

Development of Chalcogenophene-Based π - Conjugated Molecules and Their Applications in Optoelectronic Devices

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論 文 名 : Development of Chalcogenophene-Based π -Conjugated Molecules and
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(カルコゲノフェンを基盤とする π 共役分子の開発と光電子デバイスへの応用)

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論 文 内 容 の 要 旨

Chalcogenophene-based π -conjugated molecules have seen widespread attention in organic semiconductors, particularly for organic field-effect transistors (OFETs) and organic photovoltaics (OPVs). An intensive effort has been devoted to seeking high-performance materials. Their properties are significantly dependent on the molecular structure, such as which element to introduce, how to extend the π -conjugation, fused/non-fused, and so forth. Proper molecular design can modulate various properties, including absorption, photoluminescence, energy levels, self-organized behavior. Therefore, this dissertation focused on developing novel chalcogenophene-based π -conjugated molecules with unique structural features and fascinating characteristics in each Chapter. The structure–property relationship was investigated in detail to establish a design strategy going beyond the traditional framework for further development.

Chapter 2 deals with a new design strategy employing a U-shaped thienoacene as an alternative molecular configuration to conventional linear-shaped thienoacenes. It was revealed that U-shaped thienoacene had both high solvent solubility and self-assembling ability, allowing to produce highly crystalline thin films via a facile dip-coating method. It should be worthwhile that U-shaped molecules formed unique bilayer packing in their thin films with a head-to-head arrangement. OFETs based on these thin-films exhibited high carrier mobilities despite their simple and low-cost solution process.

In Chapter 3, U-shaped heteroacene-based organic semiconductors were further explored, motivated by the findings in Chapter 2. The effect of the introduction of heavy chalcogen atoms into the U-shaped heteroacenes was systematically investigated in terms of the number and positions of chalcogen substitution. It was revealed that a small alteration on the same molecular scaffold, even changing one of three chalcogen atoms, could largely modulate the optoelectronic properties, as well as packing structure in their crystals. The origin of the unique bilayer lamellar structure and high carrier mobility was elucidated by X-ray single-crystal analysis and quantum chemical calculations.

Chapter 4 described the development of perylenediimide (PDI)-fused heterohelicenes by combining hetero[7]helicenes and two PDIs forming helically-annulated π -conjugation. Heterohelicenes showed optoelectronic properties and self-organization behavior that reasonably reflect the characteristics of both helicene and PDIs. It was demonstrated that helical π -extended molecular structure contributed to the chiroptical response (i.e., circular dichroism and circularly polarized luminescence) and the alleviated crystallinity favorable for bulk heterojunction layer in OPVs. As a result, OPVs employing PDI-fused heterohelicenes as non-fullerene acceptors exhibited high power conversion efficiency values exceeding

monomeric unmodified PDI. Enantiomer-dependent solid-state properties were also investigated in terms of self-organized nanostructures, thin-film morphologies, and OPV performances.

Chapter 5 found that thiophene-based p-type semiconducting polymer containing thienylene–vinylene–thienylene units showed a liquid-crystalline nature. The alternation of the self-organized nanostructures in both bulk and thin films was confirmed in detail through X-ray diffraction measurements. The hole mobilities in thin-film OFETs were enhanced by appropriate thermal treatment via mesophase temperature due to enhanced molecular ordering. Additionally, by virtue of its thermoplasticity, this polymer could be processed into fine microfibers, functioning as a p-type active channel for charge transport.

In Chapter 6, a six-ring-fused thienoacene featuring S-shaped π -core was developed for solution-processable OFET material. Generally, solvent solubility and crystallinity are in a competitive relation with each other, which should be solved for solution-processable organic semiconductors. However, S-shaped thienoacene had excellent solvent solubility and self-organized behavior, enabling thin-film fabrication via a dip-coating method even at room temperature. Thin-film OFET exhibited high carrier mobilities comparable to amorphous silicon.

In Chapter 7, the dissertation is summarized, and perspectives are discussed.

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