論文 / 著書情報
Article / Book Information

題目(和文)	深いLUMOレベルを目指した液晶性有機半導体の合成と特性に関する研究
Title(English)	Study on Synthesis and Characterization of Liquid Crystalline Organic Semiconductors toward Having Low-LUMO Level
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11343号, 授与年月日:2019年12月31日, 学位の種別:課程博士, 審査員:飯野 裕明,梶川 浩太郎,間中 孝彰,大見 俊一郎,石川 謙,加藤 隆志,清水 洋
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11343号, Conferred date:2019/12/31, Degree Type:Course doctor, Examiner:,,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Outline of Thesis

Study on Synthesis and Characterization of Liquid Crystalline Organic Semiconductors toward Having Low-LUMO Level

By Yang Ming-Cong, supervised by Prof. Hiroaki Iino and Prof. Takashi Kato

This thesis consists of the following seven chapters.

Chapter 1 is the introduction part of this thesis. Organic electronics, organic semiconductor materials including liquid crystalline organic semiconductors, the mesophases of liquid crystals, and the advantages of liquid crystalline organic semiconductors are introduced in this chapter, which form the background of this study. The motivation and research objective of this thesis are also described.

Chapter 2 is the experimental section of this thesis. The materials used in this study, purification methods, and fabrication and characterization techniques are introduced in this chapter.

The main experiment part is from chapter 3 to chapter 6 as following.

In chapter 3, the pyridine with six-electron π-conjugated system and nitrogen atom having a sp2 hybridized orbital show stronger electron affinity than benzene with same six-electron π-conjugated system due to the electron negative of nitrogen atom larger than carbon atom. Thus, the nitrogenous aromatic compounds with sp2 hybridized orbital nitrogen, namely imine group, have strong electron affinity. In combination with quantum chemical calculation, the chrysene and the chrysene analogs with two sp2 nitrogen in different position of structure had been simulated and showed their lowest unoccupied molecular orbital (LUMO) level from 0.195eV to 1.051eV in single molecule state. In previous research, one of them called isoquino[8,7-h]isoquinoline (IQIQ) had been synthesized and studied in liquid crystalline phase and electron transport, which exhibited the LUMO level of -3.3 eV by experiment and of 0.83eV by calculation. The LUMO level of dibenzo[c,h][2,6]naphthyridine(DBN) was estimated as 1.051eV lower than the LUMO level of IQIQ. Thus, the DBN had been determined as the π-conjugated moiety of objective liquid crystal molecule. Furthermore, the asymmetric structure modification of DBN was done in thesis because this structure is helpful to gift the material highly ordered mesophase. The mono-side chain DBN of 2-decyldibenzo[c,h][2,6]naphthyridine (C10-DBN) showed only crystal phase with

liquid-like state by X-ray pattern but without typical liquid crystal texture by POM image, indicating it may be at critical state to liquid crystal phase. Thus, three kinds of strategies were applied for structure modification of C10-DBN. First is that increasing length of side chain of C12-DBN; second is that inducing the chlorine in para position to side chain of structure of C10-DBN providing the dipole moment or as the reacted point for any other particles; third is phenyl modification of DBN such as phenyl-BTBT-C10 that show highly order mesophase, i.e., SmE and present good quality in thin film fabrication with high mobility in polycrystalline thin film with bilayer structure. The synthesis route for three strategies were designed and improved to good yield. The first strategy did not appear typical texture of liquid crystal phase but both of second and third strategies have liquid crystal phase, such as Cl-DBN-C10 showed SmA and SmE phases, Ph-DBN-C10 showed SmA and SmH phases and DBN-Ph-C10 showed only SmA phase. However, the LUMO level of DBN core after phenyl modification exhibited shallower value of -3.1 eV. On the other hand, the LUMO level of Cl-DBN-C10 showed -3.4 eV. The charge carrier transport properties of Cl-DBN-C10 in SmA phase were measured by Time of Flight (TOF) technique, whose mobility depended on Poole-Frenkel like electric field and temperature dependence and was on the order of 10^{-5} cm^2/Vs. Cl-DBN-C10 derivative had large permanent dipole moment and the charge carrier transport is analyzed by Gaussian disorder model with large energetic distribution of density of state of 109 meV. Unfortunately, transient photocurrent curves in highly ordered phase (SmE) could not have well-defined even if transient photocurrent curves were plotted with the double logarithm. This may be attributed to the impurity in SmE phase trapping the photo-generated carriers.

