Studies on Supramolecular Assembly Structures and Physical Properties of Benzene Tricarboxylic Acid Derivatives Bearing Different Alkylamide Chains

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§ 1 General Introduction. Supramolecular liquid crystalline and gelation materials have been fabricated via non-covalent intermolecular interactions, which have attracted much attention for constructing dynamic molecular system in terms of simple preparation procedure, external-stimuli responsibility, and multi-functionality. Both the assembly structures and physical properties are expected from the building blocks bearing the non-covalent intermolecular interactions such as electrostatic, hydrogen-bonding, charge-transfer, and van der Waals interactions. Therefore, it is important to utilize the simple building blocks with specific non-covalent interactions to design various functional materials and also to understand the stepwise molecular assembly processes. Liquid crystal (LC) is an intermediate state between the crystal and liquid phases, showing the typical long-range orders and fluidic responses. Supramolecular LC materials have been developed by the introduction of specific functional structural units via the non-covalent intermolecular interactions. Similarly, supramolecular gels also can be designed from the functional structural units via the non-covalent intermolecular interactions. The present thesis mainly focused on simple benzoic acid derivatives bearing different length and number of –CONHC\(_n\)H\(_{2n+1}\) chains (Scheme 1), wherein the non-covalent interactions can be adjusted through the designs of hydrophobic, hydrogen-bonding, and electrostatic interactions. In particular, both the liquid crystalline and gelation behaviors have been investigated in supramolecular assemblies utilizing the non-covalent interactions, resulting in hierarchical supramolecular assembly structures with different kinds of physical responses.

§ 2 Molecular Assemblies of Isophthalic Acid Derivatives Bearing a –CONHC\(_n\)H\(_{2n+1}\) Chain. Simple isophthalic acid derivatives (CnIP) bearing one alkylamide chains (–CONHC\(_n\)H\(_{2n+1}\): n = 6, 10, 14, and 18) with different alkyl chain length at the 5-position were prepared and corresponding hydrogen-bonding molecular
assembly structures were examined. The hydrogen-bonding sites of two carboxylic acid groups enabled the linear and ring-type molecular assembly structures (Scheme 2), wherein both the organogel and liquid crystal formations were evaluated in the modification of magnitude of hydrophobic interaction. The organogelation ability of CnIP derivatives increased with the elongation of alkyl chain length. For instance, the shortest chain compound of C6IP did not form the gelation state. In contrast, C10IP, C14IP, and C18IP ones had the organogelation behavior.

Ring-shaped O–H⋯O hydrogen-bonding hexamers were obtained in the organogel state of (C14IP)$_6$(H$_2$O)$_n$ and (C18IP)$_6$(H$_2$O)$_n$, which were further assembled to a tubular molecular assembly via interhexamer N–H⋯O= hydrogen-bonding interactions. The formation of organogel state in C$_2$H$_5$OH–H$_2$O was consistent with the fibrous one-dimensional (1D) molecular assembly with a tubular structure. The ability to form thermotropic liquid crystalline phase was also enhanced with the elongation of alkyl chain. Although the C6IP and C10IP did not show thermotropic liquid crystalline phase, the C14IP and C18IP can form the lamellar and hexagonal columnar (Col$_h$) liquid crystal phases, respectively. Especially, the lamellar phase of unhydrated C18IP transformed to Col$_h$ phase by the introduction of guest H$_2$O molecules during the xerogel formation. The different gelation and liquid crystalline behaviors indicated that the balance between intermolecular hydrogen-bonding and hydrophobic interactions played a key role for the formation of different types of liquid crystalline phases. Much longer alkyl chains enhanced the hydrophobic interaction and stabilized the gelation state due to the formation of three-dimensional fibrous network, which stabilized the liquid crystal phase and resulted in the transformation from Col$_h$ to lamellar phase. In addition, the 1D hydrophilic pore of hexameric (CnIP)$_n$ units filled by H$_2$O molecules formed the suitable environment to include various ion pairs such as LiCl, NaCl, KCl, and H$_2$SO$_4$, where the ion conductivity can be modulated.

