

博士論文

**Construction of Supramolecular
Liquid-Crystalline Complexes
through Multi-Component Self-Assembly**
(多成分自己集合による液晶性超分子錯体
の構築)

内田 淳也

Chapter 1. Introduction

Molecular self-assembly can produce a variety of supramolecular architectures from molecular to macroscopic scale. Self-assembly of biomolecules spontaneously forms dynamic and ordered hierarchical structures with high biological functions. In view of materials science, the bottom-up synthesis of molecular aggregates with low energy consumption is a useful approach to develop functional molecular assemblies.

Liquid crystals are self-assembled materials forming dynamic and ordered structures in the condensed states. Self-assembly of liquid crystals has been applied for the development of functional materials because of the dynamic order and responsiveness to external stimuli. The author focuses on the design of supramolecular liquid crystals. Pioneering works on supramolecular liquid crystals are hydrogen-bonded liquid crystals. Discrete supramolecular mesogens are formed through hydrogen bonds to stabilize liquid-crystalline (LC) phases. The noncovalent approach has been extended to the introduction of supramolecular objects into LC states, leading to the combination of functions of supramolecular complexes and dynamic order of liquid crystals. The target materials in this thesis are supramolecular complexes formed through multi-component self-assembly. Rationally designed small components can be assembled to produce well-defined structures as well as polymeric structures. It is notable that some of these complexes are difficult to prepare by conventional synthetic procedures. However, application of these supramolecular structures for LC materials is still limited.

In the present thesis, construction of supramolecular LC complexes through multi-component self-assembly is described. In chapter 2, structure-property relationships in LC forklike mesogens have been studied to obtain insights of detailed assembled structures of forklike molecules. In chapters 3 and 4, design and synthesis of LC giant spherical complexes and their application for nanostructured self-healing gels have been demonstrated through self-assembly of forklike mesogenic ligands and palladium salts. Metallo-supramolecular LC polymers for stimuli-responsive materials and supramolecular LC networks showing shape memory effects have also been constructed in chapter 5 and chapter 6, respectively.

Chapter 2. Structure-Property Relationships in Liquid-Crystalline Forklike Mesogens

This chapter describes self-assembled behavior of forklike mesogens. Cyclohexylphenyl group is a typical rodlike moiety to induce LC properties. A series of mesogen-containing compounds is designed by attaching the rodlike moieties to one phenyl ring through flexible oxyethylene spacers. The number and position of mesogenic substituents are systematically changed to study structure-property relationships. Thermal and mesomorphic properties of these molecules are reported in this chapter. Forklike mesogens with two or three mesogenic side chains show LC phases over wide temperature ranges. The LC properties of forklike mesogens are dependent on the number and position of mesogenic moieties. Infrared spectroscopy provides information on the relationships between molecular structures, conformation, and assembled structures of forklike mesogens. The details of this work are reported in paper [1].

Chapter 3. Self-Assembly of Giant Spherical Liquid-Crystalline Complexes

This chapter describes design of giant spherical LC complexes through multi-component self-assembly. Introduction of liquid crystallinity into nonmesomorphic spherical molecules has attracted attention because it allows for the combination of the functions of the spherical molecules with anisotropic order of liquid crystals. In this context, a new family of giant spherical LC molecules is developed by coordination-driven self-assembly. Mesogenic ligands are prepared by attaching forklike mesogens to bis(pyridyl) ligands. Self-assembly of 24 forklike mesogenic ligands and 12 palladium salts leads to the formation of spherical complexes decorated with 72 rodlike mesogens on the surface of the spheres. The giant structures of the self-assembled complexes are characterized by nuclear magnetic resonance spectroscopy and mass spectrometry. Lyotropic LC properties are observed for these complexes in concentrated organic solution. The LC assembled structures of the

spherical complexes are dependent on the length of rodlike moieties. The details of this work are reported in paper [2].

Chapter 4. Dynamic Nanostructured Gels Exhibiting Self-Healing Properties

In this chapter, formation of dynamic network structures based on spherical complexes is described. Structurally dynamic and adaptive materials with mechanical toughness and stimuli responsiveness have been developed through reversible covalent bonds such as Diels-Alder adducts, disulfide bonds, and acylhydrazone exchange. Use of supramolecular crosslinkers formed by multi-component self-assembly may be a promising approach to develop highly crosslinked dynamic networks. A spherical complex with 24 aldehyde groups at the periphery has been synthesized by self-assembly of 24 aldehyde-functionalized ligands and 12 palladium salts. Hybridization of this complex with poly(ethylene glycol) bearing acylhydrazide groups at both ends in organic solvent results in the formation of polymer gels. The obtained polymer gels are free-standing and self-healable probably due to the formation of acylhydrazone bonds, which is supported by infrared spectroscopy. The LC order of the mesogen-containing spherical complexes developed in chapter 3 has been introduced into the dynamic network to give a self-healing supramolecular nanostructured material. The details of this work are reported in paper [2].

