer membranes such as Nafion exhibit high proton conductivity of 10^{-1} S cm^{-1} in the presence of mobile water molecules in the membranes.[5] The formation of continuous water channels and their macroscopic alignment are important to enhance the proton conductivity. However, the proton conductivity above 100 °C gradually decreases because of the evaporation of water.[6] Therefore, the development of anhydrous proton conductors is necessary for the next generation of fuel cells.[4a,7] However, the preparation of water-free proton transporting materials is still challenging because they usually exhibit lower ionic conductivities than those containing water. Our intention is to construct anhydrous proton nanochannels by using self-assembly of thermotropic LC ionic molecules.[2] In particular, we aim to develop new LC materials that show an *Ia*3*d* type of $\mathrm{Cub_{bi}}$ structure[2c−e,8] forming 3D interconnected ionic channels, which are efficient ion transporters.

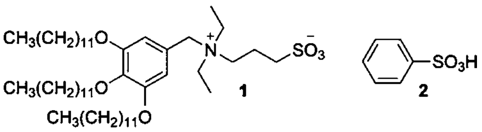

Figure 1. Molecular structures of zwitterionic compound **1** and benzenesulfonic acid **2**.

Here, the key to the material design is to use the interaction arising between a zwitterionic thermotropic liquid crystal and a nonvolatile acid for the construction of thermally stable proton channels. In the present study we have developed anhydrous proton-conductive nanostructured materials based on the complex of **1** and **2** (Figure 2). Wedge-shaped ammonium-type sulfobetaine **1** was designed to potentially exhibit $\mathrm{Cub_{bi}}$ LC structures forming ionic channels in a wide temperature range (Figure 1).[2d,8b] In addition, it is expected that anhydrous proton transportation in the ionic channel of **1** occurs after addition of an appropriate proton source.[9] Compound **2** was chosen as the source in anhydrous conditions in the present system because of its relatively strong acidity ($\mathrm{p}K_a = -2.8$)[10] and high boiling point of 190 °C. We considered that the interaction between **1** and **2** may produce mobile protons after dissociation of the acid and stabilize the self-assembled 3D ion channels based on $\mathrm{Cub_{bi}}$ phases. The advantage of using two-component systems instead of using a single component lies in the feasibility to tune the self-assembled structures and conductivity by changing the species of acids and the mixing ratio. It is generally difficult to design materials that exhibit thermotropic LC $\mathrm{Cub_{bi}}$ phases,[8e,f] but the use of thermotropic ionic $\mathrm{Cub_{bi}}$ LC materials may be a promising approach to the

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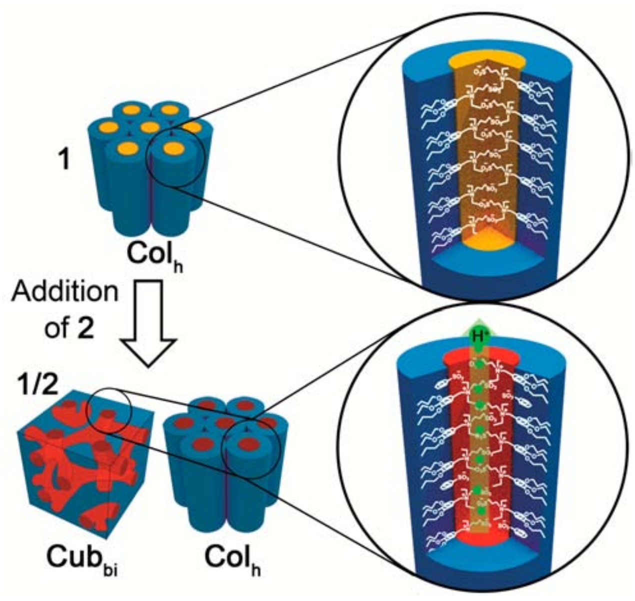

Figure 2. Schematic illustration of the self-assembled structures of **1** in the Col$_h$ phase and the complex of **1** and **2** in the Cub$_{bi}$ and Col$_h$ phases.

development of high-temperature 3D anhydrous proton conductors.