§3 Phase modulation on liquid crystals by constructing H-bonding network of 3,5-bis(tetradecylamino)carbonyl benzoic acid. The replacement of one –COOH group of C14IP by one additional –CONHC$_{14}$H$_{29}$ group yielded a different benzoic acid derivative of 3,5-bis(tetradecylamino)carbonyl
benzoic acid (C14BA), which has two alkyl chains and one –COOH group. Although one chain compound of C14IP formed the Colₐ phase above 270 °C, the enhancement of hydrophobic interaction in C14BA showed the lamellar-type liquid crystalline phase at relatively low and wide temperature range from 115 to 164 °C. In addition, the liquid crystalline phase was modulated by the introduction of additional hydrogen-bonding interactions using the proton-accepting guest molecules such as 4,4'-bipyridine (Bipy) and imidazole (Im). The lamellar type liquid crystalline phase was obtained from the hydrogen-bonding dimeric (C14BA)₂, where the hydrophilic hydrogen-bonding sites and hydrophobic alkyl chains were alternatively assembled to each other along the layer direction. The introduction of hydrogen-bonding acceptors of Bipy or Im affected the hydrogen-bonding dimeric structure of (C14BA)₂, resulting in new lamellar phases with different layer spacing. Furthermore, the additions of proton-conducting Im molecules resulted in a new liquid crystalline phase of rectangular columnar phase (Colᵣ), which demonstrated the structural modulation of intermolecular hydrogen-bonding and proton transferred assemblies through the formation of –NH⁺•••O= type electrostatic interactions in the liquid crystalline phase. Stepwise change in the molar content of Im in hydrogen-bonding binary complexes of (C14BA)₂(Im)ₙ (n = 1, 2, and 4) effectively changed the magnitude of proton conductivity. The protonic conductivity of binary complex (C14BA)₂(Im)₄ reached 4.1 × 10⁻⁶ S cm⁻¹ at 348 K, which was two orders of magnitude higher than those of (C14BA)₂(Im), (C14BA)₂(Im)₂, C14BA, and Im, due to the formation of the proton-transferred state and the proton conducting hydrogen-bonding pathway in the liquid crystalline state (Scheme 3). The combination of the hydrogen-bonding donor of C14BA with different hydrogen-bonding acceptors is one of the effective approaches to modulate the molecular assembly structures in liquid crystalline materials, and the physical property of protonic conductivity was also designed by control in the hydrogen-bonding network in supramolecular liquid crystalline phase.

§4 Multi-stimuli responsive supramolecular organogel based on alkylamide-substituted isophthalic acid derivative bearing a –CONHC₁₈H₃₇ chain. Among CnIP derivatives, the longest alkyl chain derivative of C18IP can form stable organogel state, which was further examined from the viewpoint of specific gelation ability. The
supramolecular organogel of C18IP was responsive to the outer stimuli such as temperature, ultrasonic, and change in pH. The C18IP in C₂H₅OH-H₂O (v/v = 4:1) showed the sol-gel transition by simply thermal cycle, which could be activated by the association-dissociation of the non-covalent interactions. Interestingly, C18IP in C₂H₅OH-H₂O also showed the quick sol-gel transformation under the ultrasonic condition within one minute due to the cavitation effect. The application of ultrasonic suppressed the formation of thermodynamically stable crystalline state and resulted in organogel one. The C18IP organogel also responded to the change in pH through the association-dissociation of hydrogen-bonding interaction. Low pH condition stabilized the organogel state due to stabilization of the hydrogen-bonding interactions. On the contrary, the organogelator of C18IP can transform to a hydrogelator (Na⁺)₂·C18IP²⁻ by the addition of aqueous NaOH. The intermolecular hydrogen-bonding interactions between the –COOH groups of C18IP were transformed to the electrostatic ones of –COO⁻Na⁺ units, resulting in the transformation between organogel and hydrogel. The thermal stability of electrostatic xerogel state of (Na⁺)₂·C18IP²⁻ was much higher than that of hydrogen-bonding C18IP xerogel due to the formation of effective electrostatically assembled lamellar-type structure, which also formed the Col₅ phase from the xerogel state at the temperature range from 100 to 300 °C. The simple isophthalic acid derivative C18IP was applied to develop the multi-stimuli responsive organogel. In addition, the transformation from the organogel to the hydrogel was succeeded by replacing the interaction sites from hydrogen-bonding to electrostatic one, which increased the hydrophilic property and also hydrogelation ability. The facile transformation will further enlarge the application of such soft materials.

§5 General Conclusion. In summary, supramolecular liquid crystalline and gelation behaviors based on simple hydrogen-bonding isophthalic acid derivatives were investigated in structural parameters of length and number of –CONHCₙH₂n₊¹ chains. In the systematic study of CnIP derivative with one –CONHCₙH₂n₊¹ chain, both the liquid crystalline and gelation abilities were enhanced with increasing in the alkyl chain length due to the enhancement of hydrophobic interaction. The intermolecular hydrogen-bonding interactions at two –COOH groups of CnIP formed the two kinds of hydrogen-bonding molecular assembly structures, which were the one-dimensional zig-zag chain and the ring-shaped (CnIP)₆ hexamer according to the parameter n. The ring-shaped O-H···O hydrogen-bonding hexamers were further assembled to the tubular molecular assembly via inter-hexamer N-H···O= hydrogen-bonding interaction, and the hydrophilic tubular cavity could be filled by the different ion pairs to show the ion conductivities. C14BA bearing two –CONHCₙH₂n₊¹ chains effectively modified the balance between hydrophilic and hydrophobic interactions, resulting in the lamellar phase formed by the dimeric (C14BA)₂. The liquid crystalline phase of hydrogen-bonding dimeric (C14BA)₂ was modulated by the introduction of N-heterocycle proton-accepting guest molecules such as Bipy and Im. The magnitude of proton
conductivities was enhanced by the complexation with Im. Thermally stable organogel of C18IP was examined from the viewpoint of the responses for the external stimuli, where an interesting transformation from organogel to hydrogel was observed by the modification of intermolecular interactions. The soft materials such as liquid crystal and gel have a potential for the applications of ion sensors, unhydrated proton conductors, and external stimuli responsive gel sensors. The present work may open a new possibility for a controllable fabrication of functional liquid crystals and gels.