

# 博士論文

## **Control of Assembled Structures and Functions of Luminescent Liquid Crystals**

(発光性液晶材料の集合構造および機能制御)

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Functions of  $\pi$ -conjugated molecular assemblies such as luminescence and conductivities are largely dependent on the assembled structures because of the intermolecular interactions. Thus, the control over the assembled structures of the  $\pi$ -conjugated molecules is crucially important in order to bring out the desired luminescence properties and conductivities. Self-assembly is one of the promising approaches to the control of assembled structures because the bottom up process of self-assembly leads to the formation of well-organized nanostructures.

Liquid crystal is one of the representative self-assembled materials. Depending on the molecular design, they form various nanostructures through self-assembly. Nanosegregation in the liquid-crystalline (LC) states promotes the organization of the functional groups, which endows the materials with new functions. LC molecules based on  $\pi$ -conjugated moieties form 1D or 2D nano-ordered structures which enables the anisotropic and efficient charge carrier transport, and anisotropic luminescence. Furthermore, liquid crystals possess the dynamic nature and they show the changes of their alignment and the transformation of their assembled structures induced by external stimuli such as mechanical force, heat, and environmental changes. Therefore, the use of liquid crystals enables the development of dynamic functional materials whose assembled structures and functions can be controlled and switched by external stimuli. For example, mechanochromic or thermochromic luminescent liquid crystals which change their luminescent colors in response to mechanical force or heat have been developed. However, the number of the reports relating to the stimuli-responsive luminescent liquid crystals is still limited. Control of their luminescence and stimuli-responsive properties is difficult because chemical derivatization often causes the loss of the stimuli-responsive properties.

In this thesis the author focuses on the further control of the assembled structures and luminescence properties of liquid crystals through external stimuli. In chapters 1 and 2, the relationship between the molecular structures and stimuli-responsive properties of mechanochromic luminescent liquid crystals has been examined in order to establish the molecular design to bring out desired luminescence and stimuli-responsive properties. In chapter 3, a new approach to the tuning of luminescence of liquid crystals through co-organization with ionic liquids has been demonstrated.

## **Chapter 1. Mechanochromic Luminescent Liquid Crystals Containing Oligothiophene Moieties**

This chapter describes development of mechanochromic luminescent liquid crystals based on oligothiophene moieties. For the earlier examples of mechanochromic luminescent liquid crystals, condensed ring moieties are introduced as the luminescent cores. On the other hand, the material design in this chapter is based on rod-shaped oligothiophene  $\pi$ -conjugated moieties with different conjugation length. The compound containing a bithiophene moiety exhibits two different LC phases depending on the cooling process from the isotropic liquid phase. Slow cooling leads to the formation of a rectangular columnar LC phase showing green luminescence, whereas a cubic LC phase exhibiting yellow-green luminescence is obtained by rapid cooling from the isotropic liquid phase. After applying mechanical shearing, the compound in the cubic phase shows a phase transitions to a columnar phase and the luminescent color changes to blue-green. On the other hand, the compound based on a quarter thiophene moiety exhibits only rectangular columnar phases on the cooling process. This quarter thiophene derivative also shows a shear-induced phase transition to a different columnar phase accompanied by the change of the luminescent color from orange to yellow. Emission spectra of the bithiophene derivative were measured to study the photoluminescence properties. In the cubic phase, a broad structureless emission band centered at 553 nm was obtained, suggesting that the yellow-green luminescence in the cubic phase can be ascribed to the formation of excimer. In contrast, a structured emission band was detected at 497 nm in the shear-induced columnar phase. In order to examine the formation of hydrogen bonds, infrared (IR) spectra were obtained. In the cubic phase, the C=O stretching band was observed at  $1650\text{ cm}^{-1}$ , which was located at a lower wavenumber region compared to that in the isotropic liquid phase ( $1685\text{ cm}^{-1}$ ). This result indicates the formation of intermolecular hydrogen bonds in the cubic phase. In the shear-induced columnar phase, the peak was shifted to  $1656\text{ cm}^{-1}$  and at the same time, a shoulder was detected at  $1682\text{ cm}^{-1}$ . Based on these results, the shear-induced luminescent color changes are attributed to inhibition of excimer formation in the shear-induced columnar phase due to the partial dissociation of intermolecular hydrogen bonds.

## **Chapter 2. Mechanoresponsive Liquid Crystals Exhibiting Reversible Luminescent Color Changes at Ambient Temperature**

This chapter presents the design and syntheses of mechanochromic luminescent liquid crystals to tune their stimuli-responsive properties. After applying mechanical shearing, the earlier examples of mechanochromic luminescent liquid crystals require to be heated and subsequently cooled in order to recover their initial luminescence because the shear-induced LC phases are thermodynamically more stable than the initial LC phases. LC phases and their stabilities are tunable through molecular design. Therefore, changing the molecular structures is one of the promising approaches to the tuning of stimuli-responsive properties. The molecular design in this chapter is based on the oligothiophene luminescent cores with different conjugation length and flexible substituents attached to the luminescent cores. The compound based on a bithiophene moiety exhibits an optically isotropic liquid-crystalline (OI) phase on cooling at a rate of  $5 \text{ K min}^{-1}$  from the isotropic liquid phase. After applying mechanical shearing to the compound in the OI phase, it shows a phase transition to a birefringent mesomorphic (M) phase, and its luminescent color changes from green to blue-green. After aging the M phase at ambient temperature, it spontaneously shows the phase transition to the initial OI phase and luminescent color also recovers. The results of XRD measurements support the shear-induced phase transitions and the recovery of the OI phase through the aging process. Differential scanning calorimetry (DSC) was used to examine the stability of each LC phase. During the heating process, an exothermic peak corresponding to the M–OI phase transition was detected at  $44 \text{ }^\circ\text{C}$  and this phase transition was thermally irreversible. The sample obtained by aging the M phase did not show the corresponding peak. These results suggest that the shear-induced M phase is thermodynamically and kinetically unstable, and the M–OI phase transition proceeds even at ambient temperature. Luminescent spectra and lifetimes were measured to examine the photophysical properties. The compound in the OI phase shows a broad emission band centered at  $540 \text{ nm}$  whereas it exhibits a structured emission band at  $492 \text{ nm}$  in the M phase. The compound in the OI phase possesses longer lifetime components compared to the shear-induced M phase. These results indicate that the shear-induced color changes are ascribed

