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題目(和文)	有機薄膜トランジスタおよび熱電変換素子への応用を目指したベンゾビスチアジアゾール誘導体から成る半導体高分子の開発
Title(English)	Rational Design of Semiconducting Polymers Based on Benzobisthiadiazole Derivatives for Organic Thin Film Transistors and Thermoelectric Devices
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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質　専攻	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 ）

Conjugated semiconducting polymers are promising materials for organic field-effect transistors (OFET), organic photovoltaics (OPV), and organic thermoelectrics (OTE) due to their versatile chemical synthesis, solution-processability at low temperature and mechanical flexibility.

In the present thesis, new semiconducting polymers based on benzobisthiadiazole (BBT) and its related heterocycles [thiadiazolo-benzotriazole (SN), selenadiazolo-benzotriazole (SeN) and selenadiazolo-benzothiadiazoles (SeS)] were developed by using Pd-catalyzed Suzuki and Stille polycondensation. Taking into account their characteristic features, these materials were applied to OFET and OTE. The relationship between the polymer structure and the device performances were investigated and discussed in details.

Chapter 1 introduced the discovery, development, and applications of semiconducting polymers. OFET and OTE device structure, operation, and characterizations were summarized. Most importantly, a general polymer design guideline for high-performance OFET and some representative examples of BBT-based semiconducting polymers were described in combination with some representative polymers in OTE application.

Chapter 2 summarized the general experimental procedures, such as fabrication and characterization of polymer thin film transistors (TFTs), OTE devices, atomic force microscopy (AFM) measurements and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements.

Chapter 3 reported a new series of BBT-based donor-acceptor (D-A) copolymers with different π-conjugated bridges developed for air-stable ambipolar polymer TFTs. The prototype polymer PBBT-FT without additional π-conjugated bridges showed p-type dominant TFT performances. However, PBBT-T-FT with the thiophene bridges displayed lower but more balanced μ_h and μ_e values. This trend was further accelerated when the electron-accepting thiazole bridges were employed. The

PBBT-FT-based devices showed remarkable stabilities under ambient conditions with the μ_h of ~0.1 $cm^2 V^{-1} s^{-1}$ and the μ_e of ~0.002 $cm^2 V^{-1} s^{-1}$ being retained even after one month. This study offers a better understanding of the effects of the π-conjugated bridges on the ambipolar transport and reveals that BBT-based D-A copolymers are promising materials for high-performance stable TFTs.

Chapter 4 focused on the design and synthesis of novel [1,2,5]selenadiazole[3,4-*f*]benzothiadiazole and [1,2,5]chalcogenazolo[3,4-*f*]benzo[1,2,3]triazole-based π-conjugated polymers. Thus, a new series of copolymers containing BBT derivatives, namely PSN, PSeN, and PSeS, were designed and synthesized. The heteroatoms substitution within the triple-fused-ring structure offered the opportunity to tailor the optoelectronic properties, molecular organizations, and charge carrier transport properties in polymeric TFTs. PSN showed *p*-type unipolar TFT performances with a high hole mobility up to 0.65 $cm^2 V^{-1} s^{-1}$. Moreover, the majority charge-carrier was further converted to electron when nitrogen atom was replaced by sulfur atom. Thus, PSeS exhibited *n*-type dominant charge transport properties with electron mobilities up to 0.087 $cm^2 V^{-1} s^{-1}$. This simple and effective approach will guide the way into developing high-performance ambipolar and/or n-channel semiconducting polymers for TFTs.

Chapter 5 focused on the rational design of highly crystalline benzotriazolothiadiazole-based conjugated polymers with tunable polymer packing orientation and charge polarity in high-performance organic thin film transistors. A remarkably high hole mobility of 3.22 $cm^2 V^{-1} s^{-1}$ was obtained for the conventional top contact/bottom gate TFT devices based on PSNVT-DTC8. It should be noted that this value is the highest among the previously reported BBT and its analogues-based semiconducting polymers. The oxygen atom substituted PSNVF-DTC8, composed of potentially bio-renewable furan rings, also exhibited the high hole mobility over 1 $cm^2 V^{-1} s^{-1}$, whereas the nitrogen atom substituted PSNVTz-DTC16, composed of electron-accepting thiazole rings, displayed n-type dominant ambipolar charge transport properties with an electron mobility up to 0.16 $cm^2 V^{-1} s^{-1}$. The design strategies in this study will open a new door to developing more excellent semiconducting polymers for next-generation organic electronics.

Chapter 6 reported a new series of electron-deficient semiconducting polymers based on BBT derivatives, namely pSN-NDI, pSeN-NDI, pBBT-NDI, and pSeS-NDI. It was found that the E_{LUMO} of pBBT-NDI and pSeS-NDI reached as deep as −3.93 eV and −4.03 eV, respectively, which is favorable for easy injection and efficient transport of electrons. Polymer TFTs with gold source and drain electrodes resulted in unipolar electron transport properties with electron mobility (μ_e) up to 0.039 $cm^2 V^{-1} s^{-1}$

tested under ambient conditions. Furthermore, pBBT-NDI showed remarkable air-stability, maintaining 80 % of its original μ_e values after one month storage in air.

Chapter 7 focused on synthesis and characterization of high-performance electron deficient BBT-naphthodithiophenediimide copolymers. Unipolar n-type TFT and OTE devices were fabricated. Although both polymers exhibited similar energy levels with inherently low lying LUMO below -4.4 eV, PNDTI-BBT-DP with 3-decylpentadecyl having a greater distance of the bifurcation point from the polymer backbone demonstrated higher μ_e of 0.31 $cm^2 V^{-1} s^{-1}$, σ of 5 S cm^{-1} and PF of 14.2 μW $m^{-1} K^{-2}$. Thus, it can be concluded that tuning the intermolecular interaction and consequently the crystallinity by the alkyl side chain is a promising strategy for developing superior OTE materials.

Finally, Chapter 8 summarized the achievements of each chapter.