

# 博士論文

## **Control of Structures and Alignment of Supramolecular Assemblies** (超分子集合体の構造と配向の制御)

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## Chapter 1. Introduction

Control of molecular self-assembly is a key technology in material science. In natural system, a variety of biomolecules spontaneously form ordered hierarchical structures. Dynamic assembled behaviors of these supramolecular architectures through response to external stimuli enables the construction of complex supramolecular systems with high biological functions.

Liquid crystals and self-assembled fibers are representative self-assembled materials having dynamic order and responsiveness to external stimuli. Self-assembly of these materials has been studied for the development of functional materials. For further functionalization, stimuli-responsive materials have been developed by utilizing external stimuli. Recent advancement in liquid-crystalline (LC) materials has shown anisotropic control of ion conductive pathways or switching of photoluminescent functions regulated by photo- or mechano-stimuli. Anisotropic aggregation of one-dimensional molecular assemblies in solution states has been achieved by using external fields such as LC and electric fields, resulting in polarized emission and enhancement of optical properties. However, control of dynamic molecular assembled behaviors through external stimuli or fields is still limited. Further control and understanding of the dynamic self-assembling behavior are significant challenging to obtain highly functional supramolecular materials.

In this thesis the author describes further control of structures and alignment of supramolecular assemblies utilizing external stimuli. Introduction about molecular assembled materials is presented in chapter 1. In chapters 2 and 3, development and alignment control of new stimuli-responsive self-assembled fibers consisting of  $\pi$ -conjugated gelators and a radical-based gelator are described. LC fields has been used to control the alignment of the fibers to obtain anisotropic functions. Metastable-stable phase transition induced by thermal stimuli has been applied to control  $\pi$ -electronic functions in chapter 2. Chapters 4 and 5 focus on control of dynamic molecular assembled behavior of LC materials. In chapter 4, the effects of dynamic LC ordered structures on the formation of self-assembled fibrous structures in LC templates are described. In chapter 5, study on ultrafast cooperative molecular motions of photo-responsive LC molecules by controlled UV light irradiation is described.

## **Chapter 2. Development and Alignment Control of Bistable Photoconductive Self-Assembled Fibers Exhibiting Metastable-Stable Phase Transitions**

In this chapter, development and alignment control of self-assembled fibers showing switchable photoconductive properties associated with metastable-stable phase transitions are described. Metastable states of molecular assemblies are well utilized in living systems. Recently, self-assembled fibers showing metastable-stable phase transitions have been reported, although their functions have hardly been explored. The author intends to control electronic functions of self-assembled fibers by utilizing metastable-stable phase transitions. The designed  $\pi$ -conjugated compounds formed fibrous aggregates in organic solvents, which was examined by scanning microscopic (SEM) observation. Kinetic control of self-assembly pathways gave the energetically distinct fibrous assemblies in a kinetically trapped metastable state and a thermodynamically favored state, which was confirmed by UV-vis absorption spectroscopy, differential scanning calorimetric (DSC) analyses and X-ray diffraction measurements. Electronic properties of these gels were examined by stationary-state photoconductivity measurements. Notably, switching of photocurrent responses was observed upon thermally-induced phase transitions. These results suggest that structural rearrangement of the  $\pi$ -stacked assemblies upon metastable-stable phase transition effects on the dynamic photoconductive behaviors. Anisotropically oriented fibers on electrodes were obtained by using a homogeneously oriented LC smectic field. Higher photocurrent was monitored with the fibers aligned perpendicular to the electrodes than parallel ones upon UV light irradiation. This result indicates that control of fiber orientation contributes to the efficient charge carrier transport.

