論 文 の 内 容 の 要 旨

論文題目　**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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π-Conjugated molecules that exhibit liquid-crystalline (LC) phases form molecular stacks that enable anisotropic charge carriers transport properties. Liquid crystals are solution processable, and their abilities to form smooth thin films are essential for low-cost and optimal device performance. Additionally, the fluidity and self-assembled properties of these π-conjugated self-assembly systems have also allowed for 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 these external stimuli. The objective of this study is the demonstration of LC π-conjugated moieties with both charge carriers transport and stimuli-responsive materials that could be applicable as optoelectronics and sensors. Three approaches to these stimuli-responsive materials have been proposed in this study.

In **Chapter 1**, the general introduction about LC π-conjugated molecules and the objectives of this study are presented.

In **Chapter 2**, exploiting the π-π stacking interactions, columnar X-shaped liquid crystals that show both hole carriers transport and mechanochromic properties are presented. Pyrene is fourfold conjugated with phenylbithiophene moieties and tethered with eight or twelve alkoxy chains at their extremities to form various LC columnar assemblies. Both X-shaped molecules exhibit hole mobilities in the order of 10^{-4} to 10^{-5} cm^2 V^{-1} s^{-1} by time-of-flight (TOF) photoconductivity measurements. Mechanically shearing the columnar phase of the X-shaped molecule with eight alkoxy chains induces a significant blue shift in emission colour. The possible π-stacking assemblies and the mechanism for these properties are proposed, suggesting that mechanical shearing

induces a new shear-induced phase with decreased π-π overlap. Furthermore, a fibrous-network-forming gelator molecule is introduced to the X-shaped liquid crystals that lead to the formation of a LC gel. A small increase in the measured hole mobilities is observed, suggesting the suppression of the molecular fluctuations through the fibrous networks.

In **Chapter 3**, supramolecular self-assembly of guanine derivatives for the construction of LC assemblies with charge carriers transport properties and ion-responsive emission functions is described. This molecular design is inspired by the versatility of guanine in forming different polymorphs. Guanine-oligothiophene conjugates attached with alkoxy chains that exhibit thermotropic LC columnar or bicontinuous cubic phases have been demonstrated. TOF photoconductivity measurements show that guanine-oligothiophene conjugates exhibit either ambipolar or electron carriers transport in the order of 10^{-3} to 10^{-4} $cm^2 V^{-1} s^{-1}$. The charge carriers properties of these guanine-oligothiophene conjugates are proposed to be dependent on their self-assembled structures in the LC phases. In addition, the introduction of potassium trifluoromethanesulfonate (CF_3SO_3K) induces the formation of different Col phases for the guanine-oligothiophene conjugates samples, accompanied by redshifts in the photoluminescent colours in the bulk states. These redshifts are proposed to be due to the formation of G-quadruplexes in the presence of K^+ and subsequently better π-π stacking interactions.

In **Chapter 4**, LC tetraphenylethylene (TPE) derivatives with aggregation enhanced emission (AEE) properties for efficient long-wavelength emissive properties in the LC states are introduced. These X-shaped TPE-derived liquid crystals show thermoresponsive photoluminescent responses and hole and electron carriers transport properties. Their self-assembled structures have also been proposed and discussed.

In **Chapter 5**, the conclusion and perspectives of this study are presented. The three approaches towards the design of π-conjugated stimuli-responsive and multi-functional self-assembled liquid crystals have been summarised. The strategies demonstrated in this study could potentially lead to the development of next-generational stimuli-responsive materials for applications in organic electronics or sensors.