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Novel Calamitic Liquid Crystals Based on N-containing Mesogens

**-Synthesis, Characterization of Liquid Crystallinity,
Self-organization and Electrical Properties-**

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Abstract

In this research, we proposed a new study to utilize a liquid crystalline molecule as a materials platform so as to induce new and/or enhanced properties by designing N-containing moieties as mesogenic skeleton. Three kinds of liquid crystalline semiconductors based on functional N-containing heteroaromatic skeletons were prepared through facile synthetic routes, namely, benzo[c]cinnoline(BC), monoimide-substituted, and isoquino[8,7-h]isoquinoline (IQIQ) derivatives.

Through this study on the synthesis, liquid crystallinity and electric properties of liquid crystals based on N-containing heteroaromatic skeletons, the expected properties were realized: Induced ferroelectricity has been realized in liquid crystalline benzocinnoline derivativewith broad SmC phase; The dipole moment along the molecular long axis in the rod-shaped mesogens can facilitate and stabilize the formation of smectic mesophases; Highly ordered smectic mesophases combined with low LUMO levels were realized demonstrating their potential applications in n-channel FETs. Generally, the synthesized calamitic liquid crystals based on N-containing mesogens in this thesis become promising candidates in ferroelectric liquid crystals and n-channel FETs.

Chapter 1: Introduction

In the chapter 1, firstly, the research progress on organic semiconductors and liquid crystalline semiconductors has been reviewed, and also the research background was discussed. Taking account of the unique properties of liquid crystals, it is worth expecting that liquid crystals could be a material platform for developing new properties when various functional units are incorporated into their characteristic molecular systems. In addition, N-containing moieties are important functional units for optic and electronic materials. The incorporation of N-containing moieties into the central mesogenic skeleton can effectively induce large π -polarization thereby giving rise to the directed molecular dipole or strong electron affinity. Hence, in my research, some liquid crystalline semiconductors based on N-containing heteroaromatic skeletons as main functional units have been prepared and characterized to find some new properties such as

1. Induce strong dipole moment perpendicular against the molecular long axis for liquid crystalline semiconductors with ferroelectricity.
2. Induce and enhance the molecular self-organization into smectic mesophase in liquid crystals bearing dipole moment along the long axis.
3. Liquid crystalline semiconductors combined with low LUMO levels and highly ordered mesophases for n-channel OFET.

Chapter 2: Experimental methods

In the chapter 2, experimental methods are described in detail. We tried to prepare every compounds using short synthetic route to avoid the contamination of chemical impurities. After obtaining the relative compounds, their molecular structures were confirmed by ^1H NMR and MS spectrum. And then the phase transition could be measured by using DSC and POM, in which molecular orientation was checked by X-ray diffraction. Finally, high-purity samples can be used to

transient photocurrent measurements by time of flight technique, and thus the charge carrier mobility can be extracted.

Chapter 3: Smectic liquid crystals based on benzocinnoline framework

In the chapter 3, a series of liquid crystals based on polar BC framework were prepared through facile and versatile synthetic strategies. Dialkylated BC derivatives of 10-Ph-BC-Ph-10 and 12-Ph-BC-8 showed SmC phase over a wide temperature range ($>150^{\circ}\text{C}$) and highly ordered SmG (or SmJ) and SmH (or SmK) phases, while monoalkylated derivatives of Ph-BC-8 and BC-Ph-8 showed only low-ordered mesophases of Nematic and SmA phases. The pronounced reversible redox waves and low-lying LUMO levels of these derivatives approximately -3.2eV estimated by CVs revealed their potential n-type charge transport nature. In addition, temperature-dependent transport behaviors revealed by time-of-flight method in SmA and SmC phases make us acquire a good knowledge of that dipole moment existed in polar mesogens will enhance the energetic disorder resulting in a temperature-dependent mobility. Furthermore, the wide temperature range of the SmC phase in dialkylated BC derivatives in addition with their large dipole moments (> 3.4 Debye) perpendicular to the long molecular axis made them become promising candidates for ferroelectric liquid crystals. A clear switching behavior in POM textures was observed, which was originated from ferroelectricity induced in the SmC* by a small amount of chiral dopant.

Chapter 4: Smectic liquid crystals based on monoimide-fused framework

In the chapter 4, a series of novel liquid crystals based on monoimide-fused

aromatic skeleton, with large dipole along the long molecular axis, were prepared with moderate yields. Low ordered SmA phase in a head-to-tail arrangement within the layers was achieved for NAPI-Tp(2)-8, while highly ordered smectic mesophases for DiCN-NAPI-Ph-12 and ANTI-Ph-12. Temperature-dependent unipolar electron transport behavior in the SmA phase of NAPI-Tp(2)-8 by TOF technique was revealed with mobility on the order of $10^{-5} \text{ cm}^2/\text{Vs}$ at a limited temperature range of 20K, which was resulted from the big dipole moment randomly distributed mesogenic molecules within the SmA phase. Highly ordered smectic mesophases and low LUMO levels below -3.6eV were realized in DiCN-NAPI-Ph-12 and ANTI-Ph-12 revealed that they are potential materials for n-channel FET.

Chapter 5: Smectic liquid crystals based on isoquinoisoquinoline framework

In the chapter 5, a series of new calamitic liquid crystals based on aza-fused IQIQ skeleton were successfully synthesized through facile and versatile synthetic route in a moderate yield. 10-IQIQ-10 only exhibited low ordered smectic mesophase, while didodecyl-substituted 12-IQIQ-12 and ditetradecyl-substituted 14-IQIQ-14 exhibited highly ordered smectic mesophases. In addition, the dicynated compound DiCN-Chrysene-12 also presented the emergence of highly ordered smectic mesophase. Charge carrier transport property of 12-IQIQ-12 was characterized by TOF technique, revealing that electron and hole mobilities are on the order of $10^{-4} \text{ cm}^2/\text{Vs}$, which depends neither temperature nor electric field. Low LUMO level of -3.33eV for 12-IQIQ-12 and -3.72eV for DiCN-Chrysene-12, suggesting that they are potential electron-transporting candidates. Highly ordered smectic mesophases combined with low LUMO levels in these derivatives revealed that they were promising candidates for n-channel FET.

Chapter 6: Conclusion and perspective

Through this study on the synthesis, liquid crystallinity and electric properties of liquid crystals based on N-containing heteroaromatic skeletons, the expected properties were realized such as the controlled directed molecular dipole and strong electron affinity. The conclusion is generally summarized: 1. Induced ferroelectricity has been realized in liquid crystalline benzocinnoline derivativewith broad SmC phase; 2.The dipole moment along the molecular long axis in the rod-shaped mesogens can facilitate and stabilize the formation of smectic mesophases; 3. Highly ordered smectic mesophases combined with low LUMO levels were realized demonstrating their potential applications in n-channel FETs. Generally, the synthesized calamitic liquid crystals based on N-containing mesogens in this thesis become promising candidates in ferroelectric liquid crystals and n-channel FETs.

Publications

1. Tengzhou Yang, Hiroaki Iino, Junichi Hanna; Novel Smectic Liquid Crystals Based on Benzo[c]cinnoline: Their Synthesis, Mesomorphism, Opto-and Electro-Chemical Properties; **Liquid Crystals**, *Doi: 10.1080/02678292.2016.1229056*.
2. Tengzhou Yang, Hiroaki Iino, Junichi Hanna; Novel Smectic Liquid Crystals Based On Electron-Deficient Mesogen of Isoquino[8,7-h]isoquinoline; **Chemistry Letters**, Vol. 45, No. 9 (2016). *Doi: 10.1246/cl.160559*.