In chapter 4, in order to confirm the effect of permanent dipole moment leading to small mobility and large energetic distribution in Cl-DBN-C10, the DBN with symmetrical dialkylated side chain of octyl (C8), decyl (C10), dodecyl (C12) were synthesized in good yields, and all of them exhibited liquid crystal phase, which was studied by variable temperature X-ray diffraction (XRD), differential scanning calorimetry (DSC), and polarization optical microscopy (POM). Two of them, 2,8-didecyldibenzo[c,h][2,6]naphthyridine (C10-DBN-C10) and 2,8-didodecyldibenzo[c,h][2,6]naphthyridine (C12-DBN-C12), showed low ordered smectic mesophase of smectic C (SmC) phase, while the other, 2,8-dioctyldibenzo[c,h][2,6]naphthyridine (C8-DBN-C8), showed a highly ordered smectic phase of smectic G (SmG), in addition to SmC phase. However, the mobility of C10-DBN-C10 without dipole moment showed similar value to that of Cl-DBN-C10, indicating that the low mobility was not determined by permanent dipole moment in DBN system or this was ionic transport. Thus, excluding the ionic transport at first by

testing if mobility of C10-DBN-C10 has electric field dependence and found that the low mobility may be attributed to the van der Waals disorder, quadrupole effect, or trapping effect, which need further study in the following chapter.

In chapter 5, C8-DBN-C8 has been studied to confirm that the low mobility and electric field dependence of mobility had general concept rather than special character of C10-DBN-C10. The carrier transport properties are characterized by TOF experiments, not only revealing that electron and hole mobility on 10^{-5} $cm^2V^{-1}s^{-1}$ in SmC phase, but also is Pool-Frenkel like electric field dependence and temperature dependence of mobility, which is same as that of C10-DBN-C10. The multiple trapping model and the Gaussian disorder model are used to analyze the charge carrier transport properties, and the electron transport in the SmC phase of C8-DBN-C8 matched the Gaussian disorder model very well, indicating description of the localized state in SmC phase as the energetic and positional Gaussian distribution for electron. The comparison of energetic disorder and mobility of C8-DBN-C8 with these of C12-CR-C12 and C12-IQIQ-C12 concluded that the mobility could be reduced by disorder, i.e., imine group in conjugated system which was consisted with the larger disorder parameter of 85meV of C8-DBN-C8 estimated by Gaussian disorder model. Furthermore, the large disordered system in DBN derivatives came from the induced dipole moment in π conjugated systems of C8-DBN-C8 and C12-IQIQ-C12 by imine group, which induced larger energetic disorder of the electronic polarization energy that is determined by the interaction between ionized molecule and surrounding molecules, and the mobility of DBN and IQIQ derivatives are decreased.

In chapter 6, the LUMO level of DBN derivatives, -3.3 eV, is difficult to make the organic field effect transistor (OFET) under atmospheric conditions. The lower LUMO level than -4.3 eV is necessary for air-stable OFET materials. To obtain further lower LUMO level, I pay attention on other molecules of tetracene which have lower LUMO level than that of DBN derivatives by quantum chemical calculation and it is easy to be incorporated quinone moiety into the four rings system, which is strong electron acceptor that is helpful to realize the materials having deeper LUMO level. I synthesized three derivatives and evaluated the liquid crystallinity and the LUMO levels. And the charge carrier transport properties of these derivatives were measured by TOF technique.

In chapter 7, I summarized the research results achieved from each of the above chapters and described the future perspective of this study.