

博士論文

**Development of π -Conjugated Self-Assembled
Liquid Crystals for Stimuli-Responsive Materials**

(刺激応答性材料のための自己組織性 π 共役液晶の開発)

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Chapter 1: Introduction

π -Conjugated molecules that exhibit liquid-crystalline (LC) properties have attracted wide attention for their ease of forming molecular stacks that enable anisotropic charge carriers transport properties.^{1, 2} The solution processability of these liquid crystals and their abilities to form smooth thin films are essential for low-cost and optimal device performance. The fluidity and self-assembled properties of these π -conjugated self-assembly systems also allow stimuli-responsive materials properties to be realised. These properties have been exploited in mechano-force-responsive (mechanochromic), ion-responsive and thermoresponsive materials that change their molecular arrangement structures and luminescent colour with respect to external stimuli. The author envisions that the syntheses of π -conjugated moieties with LC properties would allow for the realisation of both charge carriers transport and stimuli-responsive multi-functional materials that could potentially be applicable as optoelectronics and sensors devices.

charge carriers transporting properties and combined with mechanochromic, ion-responsive and thermo-responsive luminescent properties for **Chapter 2, 3** and **4** respectively. The author envisions that unique molecular design through supramolecular interactions such as π - π stacking, hydrogen bonding and ion-dipole interactions would lead to the development of self-assembled functional liquid crystals with charge-transporting stimuli-responsive functions.

Chapter 2. Columnar liquid-crystalline assemblies of X-shaped pyrene-oligothiophene conjugates: Photoconductivities and mechanochromic functions

Oligothiophene derivatives have promising applications in electronic devices due to their luminescent properties and charge carriers transporting properties. On the other hand, pyrene derivatives have also been widely incorporated into liquid crystals that exhibit mechanochromic properties. Herein, the author reports on the syntheses of X-shaped pyrene-oligothiophene conjugates consist of a disc-like pyrene core that is four-fold conjugated with bithiophenes moieties, tethered with eight or twelve alkoxy chains. These X-shaped molecules form hole transporting LC columnar phases (Col), with molecular assemblies that are tuneable by mechanical stimuli that results in a change in the emission colour.

Compound **PO-1a** forms hexagonal columnar phases (Col_{h1}, Col_{h2}), while **PO-1b** shows tetragonal columnar (Col_t) and rectangular columnar phases (Col_r) over a large range of temperature, as determined by differential scanning calorimetry (DSC), X-ray diffraction (XRD) spectra and visual inspection with polarising optical microscopy (POM). Time-of-flight (TOF) photoconductivities measurements have revealed that both X-shaped molecules exhibit hole carriers transport properties in the order of 10^{-4} to 10^{-5} cm² V⁻¹ s⁻¹.

Mechanically shearing the sample of **PO-1a** induces an emission colour change from dark red to bright orange, which is observable by visual inspection and fluorescence spectroscopy. This shear-induced phase is proposed to be due to the disorder to the columnar stacking structure triggered by the shearing force, which is supported by DSC heating traces and wide-angle X-ray diffraction (WAXRD) spectra.

The blue-shift in the emission wavelength can be ascribed to the decreased π - π overlap in the disordered shear-induced phase. The author has then proposed the thermal transition scheme of the different Col phases of **PO-1a** based on the above DSC, WAXRD, spectrofluorometric data, and previously reported helical packing assemblies of pyrene derivatives.³ As far as the author knows, it is believed that this X-shaped molecule **PO-1a** is the first example of a LC material that shows both charge transport and mechanochromic properties. On the other hand, **PO-1b** exhibits no observable mechanochromic properties, which is presumably ascribed to the more rigid Col_r phases.

The author has further conducted a study into the effect of introducing gelator molecules that form fibrous networks to the X-shaped liquid crystals. It is discovered that the resulting LC gel apparently slightly increases the measured hole mobilities for **PO-1a** but not **PO-1b**. It is thought that the increase in hole mobilities is likely ascribed to the suppression of the molecular fluctuations of **PO-1a** through the fibrous network. As for **PO-1b**, as discussed before, the already existing rigidity of **PO-1b** is thought to be the reason behind the minimum effect of gelation has on its hole carriers transport properties.

Chapter 3: Guanine-oligothiophene conjugates: liquid-crystalline properties, photoconductivities and ion-responsive emission of their nanoscale assemblies

The introduction of hydrogen-bond-forming motifs to π -conjugated groups have attracted intense attention for the construction of supramolecular self-assembled nanostructures.¹ Nucleobases such as guanine are intriguing with their versatile ability to form ribbon-like or disk-like polymorphs, while also exhibiting charge carriers transport properties.

