論　文　の　要　旨

題　目　Synthesis of novel π-conjugated oligomers and D-A type copolymers for optoelectronic applications

（光電子デバイスへの応用を目指したπ-共役オリゴマーおよびD-A型コポリマーの合成）

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In the past years, the research of conjugated conductive organic materials (COMs) has developed energetically. Not only the synthesis of COMs, the characterization and processing were also developed owing to the large efforts of both academic and industrial research laboratories. The essential structural characteristics of COMs are the conjugate π-electron systems, which is formed by the p_z orbital of sp^2-hybridized C atoms in the molecules. The electronic properties of a molecule depend on factors like the conjugation length or the presence of electron donating or withdrawing groups. Thus organic chemistry offers a wide range of possibilities to tune the optoelectronic properties of COMs.

COMs have a very promising future, and they permit the fabrication of solar modules with several potential advantages, including light weight, flexibility, low cost synthesis and production, the possibility of creating large-area devices, and easy manufacture of thin film devices by vacuum evaporation/sublimation or solution cast or printing technologies. Furthermore, COMs thin films may show high absorption coefficients. Several excellent advantages and properties lead to the general optoelectronic applications. An important device application of COMs is in organic photovoltaic cells (OPVCs). In spite of their high absorption coefficient, which exceeds 105 cm^{-1} in most materials, the application of COMs in OPVCs faces the problem of the large exciton binding energy which prohibits efficient exciton dissociation. This can be overcome by making use of a photoinduced charge transfer between an electron donor like conjugated polymer and the fullerene $PC_{61}BM$ as an acceptor. Due to the short exciton diffusion length of typically 10nm, efficient OPVCs use the so-called bulk-heterojunction concept of mixing donor and acceptor in one single layer. In spite of the huge progress recently achieved, there are still challenges to achieve sufficient lifetime of OPVCs under ambient conditions or the availability of low-band gap materials to make better use of the solar spectrum. The organic field effect transistor (OFET) was another application of COMs we have paid attention to. That uses an electric field to control the shape and hence the conductivity of a channel of one type of charge carrier in COMs. Spin-coating is a widely used technique for the production of small area thin film. I also use this method to fabricate the photovoltaic devices.

My research attention was paid to the conductive polymers and oligomers. In this thesis, I describe the synthesis of novel π-conjugated oligomers and D-A type copolymers for optoelectronic applications. The main contents of this thesis were arranged as follow.

In chapter 1, general introduction of COMs included the historical background, wide applications, basic principles and instrumentation. In the last part, I illustrated the purpose of this study.

In chapter 2, tow novel conjugated copolymers (**PM1**: poly[(4,8-dihexyloxylbenzo[1,2-*b*;4,5-*b*']-dithiophene)-*alt*-((*E*)-2,3-bis(2-thienyl)acrylonitrile)] and **PM2**: poly[(4,8-didecyloxylbenzo[1,2-*b*;4,5-*b*']dithiophene)-*alt*-((*E*)-2,3-bis(2-thienyl)acrylonitrile)]) comprising (E)-2,3-bis(2-thienyl)acrylonitrile and benzo[1,2-b;4,5-b']dithiophene derivatives are designed and synthesized to be applied as an electron donor material in polymer solar cells blended with $PC_{61}BM$ as an electron acceptor. These copolymers show a good thermal stability with a 5% weight loss temperature beyond 340 °C, and their films exhibit a broad absorption band with a low optical bandgap of ca. 1.84 eV. Polymer solar cells based on **PM2**, prepared under optimized preparation conditions, are found to exhibit a short-circuit photocurrent of

10.71 mA/cm^2, an open-circuit photovoltage of 600 mV, a fill factor of 65%, and a power conversion efficiency of 4.17% under AM 1.5 illumination conditions, 100 mW/cm^2.

In chapter 3, conjugated polymers (Poly[(benzodithiophene-2,6-diyl)(2,5-thienylene)] (**PS0**) and its derivatives with π-conjugated side-chains (**PS1**: thienylethenyl and **PS2**: thienylcyanoethenyl)) were designed and synthesized in order to study the effects of the conjugated side-chains on the optical, electrochemical, and photovoltaic properties of the copolymers. It was found that the electronic properties and energy levels of the copolymers can be effectively tuned through changing a conjugated side-chain attached to a polymer backbone. The conjugated side-chain type polymers exhibited better light harvesting ability and deeper HOMO energy levels. Polymer solar cells based on copolymer/$PC_{61}BM$ exhibited power conversion efficiencies of 2.85%, 3.44%, and 4.49%, respectively, for **PS0**, **PS1**, and **PS2** under a simulated solar light (AM1.5G, 100 mW/cm^2), compared with 4.17% for a main-chain type copolymer corresponding to **PM2**. The results reveal that the introduction of the conjugated side-chain with an electron-deficient group to a polymer backbone is an effective approach for improving the performance of the photovoltaic materials.

In chapter 4, Five sorts of soluble oligothiophenes (trimer to undecamer) containing 3,4-ethylenedioxythiophene (EDOT) were synthesized, and their optical and electrochemical properties were investigated in relation to the chain length of oligothiophenes and the number of EDOT units. The introduction of the EDOT unit into a main oligothienylene unit induced a red shift of absorption bands and a negative shift of oxidation potentials. The conductivity of an electrochemically oxidized film of undecamer was found to be around 1 S/cm. A thin-film field effect transistor was preliminary fabricated with neutral undecamer films and the hole mobility was determined.

In Chapter 5, summary of this dissertation was described finally.