Previously, proton conductivities of aqueous lyotropic liquid crystals were reported.[11,12] These materials were composed of mixtures of phosphonium or pyridinium salts and bis-(trifluoromethylsulfonyl)imide. They exhibited significant decreases of conductivities around 100 °C due to the evaporation of water, resulting in the disappearance of their liquid crystallinity.

The mixtures of **1** and **2** (**1**/**2**) that exhibit thermotropic LC Cub$_{bi}$ phases have been successfully obtained as homogeneous solids after the evaporation of the tetrahydrofuran solution containing the requisite amounts of **1** and **2**. The samples were properly dried under vacuum at 90 °C for a period of 12 h. It is noteworthy that, in contrast to the single component of **2**, mixtures **1**/**2** do not show hygroscopic behavior. The phase diagram of the mixtures up to 50 mol% of **2** is shown in Figure 3.[13,14] We have found that these mixtures containing 20−40 mol% of **2** exhibit Cub$_{bi}$ phases with an *Ia*3*d* symmetry over a wide temperature range as well as LC Col$_h$ phases. It is of interest that the mixtures of **1**/**2** show the Cub$_{bi}$ phases while compound **1** exhibits only a Col$_h$ phase from room temperature to 200 °C (Figures 2 and 3). For example, the mixture of **1** containing 30 mol% of **2** [**1**/**2**(30)] exhibits the crystalline (Cr)−Cub$_{bi}$ phase transition at 50 °C and the Cub$_{bi}$−Col$_h$ phase transition at 115 °C upon heating. The Col$_h$ phase is observed up to the decomposition temperature around 200 °C. On the other hand, the equimolar mixture exhibits only a Cub$_{bi}$ phase, and it becomes the isotropic liquid at 119 °C. As for the mixture **1**/**2**(10), biphasic mixtures of Col$_h$ and Cub$_{bi}$ are seen from room temperature to 78 °C. The Cr−Cub$_{bi}$ and Cub$_{bi}$−Col$_h$ phase transition temperatures tend to increase with the increase of **2**. The widest temperature range of a Cub$_{bi}$ phase is achieved for the mixture **1**/**2**(40), from 67 to 130 °C.

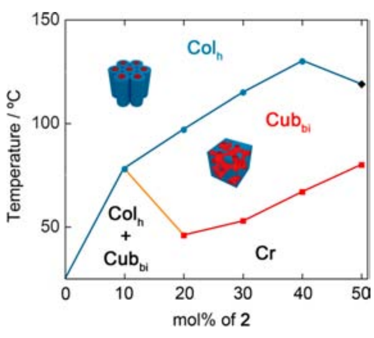

Figure 3. Phase diagram for the mixtures of **1** and **2** as a function of temperature and the mol% of acid **2**.

The results of X-ray diffraction measurements of **1** and **1**/**2** in the LC phases suggest that the zwitterionic moieties are interlocked by the formation of intermolecular ionic pairs in the center of the columns and the alkyl chains are interdigitated (Figure 2, right part, and Supporting Information, Figure S9). The diffraction patterns of **1** and **1**/**2** in the Col$_h$ phases (Supporting Information) at 140 °C reveal intercolumnar distances of 32.9 and 33.1 Å, respectively. The estimated molecular length of **1** in the extended conformation is 28.4 Å.