Herein, the author reports on the design of *N*-9-alkylated guanine derivatives that are conjugated with oligothiophene moieties at the C-8 position for the construction of supramolecular self-assembled LC assemblies showing charge carriers transport properties and ion-responsive emission responses. Five guanine-oligothiophene conjugates have been synthesised, namely guanine-monothiophene derivative **GO-1**, guanine-bithiophene derivatives **GO-2a**, **GO-2b** and guanine-terthiophene derivatives **GO-3a**, **GO-3b**. Investigated through DSC thermograms, WAXRD spectra of POM images, **GO-1** and **GO-2a** are found to show only isotropic (Iso) phase, while **GO-2b** and **GO-3b** exhibit Col_h phases over a wide range of

temperatures. For **GO-3a**, an unexpected bicontinuous cubic (Cub_{bi}) phase with an *Im3m* space group is observed, which is quite rare for π -conjugated molecules, as far as the author knows.

Through TOF transient photocurrent curves, **GO-2b** and **GO-3b** in the Col_h phases exhibit only electron carriers transport, while **GO-3a** in the Cub_{bi} phase shows ambipolar carriers transport, with measured electron and hole carriers mobility in the order of 10^{-3} to 10^{-4} cm² V⁻¹ s⁻¹. The lack of hole carriers transport properties of the Col_h phases has prompted the author to explore the possible molecular assembly structures of these guanine-oligothiophene conjugates. Through further study by WAXRD, Fourier transformed infrared (FTIR) spectroscopy, and computational calculation by density functional theory (DFT), the author has attributed the hole trapping behaviour in the Col_h phases of **GO-2b** and **GO-3b** to the guanine-guanine stacking and G-quadruplex formation that are well-known for their hole trapping effect.⁴ On the other hand, **GO-3a** in the Cub_{bi} phase is proposed to self-assemble in a ribbon-like and catenary manner. The dimensions of the eight molecules in a layer of the cubic unit cell are in good agreement with the measured WAXRD peaks. Such molecular assemblies are presumably form in such a way that guanine-guanine stacking is non-dominant, resulting in less significant hole traps and allowing ambipolar carriers transport in the nanostructures. Similar molecular assemblies have also been previously reported.⁵

The ion-responsive phase transitions of the guanine-oligothiophene conjugates and the resulting photoluminescent response of the complexes were also examined. The introduction of potassium trifluoromethanesulfonate (CF₃SO₃K) with various organic to K⁺ ratios induces the formation of different Col phases for all the guanine-oligothiophene conjugates samples. The photoluminescent colour changes were characterised by fluorescence spectroscopy and visual inspection under UV irradiation. Observable spectroscopic redshifts are observed by the introduction of CF₃SO₃K, with guanine-bithiophene derivative **GO-2a** changes from green to yellow emission, and guanine-terthiophene derivative **GO-3a** transforms from yellow to orange emission. The author has attributed the redshifts in the emission colours of the complexes to the better π - π stacking structures associated with the formation of G-quadruplexes in the Col phases.

On the other hand, while the introduction of CF₃SO₃K induces the Iso to Col phase transition for guanine-monothiophene derivative **GO-1a**, its bulk state emissions show minimal change in the emission colour (sky-blue to blue). The author has reasoned that the lack of spectroscopic shift between **GO-1a** and its complexes is presumably due to the insufficient overlapping from the monothiophene moiety. In addition, introduction of K⁺ to **GO-2b** and **GO-3b** causes relatively smaller redshifts in the emission wavelengths, as these derivatives with tridodecyloxy phenyl side chains are already in the Col phases in their single component states. This supports the author's proposal that the emission change is due to better π - π overlap associated with G-quadruplexes in the Col phases as compared to other phases.

In order to gain further insight into the emission colour changes, the author has conducted studies of the emission spectra of the THF solutions of guanine-oligothiophene conjugates consisting of different concentrations in the presence of high concentration of K^+ . The investigation shows that while the emission spectra of the dilute solutions of guanine-oligothiophenes are not affected, the more concentrated solutions exhibit observable spectroscopic redshift in the presence of excess K^+ , indicating the formation of G-tetrads that subsequently form G-quadruplexes with better π - π stacking interactions.

