# 論文 / 著書情報
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# 論 文 要 旨

THESIS SUMMARY

専攻： Department of 物理電子システム 専攻
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this research, we proposed a new molecular design strategy for discotic liquid crystals, i.e., incorporation of alkyl chains into bay positions of disclike core, so as to achieve densely packed columnar mesophases with hometropic alignment, thereby suppressing molecular motion, which was expected to be beneficial for high-speed charge carrier transport.

Three different types of discotic liquid crystals have been designed and prepared through facile synthetic routes, namely, benzoporphyrin, Hexaazatrinaphthylenes (HATNA) and truxene. Their phase transitions were characterized by using DSC, POM and XRD measurements. Furthermore, the charge carrier transport was measured by time of flight technique.

In the chapter 1, firstly, the research progress on organic semiconductors has been reviewed, and also the research background was discussed. All organic semiconductors have been divided into two kinds based on their natures, namely the conventional and the self-organizing. As one of self-organizing organic semiconductors, sdscotic liquid crystals, such as triphenylenes, benzocoronenes, and phthalocyanines, can self-organize into columnar phases (hexagonal columnar phase, rectangular columnar phase and so on) when bearing long alkyl chains, in which large π-π overlaps are formed between neighboring molecules, so that charges are likely to transport along the column axis in quasi one dimensional pathway. On the other hand, two different molecular orientations in columnar phases have to be described: homeotropic and planar. In principle, electronic systems fabricated using such materials based on the columnar alignment configuration have been expected to find use in applications of organic field effect transistor (planar columnar alignment), organic light emitting and organic solar cell (homeotropic columnar alignment).

However, due to rather subtle intermolecular interplay between the conjugated cores, like attractive and repulsive forces, which inevitably causes molecular motions (translational and rotational) in columns, most of discotic liquid crystalline materials exhibit relatively low mobility ranging from $10^{-4}$ to $10^{-2}cm^2V^{-1}s^{-1}$. We are focusing on how to align columns homeotropically and thus boost charge carrier transport mobility in the homeotropic columnar mesophases of discotic liquid crystals through molecular design strategies. As discussed above, molecular motion in mesophases has been considered one of primary effect factors interfering with high-speed charge carriers, which will have to be suppressed so as to maintain fast mobility of carriers.

To meet the requirement of suppressed molecular motions, we designed discotic compounds with side chains at the bay positions of disclike cores. These kind of discotic compounds were expected to easily form homeotropic columnar alignment and also exhibit narrower intercolumnar space than peripheral substituted discotic liquid crystals, i.e., densely packed columnar lattice, which is beneficial to confine molecules within columns.

In the chapter 2, experimental methods are talked in detail. All compounds were synthesized according to the molecular design strategy. We tried to prepare every compound using short synthetic route to avoid the contamination of chemical impurities. After obtaining the relative compound, its molecular structure was confirmed by $^1$HNMR 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.

In the chapter 3, we designed a versatile route for synthesis of DLC benzoporphyrin derivatives. Through the new route, we obtained quite high efficiency, mild conditions and functional group tolerance, comparing with the previous one, which was helpful for high-purity sample for measuring charge carrier transport. Such materials were find to exhibited homeotropic columnar alignment. In the hexagonal columnar mesophase, the intercolumnar distance was estimated to be 21.6Å (the diameter of the core is 16 Å), thereby showing an intercolumnar space about 6Å, quite smaller than that of peri-substituted ones (over 10 Å).

We investigated charge carrier transport and photoconductive behaviours in two discotic liquid crystalline benzoporphyrin derivatives. Interestingly, through time of flight technique, these materials exhibited very high hole mobility over $0.1cm^2/Vs$ in Col$_{hd}$ and Col$_{rd,}$ while peri-substituted phthalocyanines just showed mobility of $10^{-3}$ $cm^2V^{-1}s^{-1}$. We contributed this result to a densely packed columnar structure, comparing with peripheral substituted DLCs. Moreover, very high photo-generation efficiency up to 2% in the columnar phase has been achieved.

In the chapter 4, we have challenged hexaazatrinaphthylene (HATNA) to form molecular columns with out-of-plane orientation for high electron transport. In this research, we discuss facile synthesis of novel hexaazatrinaphthylenes bay-substituted with alkyl, alkylethynyl, and alkylthio groups, i.e., type I, type II and type III, and their phase transition behaviors, as well as feasibility of self-directed molecular orientation on the substrates.

We found that all compounds can form long-range molecular columns with self-directed growth direction. Interestingly,

the HATNA substituted with bay alkyl groups (Type I) presented typical “edge-on” molecular alignment to form in-plane-oriented molecular columns on the substrate. On the other hands, the HATNAs with acetylene spacers (type II) exhibited perfect hexagonal lattice patterns: II-a with short side chains showed in-plane molecular columns, while II-b with longer chains obviously resulted in out-of-plane-oriented columns with “face-on” molecular alignment. In the case of III, the HATNA with sulfur atom spacers surprisingly showed molecular columns with rectangular lattices, whose molecular alignment also varied sensitively depending on the alkyl chain length.

Furthermore, CV measurements demonstrated that the introduction of various side chains could not override the electron-deficiency of the HATNA core. More importantly, we also found that the HATNA bay-substituted with octylthio groups showed high electron mobility in the bulk of Colr’ phase and even in polycrystalline phase up to $10^{-3}$ $cm^2V^{-1}s^{-1}$. This is the first time to determine valid charge carrier mobility through time of flight method in such N-containing compounds.

In the chapter 5, we proposed a new molecular design, i.e., the windmill-shaped molecule based on a disc-like truxene core, which was expected to form a densely packed columnar lattice with a shortened intercolumnar space, thereby suppressing the molecular motions and enhancing charge carrier transport in the discotic columnar mesophases. In addition, mono-side chain is adopted at a bay- position to expose the peripheral phenyl ring, thus leading to possible charge transport among the neighboring columns.

These truxenes showed highly ordered columnar phases with homeotropic alignment upon cooling, in which very narrow intercolumnar space of 5 Å was estimated. The resulting columnar structure was quite stable and so densely packed that molecular motions in mesophases were thought to be confined.

Interestingly, these DLC materials showed fast ambipolar carrier mobility over 0.1 $cm^2$ $V^{-1}$ $s^{-1}$ in both columnar and crystalline phases in spite of a relatively small core size of truxene. These results suggest the windmill-shaped DLC molecules with alkyl substituents at bay positions give densely packed columnar phases, which are advantageous over conventional DLC molecules substituted with peripheral side chains for fast charge carrier transport.

In conclusion, the molecular design strategy we proposed, i.e., introduction of short side chains into bay positions of discotic cores (such as phthalocyanine, tetrabenzoporphyrin, HATNA and truxene), is able to effectively and easily induce homeotropic columnar mesophase, which mainly originated from their low isotropic temperature and strong affinity within columnas. Furthermore, shorter side chain used in homeotropic columnar phases form a much narrower intermolecular distance around 5-10 Å between adjacent columns, contributing to suppressing the molecular motions (translational and rotational). On the other hand, what’ more important is to expose the peripheral phenyl ring , thus leading to the possibility of 2D charge carrier transport between columns and less static defects along quasi one-dimensional columns, meanwhile forcing a face-to-face stacking of molecular cores is expected to maximize intermolecular couplings, thereby enhancing charge carrier transport within columns.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).