## **Chapter 3. Development and Alignment Control of Redox-Active Self-Assembled Fibers Having Organic Radical Moieties**

In this chapter, development and alignment control of self-assembled fibers composed of a redox-active radical-based gelator are described. Organic radicals receive attentions because of their unique magnetic and redox properties derived from unpaired electrons. Magneto-active radical-based gelators forming self-assembled fibers

were reported by Kato group and their alignment was controlled. However, redox-active self-assembled fibers based on organic radicals have not been studied. Development of redox-active radical-based gelator is interesting for fast and durable redox-responsive fibrous materials. A new isoleucine-based gelator having a nitronyl nitroxide radical moiety has been described in this chapter. The nitronyl nitroxide has ambipolar redox properties to give the cations and anions from the neutral radicals. The designed compound formed fibrous aggregates in typical organic solvents and LC molecules, which were examined by scanning electron microscopy. Cyclic voltammetry (CV) and in situ visible absorption spectroscopic measurements revealed the ambipolar redox behavior showing quasi-reversible one-electron oxidation and reduction associated with multicolored electrochromism of the gelators in a solution state. The redox properties of the gelators in the fibrous aggregated state were also studied by CV measurements. Macroscopic alignment of the redox-active fibers has been achieved by using a homogeneously oriented LC smectic field.

#### **Chapter 4. Thermally Tunable Formation of Self-Assembled Fibrous Structures in Liquid-Crystalline Templates**

In this chapter, tuning of self-assembled fibrous structures in LC smectic templates through control of the order of LC structures is described. Morphologies of self-assembled fibers like aligned fibrous structures are important for material properties such as mechanical, optical, transporting and biological properties. LC fields have been studied as anisotropic templates for self-assembly of low-molecular-weight gelators. In LC smectic A templates, one-directionally aligned self-assembled fibers have been obtained. However, further control of complex fibrous structures is still challenging. The concept shown in this chapter is tuning of anisotropic aggregation of gelators in LC templates through control of LC layered structures, which are dependent on thermal conditions. The formation of the fibrous assembly of a typical amino acid-based gelator in a LC smectic A phase has been demonstrated with various thermal conditions. In the templates of the smectic A layered structure, the gelator selectively formed aligned fibers in one direction or two orthogonal directions through tuning of thermal conditions. The anisotropic alignment of these fibers was examined by SEM observations. Dynamic

LC structures were studied by polarized infrared absorption measurements.

## **Chapter 5. Ultrafast Photoisomerization-Induced Cooperative Motions to Higher Molecular Orientation in Liquid-Crystalline Molecules**

In this chapter, ultrafast cooperative motions in LC smectic azobenzene molecules triggered by photoisomerization are presented. Cooperative molecular motions are fundamental nature of LC materials. Understanding of cooperative motions of LC materials is of importance for the development of new stimuli-responsive LC materials. The structural control of LC materials has been studied by combining photo-responsive azobenzene molecules. In these LC materials, photo-induced cooperative motions of LC molecules have been observed on micro to millisecond timescale. In contrast, in solution states, photoisomerization of a single azobenzene-based molecule occurs on femto to picosecond timescale. Thus, the response of liquid crystals of azobenzene molecules may initiate in a few picoseconds. However, there is no observation on photoisomerization-induced cooperative motions of LC materials on picosecond timescale. In this chapter, therefore, structural change of azobenzene-based LC molecules has been studied by picosecond time-resolved electron diffraction (TRED) measurements. Ultrafast TRED measurements on an LC azobenzene molecule, which shows a smectic B phase, revealed that linearly polarized UV light irradiation upon the homeotropically oriented LC film induced ultrafast cooperative molecular motions to higher molecular orientation on the timescale of 100 picoseconds. This observation corresponds to the timescale of the photoisomerization of the LC azobenzene molecules indicated by transient transmission measurements. Simplified molecular dynamics calculations suggest the azobenzene molecules are aligned in the direction of the UV light polarization axis by their cooperative motion induced by steric intermolecular interactions after photoisomerization.

## **Chapter 6. Conclusion and Perspective**

In the present thesis, the author describes the control of structures and alignment of self-assembled fibers and liquid crystals through use of external stimuli.