to the inhibition of excimer formation in the shear-induced M phase. Compounds based on longer  $\pi$ -conjugation length also exhibit the reversible luminescent color changes at ambient temperature and their luminescence covers the wide range of visible region. Interestingly, these compounds recover their initial luminescence faster than the compound based on the bithiophene moiety, suggesting that not only luminescent colors but also stimuli-responsive properties are tunable through the simple change of the  $\pi$ -conjugation length.

### **Chapter 3. Nanosegregated Luminescent Liquid Crystals and Control of their Luminescence through Co-organization with Ionic Liquids**

This chapter describes the nanosegregated luminescent liquid crystals and tuning of their luminescence. LC amphiphilic molecules have large tunability in their assembled structures through mixing with ionic liquids. The concept of this chapter is based on tuning of luminescence of liquid crystals through changing the environment around the luminescent cores by introducing ionic liquids into the nanosegregated LC structures. The compound described in this chapter is composed of a donor-acceptor type  $\pi$ -conjugated moiety, a hydrophilic diol group, and a hydrophobic moiety. The compound forms a hexagonal columnar phase which was confirmed by polarizing optical microscopic observation, DSC, and XRD measurements. The results of IR measurements indicate the formation of intermolecular hydrogen bonds of the diol moieties, which suggests that the compound exhibits the columnar phase through nanosegregation and the hydrophilic diol moieties are organized at the center of the columns. As the ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate was mixed with the compound. As the mole fraction of the ionic liquids increases, the intercolumnar distance gradually becomes longer. The mixtures possess higher clearing points and crystallize at lower temperature compared to the pure compound. These results suggest that the ionic liquids are organized inside the hydrophilic channels of the columns and promote the nanosegregation, leading to the stabilization of the columnar phase. Interactions between the ionic liquids and the

compound was confirmed by the IR measurements, supporting the co-organization of compounds and ionic liquids. The pure compound shows light-blue luminescence whereas blue-green luminescence is observed for the mixture. Ionic liquids organized inside the columns may stabilize the photo-induced charge transfer state of the amphiphilic molecules, which results in the change of the luminescent colors.

## **Chapter 4. Conclusion and Perspective**

The thesis presents the control of assembled structures and luminescence properties and the switching or tuning of luminescence by applying external stimuli. The approaches focused on material design in order to bring out the desired luminescence and stimuli-responsive properties of mechanochromic luminescent liquid crystals, or in order to form nanosegregated structures which dynamically change the assembled structures in response to the introduction of ionic liquids.

In chapters 1 and 2, the relationship between the molecular structures and mechanochromic properties is described. Through the molecular design shown in the chapters, luminescent liquid crystals exhibiting reversible luminescent color changes at ambient temperature have been developed for the first time.

In chapter 3, the tuning of the luminescence through co-organization with ionic liquids has been demonstrated. Although the spectral shift is not large, this chapter describes a new approach to the tuning of luminescence of liquid crystals.

In conclusion, this thesis demonstrates the potential of control over the assembled structures and luminescence properties of liquid crystals. The results obtained in this thesis are informative for the further development of luminescent molecular assemblies and their application.

## List of Publications

### Original Papers

- [1] “Mechanochromic Photoluminescent Liquid Crystals Containing 5,5’-Bis(2-phenylethynyl)-2,2’-bithiophene”  
Masato Mitani, Shogo Yamane, Masafumi Yoshio, Masahiro Funahashi, Takashi Kato  
*Mol. Cryst. Liq. Cryst.* **2014**, *594*, 112–121.
- [2] “Mechanoresponsive Liquid Crystals Exhibiting Reversible Luminescent Color Changes at Ambient Temperature”  
Masato Mitani, Shuhei Ogata, Shogo Yamane, Masafumi Yoshio, Miki Hasegawa, Takashi Kato  
*J. Mater. Chem. C* **2016**, DOI: 10.1039/c5tc03578c.
- [3] “Nanosegregated Luminescent Liquid Crystals and Control of their Luminescence through Co-organization with Ionic Liquids”  
Masato Mitani, Masafumi Yoshio, Takashi Kato  
In preparation.

### Reviews

- [4] “Mechanoresponsive Luminescent Molecular Assemblies: An Emerging Class of Materials”  
Yoshimitsu Sagara, Shogo Yamane, Masato Mitani, Christoph Weder, Takashi Kato  
*Adv. Mater.* **2016**, *28*, 1073–1095.
- [5] “デンドロンを利用した機械的刺激応答性発光材料の開発”  
(Development of Mechanochromic Luminescent Materials Having Dendrons)  
相良剛光・三谷真人・長野哲雄・加藤隆史  
ファインケミカル, 44 巻, 4 号, 21–28 頁 (2015 年).