



Design of 3D continuous proton conduction pathway by controlling co-organization behavior of gemini amphiphilic zwitterions and acids



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ABSTRACT

Gemini-type amphiphiles with benzylimidazolium-based zwitterionic head-groups have been newly designed and synthesized. They co-organize into liquid-crystalline ordered states with various acids owing to the nature of the zwitterionic parts to cause ion exchanges with these acids. Their co-organization behaviors can be tuned by various factors including the linker selection between the head-groups, the length of the long alkyl chains, the acid species, and the molar ratio between the zwitterions and acids. By tuning these factors, we have succeeded in preparing amphiphilic zwitterion/acid mixtures that form bicontinuous cubic liquid-crystalline assemblies with a 3D continuous hydrophilic surface. These cubic liquid crystals function as ion transporting matrices whose ionic conductivities are enhanced owing to the presence of a 3D continuous proton conduction pathway along the hydrophilic surface. The present material design would possess a great potential to bring an innovation to the design of proton conductive polymer electrolytes.

1. Introduction

Proton conductive polymer electrolytes are a key building block for energy conversion devices, such as fuel cells. In the several decades, a variety of material designs have been employed for developing advanced proton conductive polymer electrolytes [1–3]. Liquid crystals [4–8], plastic crystals [9,10], gels [11], block copolymers [12], MOFs [13], nanoparticles [14], and nanocomposites [15–19] have been employed for creating new proton conductive electrolytes. Especially, it has been gradually understood that the interface design is one of important designs for creating superior proton conductive materials [3,14–17,19]. For example, it was reported that the continuous alignment of acid groups in polymer matrices is a significant approach for inducing efficient proton conduction pathways [3]. For extracting the potential of this concept, the use of liquid crystals is a promising approach because self-organization of liquid-crystalline (LC) molecules produces ordered nanostructures in which the component molecules are well-aligned in a molecular scale [4,20].

Recently, we have focused on the alignment of sulfonic acid groups on a gyroid minimal surface, a class of infinite periodic minimal surfaces with 3D periodicity and continuity, to create a macroscopically continuous proton conduction pathway [21,22]. This concept has been serendipitously achieved by designing amphiphilic LC molecules having

a pyridinium-based zwitterionic moiety [21]. These amphiphilic zwitterions exhibit bicontinuous cubic (Cub_{bi}) phases in the presence of bis (trifluoromethanesulfonyl)imide (HTf_2N) forming a gyroid minimal surface where their sulfonic acid groups align in an ordered manner. By performing ion conduction measurements for the Cub_{bi} LC materials, the potential utility of the gyroid minimal surface for an ion conduction pathway has been revealed for the first time [21]. One of the reasons that there had been no report on the use of a gyroid minimal surface in such a way before is the design difficulty of Cub_{bi} liquid crystals [23,24]. It is well known that the exhibition of Cub_{bi} phases is found for only a limited number of thermotropic liquid crystals [23,25,26] and it is also observed in a limited concentration range in the case of lyotropic liquid crystals [27–29]. With these backgrounds on Cub_{bi} liquid crystals, we expect that the development of molecular design technology to intentionally produce LC molecules forming Cub_{bi} phases is important for further improvement of our material design.

In the course of studies on amphiphilic molecules, some specific molecular designs are effective for the induction of Cub_{bi} phases [30]. For example, the design of gemini-type amphiphiles is more suitable for creating Cub_{bi} liquid crystals than that of monomeric-type amphiphiles [31–36]. On the other hand, we have found that the employment of zwitterions as the head-group of amphiphiles and the control of their self-organization behavior by the addition of brønsted acids are an