Chapter 4: Cyano- and Oligothiophene-Decorated Tetraphenylethylene-based Liquid Crystals: Long Wavelength Thermoresponsive Emission and Photoconductive Functions

The π -conjugated moieties commonly employed by long wavelength emissive materials often use disc-shaped or rod-shaped molecular design that are generally weakly emissive in their bulk states due to aggregation caused quenching (ACQ), limiting their practical uses in device applications. The employment of a moiety that shows aggregation-induced or -enhanced emission (AIE or AEE) in the bulk states could solve this problem.⁶

Herein, the author presents the syntheses of thermoresponsive liquid crystals consisting of tetraphenylethylene (TPE) derivatives comprising of fourfold conjugated α -cyanostilbene (**TPE-1**) and their heteroaryl analogues with thiophene and bithiophene derivatives (**TPE-2** and **TPE-3**) which exhibit yellow, orange and red emissions, respectively. The investigation into the LC properties by DSC thermograms, WAXRD and POM observations of these X-shaped molecules revealed that while **TPE-1** and **TPE-2** shows only Col_h phases, **TPE-3** exhibits Cub_{bi} phase with $Pn3m$ symmetry in a wide temperature range, with the formation of Col_h phase occurring at higher temperature.

Through fluorescence spectroscopy, it is found that an increase in photoluminescent intensity is consistently achieved with decreasing temperature and vice-versa for all three TPE-derived liquid crystals (**Figure 7**), as expected of AEE-exhibiting derivatives. The absolute quantum yield (Φ) for **TPE-1**, **TPE-2** and **TPE-3** are measured to be 0.44, 0.28 and 0.05, respectively. In addition, the charge carriers transport properties of these TPE conjugates were studied with TOF photoconductivity measurements. While **TPE-1** exhibits only electron carriers transport in the order of 10^{-4} to 10^{-5} $cm^2 V^{-1} s^{-1}$, both **TPE-2** and **TPE-3** show ambipolar carriers transport in the order of 10^{-3} to 10^{-4} $cm^2 V^{-1} s^{-1}$.

Using the results from the DFT calculations, WAXRD, FTIR, 2D NMR spectra as well as the existing reports from the literatures, the self-assembled structures of the X-shaped TPE-derived liquid crystals are proposed. The cyano groups are thought to form hydrogen bonds with

the vinylene hydrogen atoms from the adjacent X-shaped molecule, forming column-like stacking structures in all the LC phases observed, including the Cub_{bi} phase.

Chapter 5: Conclusion and Perspectives

In this thesis, three different approaches towards the design of π -conjugated stimuli-responsive and multi-functional self-assembled liquid crystals have been discussed. The first approach is through the incorporation disc-like pyrene with rod-shaped oligothiophenes for the formation of π -stacked LC Col phases to allow for hole carriers transport and mechanochromic properties. The second approach makes use of hydrogen-bond-forming guanine that is conjugated with oligothiophene moieties to form various self-assembled LC phases such as Cub_{bi} and Col phases, enabling ambipolar or electron carriers transport and ion-responsive chromic responses. The third approach exploits the AIE- or AEE- exhibiting properties of TPE derivative and the hydrogen bonding properties of cyano group with vinylene hydrogen atoms for the development of charge-transporting thermoresponsive self-assembled liquid crystals. The strategies presented here could potentially allow for the design of next-generation stimuli-responsive materials for applications in organic electronics or sensors.

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List of publications

Original papers

1. "Columnar Liquid-Crystalline Assemblies of X-Shaped Pyrene–Oligothiophene Conjugates: Photoconductivities and Mechanochromic Functions"

Kian Ping Gan, Masafumi Yoshio and Takashi Kato

Journal of Materials Chemistry C, 2016, **4**, 5073-5080

2. "Guanine-Oligothiophene Conjugates: Liquid-Crystalline Properties, Photoconductivities and Ion-Responsive Emission of their Nanoscale Assemblies"

Kian Ping Gan, Masafumi Yoshio, Yuki Sugihara and Takashi Kato

Chemical Science, 2018, **9**, 576-585

3. "Cyano- and Oligothiophene-Decorated Tetraphenylethylene-Based Liquid Crystals: Long Wavelength Thermoresponsive Emission and Photoconductive Functions"

Kian Ping Gan, Masafumi Yoshio and Takashi Kato

in preparation

Reference paper

1. "Cyclization of (2-Alkenylphenyl)carbonyl Compounds to Polycyclic Arenes Catalyzed by Copper(II) Trifluoromethanesulfonate or Trifluoromethanesulfonic Acid"

Wei-Min Liu, Ya Lin Tnay, Kian Ping Gan, Zhen-Hong Liu, Wan Huei Tyan and Koichi Narasaka

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