While **1** alone shows low conductivity[15] on the order of 10^{-7}−10^{-8} S cm^{-1} in the Col$_h$ phase around 130 °C, the addition of anhydrous **2** to **1** leads to a drastic increase in ionic conductivity, as shown in Figure 4. These results suggest that the complexation of **1** and **2** provides mobile protons inside the channels, whereas zwitterionic compound **1** alone has no transportable ions. The conductivities of anhydrous mixtures of **1**/**2** in the Cub$_{bi}$ phases increase with an increase in temperature. The maximum conductivity of 10^{-4} S cm^{-1} in the Cub$_{bi}$ phase is achieved for the mixture **1**/**2**(30) at 130 °C. The mixtures **1**/**2**(40) and **1**/**2**(50) show slightly lower conductivities than **1**/**2**(30). The drops in the conductivity observed for all the mixtures are caused by the phase transitions from Cub$_{bi}$ to the Col$_h$ or the isotropic phase, where partial or total disconnection of the 3D proton conduction pathways occurs.

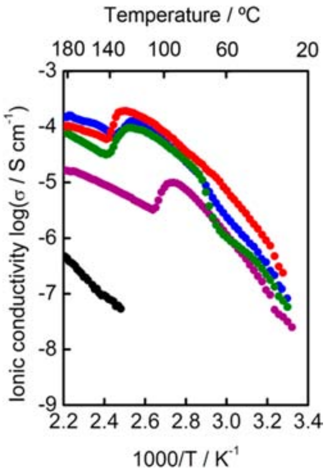

Figure 4. Ionic conductivity as a function of temperature of **1** (black), **1**/**2**(20) (purple), **1**/**2**(30) (red), **1**/**2**(40) (blue), and **1**/**2**(50) (green). Frequency range from 10 Hz to 5 MHz.

It is assumed that the ion conduction in **1**/**2** mixtures is exclusively caused by the proton and benzenesulfonate anion of **2** because the ionic groups of **1** are covalently bonded and therefore they cannot migrate under an electric field. Proton transportation typically proceeds via two generally accepted mechanisms, Grotthuss and vehicle.[16] In the case of anhydrous **1**/**2**, the proton transport might primarily occur by the Grotthuss mechanism, where the dissociated protons are hopping among the adjacent sulfonate groups.[17,18] However, the diffusion of benzenesulfonic acid may also contribute to the transport of protons. The activation energy of the ion transportation in **1**/**2**(30) under anhydrous conditions is estimated to be 59 kJ mol^{-1} in the Cub$_{bi}$ phase between 70 and 100 °C.[19]

In order to examine the interactions between **1** and **2**, ^{1}H NMR measurements were taken for the equimolar mixture in $CDCl_3$ (see Supporting Information). It was found that all the peaks of the zwitterionic backbone as well as the aromatic signal of **1** were shifted after the addition of acid **2**. These results suggest that **2** dissociates to give an ionic complex between the ammonium cation of **1** and the benzenesulfonate anion of **2**, while the proton interacts with the sulfonate of **1**.[9,11,12,20] It is noteworthy that such complexation of **1** and **2** induces both the formation of Cub$_{bi}$ phases and the proton conduction that were not achieved for **1** alone. As a control experiment we prepared mixtures of **1** with phenylphosphonic acid or trifluoromethanesulfonic acid. However, no Cub$_{bi}$ phases were observed for these mixtures; only Col$_h$ phases were seen. The acidity, shape, and volume of the acid molecules seem to play important roles in the induction of the Cub$_{bi}$ phase for the complexes of **1** and acids.

In summary, we have prepared new nanostructured complexes of **1** and **2**, forming the pathway for the 3D proton conduction. The mixtures in neat states free of water exhibit LC Cub$_{bi}$ phases over 100 °C in a wide range of temperatures. It is significant that **1**/**2** can efficiently transport protons over 100 °C in the absence of water. This material design will be important, and it has great potential for the development of high-temperature proton conductors.

■ 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.

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Notes

The authors declare no competing financial interest.

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(13) The phase transition temperatures were determined by differential scanning calorimetry, powder X-ray diffraction measurements, and polarizing optical microscopic observations.

(14) Mixtures over 50 mol% of **2** did not exhibit LC phases.

(15) Temperature dependence of the ionic conductivity was measured by an alternating current impedance method.

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