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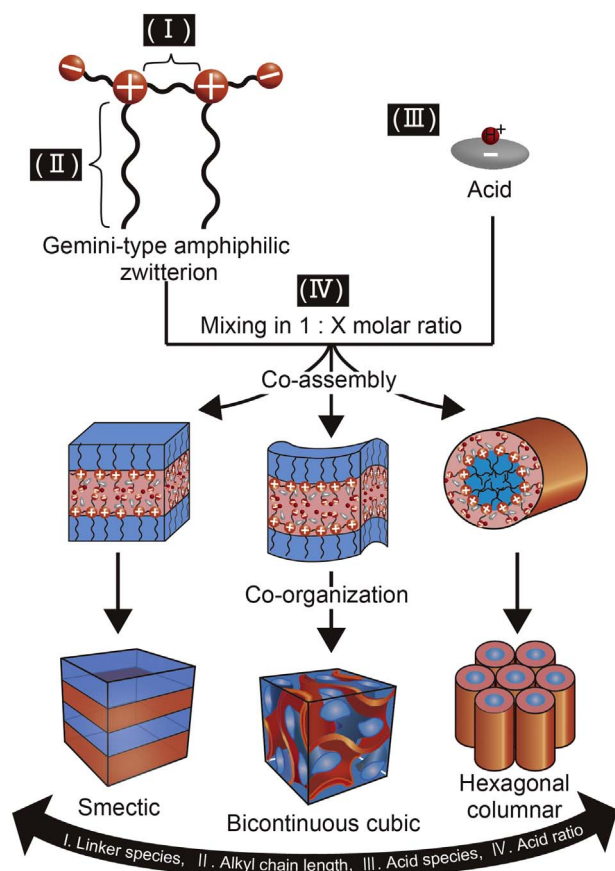


Fig. 1. Schematic illustration of the present material design for constructing ionic liquid crystalline matrices having bicontinuous cubic structures. The materials are prepared using the co-assembly and co-organization behaviors of gemini-type amphiphilic zwitterions and various acids. The nanostructure patterns are controlled by various factors, such as linker species (I), alkyl chain length (II), acid selection (III), and acid ratio to zwitterions (IV).

advantageous strategy for inducing Cub_{bi} phases [21,22,37]. We expect that the fusion of the two concepts, *gemini design* and *zwitterion design*, will pave a new way to produce Cub_{bi} LC materials in a desired manner. The concept in the present study is shown in Fig. 1. Here we report the potential advantage of gemini-type amphiphilic zwitterions for designing Cub_{bi} liquid crystals forming a 3D continuous proton conduction pathway.

2. Results & discussion

A new class of gemini amphiphilic zwitterions ($G-ZI_{n-L-n}$) has been designed and synthesized (Fig. 2a, Scheme S1). They consist of two benzylimidazolium amphiphilic parts that are connected by a linker of two different types: one is a hexyl group (L1) and the other is a diethylether group (L2). ‘n’ indicates the number of carbon atoms in the long alkyl chains. As partner acids to these $G-ZI_{n-L-n}$, a class of imide-type acids, A- CF_3 and A-Tfb, have been selected (Fig. 2b) [38]. By mixing $G-ZI_{n-L-n}$ and these acids, we have aimed to investigate the importance of various parameters, such as linker selection (I), ionophobic alkyl chain length (II), acid species (III), and the molar ratio of the acid to $G-ZI_{n-L-n}$ (IV), for designing LC materials forming Cub_{bi} phases. Furthermore, corresponding monomeric-type amphiphiles with a benzylimidazolium-based zwitterionic head group ($M-ZI_n$) have been also synthesized (Scheme S2) and their organization behaviors are compared with those of $G-ZI_{n-L-n}$ in order to reveal the effects of gemini-structure design.

