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)	論文要旨
Type(English)	Summary

博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	電気電子 電気電子	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Liquid crystalline organic semiconductors became a member of organic semiconductor materials, which give us three benefits, i.e., easily fabrication of uniform thin films, controllable molecular orientation, and high mobility. However, the electron deficient liquid crystalline organic semiconductors for electron transport or electron accepter are few compared with materials for hole transport. The electron transport materials are necessary for organic light emitting diode, organic photovoltaic cell, and n-channel organic field effect transistor (OFET), which require the deep lowest unoccupied molecular orbital (LUMO) level from -3 to -4 eV. Thus, the π-conjugated moiety for charge carrier transport of liquid crystal molecule should have enough deep LUMO level, whose LUMO level could be modulated by the chemical modification in π-conjugated moiety of liquid crystal molecule by electron withdrawing group and strong electron affinity π-conjugated moiety with linear shape expected for smectic liquid crystal phase. In this thesis, I study the molecular design and synthesis for low-LUMO level liquid crystalline organic semiconductor and evaluation of the liquid crystalline and charge carrier transport characterization.

In order to realize liquid crystals having low-LUMO level, I focused on the pyridine ring because it is six-electron π-conjugated system and nitrogen atom having a sp2 hybridized orbital, which show stronger electron affinity than benzene ring. In combination with quantum chemical calculation, the LUMO levels of chrysene and the chrysene analogies with two sp2 nitrogen in different position of structure were simulated and estimated as -0.195 eV to -1.051 eV in single molecule state. In previous research, one of them called isoquino[8,7-h]isoquinoline (IQIQ) had been synthesized and the liquid crystalline and electron transport properties had been investigated; IQIQ derivative exhibited the LUMO level of -3.3 eV by experiment. The LUMO level of dibenzo[c,h][2,6]naphthyridine (DBN) was estimated as 1.051eV lower than the calculated LUMO level of IQIQ. Thus, the DBN was determined as the π-conjugated moiety of objective liquid crystal molecule.

The asymmetric structure DBN derivatives were synthesized because asymmetric structure is helpful to exhibit highly ordered smectic phases. The mono-side chain DBN derivative, C10-DBN, showed only multi-crystal phases without liquid crystal phase. On the other hand, chlorine atom modification in para position to side chain of structure of C10-DBN providing the dipole moment, Cl-DBN-C10, and phenyl modification of DBN such as phenyl-BTBT-C10 showed smectic A (SmA) phase and

highly ordered smectic phases. Cl-DBN-C10 derivative showed low-LUMO level, -3.4 eV, measured by photoelectron yield spectroscopy. However, the LUMO level of Ph-DBN derivative exhibited shallower value of -3.1 eV than that of Cl-DBN-C10 derivative. The charge carrier transport properties of Cl-DBN-C10 were evaluated by Time of Flight (TOF) technique, whose mobility was obtained on the order of 10^{-5} cm^2/Vs in SmA phase. Interestingly, the mobility depended on electric field and temperature in the wide temperature range of SmA phase and the carrier transport properties were characterized to be an energetic distribution of the density of states (DOS) of 109meV on basis of Gaussian disorder model for the first time. Small mobility of 10^{-5} cm^2/Vs and the wide distribution of DOS were strongly suggested to the effect of permanent dipole moment in chloro-substituted DBN moiety.

In order to confirm the effect of the dipole moment leading to the low mobility and wide distribution of DOS in Cl-DBN-C10, symmetric dialkylated DBN derivatives were synthesized and evaluated the liquid crystalline phase and charge carrier transport properties. These symmetric dialklyated DBN derivatives did not have any permanent dipole moment. Two dialkylated DBN derivatives, C10-DBN-C10 and C12-DBN-C12, showed low ordered smectic phase of SmC, while C8-DBN-C8 showed a highly ordered smectic phase of SmG in addition to SmC phase. The LUMO level of dialkylated DBN derivatives showed -3.3 eV. For C8-DBN-C8 and C10-DBN-C10, the charge carrier transport properties were studied by TOF technique. In SmC phase, transient photocurrents showed well-defined transits, which gave us to evaluate exact mobility. The mobility for negative carriers are depended on electric field and temperature, which conduced that the conduction mechanism is hopping transport for electron. However, it was unexpectedly found that dialkylated DBN derivatives exhibited quite low mobility on the order of 10^{-5} $cm^2V^{-1}s^{-1}$, which is two orders of magnitude smaller than that of dialkylated chrysenes derivative. The charge carrier transport properties of dialkylated DBN derivatives were also characterized to be wide energetic distribution of DOS of 85meV on basis of Gaussian disorder model, in spite of no permanent dipole moment of DBN core. It would be attributed to van der Waals disorder by induced dipole moment effect lead by imine group in DBN core.

In summary, I designed and synthesized new rod like liquid crystal materials, DBN derivatives, which have low LUMO level and Smectic liquid crystal phases. The carrier transport properties in SmC phase of these DBN liquid crystalline phases revealed that the induced dipole moment had effect on the wide energetic distribution of DOS on basis of Gaussian disorder model, which gave us the idea to realize the small energetic distribution and high mobility.