In chapter 1, general introduction about supramolecular assembled materials and objectives of this thesis are described. In chapters 2 and 3, development and alignment control of stimuli-responsive functional self-assembled fibers has been demonstrated. In chapter 2, metastable-stable phase transitions triggered by thermal-stimuli allows the switching of photoconductive properties of the self-assembled fibers. Anisotropic orientation of the photoconductive fibers contributes to the efficient charge carrier transport. In chapter 3, redox-active self-assembled fibers having organic radicals have been developed and their macroscopic alignment has been controlled by using LC templates. In chapters 4 and 5, dynamic molecular assembled behavior of LC materials has been studied and controlled by using external stimuli. In chapter 4, tuning of the LC smectic layered structures based on thermal conditions leads to the selective formation of the self-assembled fibers with different orientation. In chapter 5, ultrafast photoisomerization-induced cooperative motions in a LC phase have been confirmed on picosecond timescale, which is the fastest cooperative molecular motion ever observed in LC states. Well-controlled UV light irradiation defines the direction of the ultrafast molecular motions to higher orientation in the LC smectic B phase.

In conclusion, the potential of control over dynamic molecular behaviors of supramolecular assemblies utilizing external environment is presented in this thesis. The results obtained in this thesis will provide new insights into the further development of high functional molecular materials using dynamic molecular behaviors.

## List of Publications

### Original Papers

- [1] “Kinetically Controlled Bistability of Self-Assembled Fibers Consisting of  $\pi$ -Conjugated Gelators: Phase Transition-Induced Switchable Photoconductivity and Alignment Control for Efficient Charge Transport”  
Daisuke Yamaguchi, Masafumi Yoshio, Go Matsuba, Takashi Kato  
To be submitted.
- [2] “Redox-Active Supramolecular Fibers of a Nitronyl Nitroxide-Based Gelator”  
Daisuke Yamaguchi, Hiroki Eimura, Masafumi Yoshio, Takashi Kato  
*Chem. Lett.* **2016**, *45*, 863–865.
- [3] “Thermally Tunable Formation of Self-Assembled Fibers in Liquid-Crystalline Smectic Templates: Selective Formation of Oriented Fibrous Structures in Two Orthogonal Directions”  
Daisuke Yamaguchi, Takashi Kato  
To be submitted.
- [4] “Ultrafast Isomerization-Induced Cooperative Motions to Higher Molecular Orientation in Smectic Liquid-Crystalline Azobenzene Molecules”  
Daisuke Yamaguchi<sup>†</sup>, Masaki Hada<sup>†</sup>, Tadahiko Ishikawa, Takayoshi Sawa, Kenji Tsuruta, Ken Ishikawa, Shin-ya Koshihara, Yasuhiro Hayashi, Takashi Kato  
*Nat. Commun.* **2019**, *10*, 4159 (<sup>†</sup>equal contribution).

### Reference Paper

- [1] “Shear-Induced Liquid-Crystalline Phase Transition Behaviour of Colloidal Solutions of Hydroxyapatite Nanorod Composites”  
Satoshi Kajiyama, Hiroki Iwase, Masanari Nakayama, Rino Ichikawa, Daisuke Yamaguchi, Hideki Seto, Takashi Kato  
In revision.

### Reviews

- [1] “Synthesis and Functionalization of Hydrogen-Bonded Supramolecular Materials”  
Takashi Kato, Daisuke Yamaguchi  
*CSJ Current Review*, Vol. 33 (Ed: The Chemical Society of Japan), Kagaku-Dojin, **2019**, Ch. 13, pp. 151–157.
- [2] “Supramolecular Association and Nanostructure Formation of Liquid Crystals for New Ordered Functional Materials”  
Takashi Kato, Monika Gupta, Daisuke Yamaguchi, Kian Ping Gan, Masanari Nakayama  
*Bull. Chem. Soc. Jpn.* to be submitted. (Review)