$G-ZI_{n-L-n}$ was obtained as crystalline compounds showing high

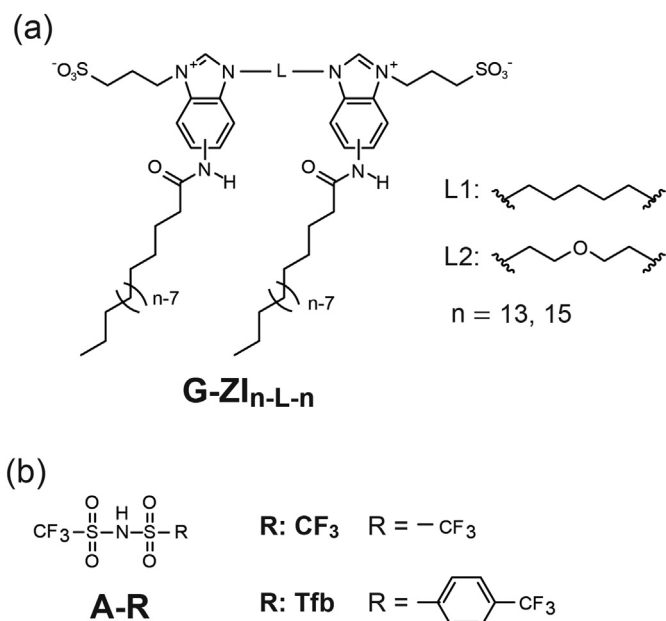


Fig. 2. Molecular structures of (a) gemini-type amphiphilic zwitterions $G-ZI_{n-L-n}$ and (b) acids A-R (A- CF_3 and A-Tfb).

melting temperature (T_m) over 200 °C. No mesomorphic behaviors are observed for themselves. The high T_m of $G-ZI_{n-L-n}$ results from the co-operation of various intermolecular interactions between the $G-ZI_{n-L-n}$ molecules, such as electrostatic interaction, hydrogen-bonding interaction, and van der Waals interaction.

Homogeneous mixtures of $G-ZI_{n-L-n}$ and various acids in 1:2 molar ratio were successfully prepared by dissolving $G-ZI_{n-L-n}$ into methanol solutions of acids and the subsequent removal of the methanol by evaporation. Complete removal of the methanol was confirmed by 1H NMR measurement (Figs. S19–S21). These mixtures exhibit thermotropic LC behaviors. Here it should be noted that the observed LC behaviors greatly vary depending on the selection of the acid species. Below we discuss the obtained results when using A- CF_3 and A-Tfb as acids.

Thermal phase behaviors of $G-ZI_{n-L-n}/A-CF_3$ mixtures (1:2 molar ratio) and $G-ZI_{n-L-n}/A-Tfb$ mixtures (1:2 molar ratio) are summarized in Fig. 3. It is notable that the exhibition of the thermotropic LC properties is observed for $G-ZI_{n-L-n}$ upon the addition of these acids. It is assumed that the added acids lead to the change of the intermolecular interactions between the $G-ZI_{n-L-n}$ molecules, which plays a significant role in endowing them with the thermotropic LC properties. To clarify this assumption, IR measurements were performed for pristine $G-ZI_{n-L-n}$ and the mixtures of $G-ZI_{n-L-n}$ and A- CF_3 or A-Tfb. Comparing the IR spectra of $G-ZI_{n-L-n}$ and those of $G-ZI_{n-L-n}/acid$ mixtures, high-frequency shifts of some peaks are found (Fig. 4a). For example, the stretching vibration of the C–H bond at the C_2 position of the imidazolium ring of $G-ZI_{13-L1-13}$ shifts from 3129 cm^{-1} to 3149 cm^{-1} upon the addition of A- CF_3 . The high-frequency shifts indicate that the weakening of hydrogen-bonding between the proton at the C_2 position and electron-rich groups around the imidazolium cation. We attribute it to the replacement of the counter anion from the sulfonate anion of $G-ZI_{13-L1-13}$ to the A- CF_3 anion through ion exchange based on the Hard and Soft Acid and Base principle [39] (Fig. 4b). Another notable change is the IR peak shift of N–H stretching band observed at around 3300 cm^{-1} . The N–H band of $G-ZI_{13-L1-13}/acid$ mixtures is observed in a higher wavenumber region compared to that of pristine $G-ZI_{13-L1-13}$. This higher wavenumber shift indicates the weakening of the hydrogen-bonding between the amide groups, which can be explained by the expansion of the intermolecular distances upon the intercalation of the A- CF_3 or A-Tfb anions between the benzylimidazolium cations.

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