

論文の内容の要旨

論文題目 Development of Spiropyran-Based Liquid-Crystalline Materials
 (スピロピラン部位を有する液晶性材料の構築)

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Molecular self-assembly is a promising approach for developing new functional soft materials. Liquid crystals are soft materials that form fluidic and ordered states of molecules. For development of new dynamically functional liquid-crystalline (LC) materials, unconventional design of the molecules and self-assembled structures from nano to macro scale is important. These new LC assemblies can be built by using a combination of specific intermolecular interactions, nanosegregation behavior, and the molecular shape of liquid crystals. On the other hand, LC assemblies that can change their LC nanostructures and molecular orientations in response to stimuli such as photoirradiation have attracted attention because these stimuli-responsive liquid crystals have great potential as ordered materials exhibiting anisotropic and dynamic function. In this thesis, the use of spiropyran compounds for development of new LC materials is described. Spiroyrans are unique compounds that show photo-, thermo-, chemo-, and solvatochromic properties. Spiroyrans have been widely used for various applications such as molecular switches, optical devices, metal sensor, and probes due to their reversible spiro-merocyanine (SP-MC) isomerization. The molecular isomerization of spiropyran from non-planar and non-ionic spiro form to planar and ionic merocyanine form is expected to promote aggregation and formation of the ordered nanostructures. However, spiropyran-based liquid crystals are very limited. In fact, to the best of our knowledge, there is no any report on the columnar LC assemblies of spiropyran compounds. Furthermore, the potential applications of spiropyran-based LC materials have not been explored until now.

In this thesis, the author is interested in using acid- and photoinduced SP-MC isomerization of spiropyran for the induction of new LC assemblies. For this purpose, four different approaches have been explored, there are: a) addition of an acid, b) photoirradiation, c) a combination of addition of acid and photoirradiation, and d) a combination of photoirradiation and addition of ionic liquids. The author also expected that if columnar LC assembly can be induced in the ionic merocyanine form of spiropyran derivatives, the resulting LC materials may show interesting ion conduction properties.

In chapter 1, an overview of liquid crystals and a basic introduction of spiropyran compounds are presented. In addition, the objectives and the outline of this thesis are stated.

In chapter 2, the development of the first example of spiropyran-based columnar liquid crystals is described. Since spiroyrans are acid-responsive, the author aimed at manipulating acid-induced SP-MC isomerization for: i) the formation of columnar phases through self-assembly of merocyanine isomers of a spiropyran fan-shaped compound and ii) the use of the columnar nanostructures formed by the merocyanine isomers as the conduction path for an ion transportation. A spiropyran-based compound having a fan-shaped trialkoxy benzene group has been designed and prepared. The induction of columnar LC phases for spiropyran derivatives is achieved by the addition of 4-methylbenzenesulfonic acid. The induction and stabilization of these columnar assemblies are ascribed to the acid-induced SP-MC isomerization and the presence of protonated merocyanine isomers. Several key factors for the induction of columnar LC assemblies such as acidities, the sizes of anions of the added acids, molar fraction of the added acids, and miscibilities of the added acids with the spiropyran derivatives have been examined. In addition, the anisotropic ionic conductivities of the LC mixtures of a fan-shaped spiropyran derivative with 4-methylbenzenesulfonic acid have been measured. One-dimensional ionic conductivities of these LC mixtures are measured by an alternating current impedance method with comb-shaped gold electrodes as reported previously. The self-assembled columnar polydomains are aligned in the direction perpendicular and parallel to the gold electrode via mechanical shearing. The ionic conductivities parallel to the columnar axis (σ_{\parallel}) for the LC mixtures are higher than those perpendicular to the axis (σ_{\perp}) in the ordered LC state. The highest σ_{\parallel} value in the columnar state is $8.5 \times 10^{-6} \text{ S cm}^{-1}$. Anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) of ionic conductivities in the columnar state is *ca.* 10. The measured anisotropic ionic conductivities are due to ion conduction and possibly including proton hopping in phenolic moieties of the merocyanine stacks in the columnar nanostructures.

In chapter 3, the development of spiropyran-based ionic liquid crystals is stated. Imidazolium-based ionic liquids having a sulfonic acid group have been used to induce LC assemblies of a fan-shaped spiropyran derivative. The binary mixtures of this spiropyran derivative with the acidic ionic liquids exhibit columnar phases with wider temperature ranges. The ionic interactions formed by the imidazolium ionic moiety should contribute to the stabilization of the columnar phases. On the contrary, the addition of an ionic liquid without a sulfonic group to the same spiropyran derivative does not lead to formation of columnar nanostructure although a miscible mixture is obtained.

In chapter 4, the induction of LC phases of nitrospiropyran derivatives is studied by four different approaches: a) addition of an acid, b) UV irradiation, c) combined effects of the addition of an acid and UV irradiation, and d) combined effects of UV irradiation and the addition of an imidazolium-based ionic liquid. The addition of an acid successfully induced LC phases for several nitrospiropyran derivatives. The induction of the mesomorphism is due to: a)

ionic interactions of these nitrospiropyran derivatives in the protonated merocyanine form, b) nanosegregation of the ionic and non-ionic moieties, and c) the filling of space by anion of the added acid. Moreover, the formation of hydrogen bonds between the phenolic OH group and the anion of the acid might also contribute to the stabilization of LC nanostructure. On the other hand, an induction of LC assemblies by UV irradiation for nitrospiropyran derivatives was expected because of the formation of ionic MC isomers. The MC isomers can form ordered nanostructures through ionic interactions. However, the results indicate that UV irradiation alone fails to induce mesomorphism. It is assumed that the formation of ionic interactions for the single component of MC isomers is not suitable for the induction of LC nanostructure. The combined effects involving UV irradiation and the addition of an acid or imidazolium-based ionic liquid also fail to induce mesomorphism for nitrospiropyran derivatives.

In chapter 5, a conclusion and perspectives of this thesis are summarized.

In this thesis, acid-induced LC assemblies of spiropyran compounds have been developed. The results clearly indicate that the complementary effects of ionic interaction, nanosegregation, hydrogen bonding, and space-filling effect of the anion of the added acid are important for the induction and stabilization of LC assemblies. The new LC materials exhibit anisotropic ionic conductivities. They are potentially to be used as one-dimensional ion conductors. In future, these materials could be further developed as media for gas sensing and gas entrapment.