Chapter 5. Metallo-supramolecular Liquid-Crystalline Polymers for Stimuli-Responsive Materials

This chapter describes the formation of metallo-supramolecular LC polymers for stimuli-responsive materials. Side-chain metallo-supramolecular LC polymers are constructed through self-assembly of the forklike mesogenic ligands and silver salts. Atomic force microscopy shows fibrous aggregates with a diameter of around 3 nm, suggesting the formation of polymeric structures by self-assembly. The metallo-supramolecular polymers exhibit smectic LC phases, which are characterized by

polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction measurements. Dissolution of the metallosupramolecular LC polymers in a host liquid crystal leads to the preparation of homogeneous LC mixtures. Responsive behavior of the LC mixtures under electric fields is investigated. The details of this work are reported in paper [3].

Chapter 6. Shape Memory Supramolecular Liquid-Crystalline Networks

This chapter presents the construction of supramolecular LC networks exhibiting shape memory effects. Supramolecular LC networks formed by multi-component self-assembly of small molecular building blocks show mechanical properties of polymer networks as well as phase transition of liquid crystals. Given this background, the forklike LC ligands are complexed with tricarboxylic acid for the preparation of hydrogen-bonded LC networks. Free-standing and moldable supramolecular LC materials are obtained by self-assembly of small molecular components probably because of the formation of rigid hydrogen-bonded framework having mesogenic moieties through flexible spacers. Moreover, the mechanical properties can be tuned by addition of silver salts into the hydrogen-bonded LC networks, which results in the development of supramolecular LC networks showing shape memory effects. The details of this work are reported in paper [4].

Chapter 7. Conclusion and Perspective

The present thesis describes the design and synthesis of supramolecular LC complexes for dynamic materials through multi-component self-assembly. Complexation of forklike mesogenic molecules with various supramolecular components plays a key role in the construction and functionalization of the supramolecular LC complexes.

In chapter 1, general introduction about self-assembled LC complexes and objective of this thesis are presented. In chapter 2, self-assembled behavior of

mesogen-containing compounds is systematically described. Molecular conformation of forklike mesogens in the LC assemblies is discussed. In chapter 3, construction of spherical LC molecules through multi-component self-assembly is demonstrated. Complexation of forklike mesogenic ligands with palladium salts allows for the formation of the giant LC spheres bearing mesogenic moieties. In chapter 4, an aldehyde-decorated spherical complex as a new supramolecular crosslinker has been designed and applied for the formation of dynamic covalent networks. Nanostructured self-healing materials have also been developed by using the mesogen-functionalized spherical complex as LC media. In chapters 5 and 6, supramolecular LC complexes with polymeric structures are presented. Chapter 5 reports the formation of metallosupramolecular LC polymers for stimuli-responsive materials. Chapter 6 describes the preparation of supramolecular LC networks exhibiting shape memory effects.

In conclusion, this thesis demonstrates design and functionalization of supramolecular LC complexes formed by multi-component self-assembly. The results presented in this thesis will provide a new direction in the development of dynamic materials based on supramolecular architectures.

List of Publications

Original Papers

- [1] “Liquid-Crystalline Fork-like Dendrons”
Junya Uchida, Takashi Kato
Liq. Cryst. **2017**, *44*, 1816-1829.
- [2] “Self-Assembly of Giant Spherical Liquid-Crystalline Complexes and Formation of Nanostructured Dynamic Gels that Exhibit Self-Healing Properties”
Junya Uchida, Masafumi Yoshio, Sota Sato, Hiroyuki Yokoyama, Makoto Fujita, Takashi Kato
Angew. Chem. Int. Ed. **2017**, *56*, 14085-14089.
- [3] “Construction of Metallosupramolecular Liquid-Crystalline Polymers and their Application for Electric Field-Responsive Liquid Crystals”
Junya Uchida, Masafumi Yoshio, Takashi Kato, in preparation.
- [4] “Shape Memory Supramolecular Liquid-Crystalline Networks”
Junya Uchida, Masafumi Yoshio, Takashi Kato, in preparation.

Reviews

- [5] “Functional Liquid-Crystalline Polymers and Supramolecular Liquid Crystals”
Takashi Kato, Junya Uchida, Takahiro Ichikawa, Bartolome Soberats
Polym. J. **2018**, *50*, 149-166.
- [6] “Functional Liquid Crystals towards Next Generation of Materials”
Takashi Kato, Junya Uchida, Takahiro Ichikawa, Takeshi Sakamoto
Angew. Chem. Int. Ed. in press.