

# 論 文 の 要 旨

題 目      Design, Synthesis and Characterization of Organic  $\pi$ -Conjugated Compounds Incorporating Group 14 and 15 Heavy Elements  
(14 および 15 族重元素を含む有機 $\pi$ 共役化合物の設計、合成および特性)

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Organic  $\pi$ -conjugated materials are a class of organic molecules or polymers with a specific electronic structure, in which the internal  $\pi$ -electron system can form a continuous conjugated structure, allowing  $\pi$ -electrons to move freely within the molecule. This group of substances is attractive because of its outstanding and adaptable structural features, a broad spectrum of optical attributes, and the wide variety of potential uses in which they can be employed. Organic  $\pi$ -conjugated materials can control the energy level at the molecular level. Through reasonable selection and design of molecular structure, the electronic energy level, band gap and optical absorption and emission characteristics of the materials can be regulated, to optimize their performance in specific applications.

In introduction presented motivation and background of this thesis. The introduction of noncovalent interaction is one of the important strategies for designing new organic  $\pi$ -conjugated molecular systems. The significance of non-covalent interactions at both inter-and intramolecular levels has been thoroughly examined in the realms of materials science and various other research domains. Introducing elements to construct new  $\pi$ -conjugated systems is an important research direction in the field of organic electronic materials. Triazoles are aromatic ring systems with a five-membered structure that consists of three nitrogen atoms in sequence and two double bonds. Apart from their distinctive structural characteristics, such as high dipole moments and molecular rigidity, triazoles have exceptional accessibility and ease of modification. Indeed, they have been extensively employed in creating functional materials for a wide range of use. Designing molecular structures and synthesizing Group 14-containing building blocks are efficient approach for constructing innovative  $\pi$ -conjugated structures. Group 14 metalloles, such as siloles and germoles are considered valuable components for the construction of functional compounds due to that the silane moiety interacts with the butadiene moiety to give rise to low-lying LUMO energies and relatively narrow band gaps. Dithienosilole serves as a typical silicon-based unit used in the creation of conjugated organic materials. Wang and coworkers have prepared dithieno[2,3-b:4,5-c']silole derivatives and prepared conjugated polymers using them as the monomers. In this unsymmetrical unit, one thiophene ring can be incorporated into conjugated oligomeric and polymeric systems and the introduction of a functional group (R) on the other thiophene ring enables fine-tuning of the electronic state of the dithienosilole unit. Meanwhile, germanium-based congeners are relatively underexplored. Therefore, the exploration of unsymmetrical dithienogermoles as a promising building block is another method for the development of functional materials

In Chapter 1, intramolecular non-covalent interactions provide a convenient method for enhancing the molecular planarity of organic semiconductors through conformational locks in their design. This approach effectively decreases the band gap, as evidenced by phospho-substituted bisbenzofuran derivatives (BFP) featuring non-covalent P $\cdots$ O interactions. Additionally, inclusion of bulkier elements may lead to stronger

noncovalent interactions. Consequently, bibenzofurans and bibenzothiophenes substituted with bismuth, antimony, and arsine have been synthesized by the author. An X-ray diffraction analysis of a single crystal indicated that  $\text{Bi}\cdots\text{O}$ ,  $\text{Sb}\cdots\text{O}$ , and  $\text{As}\cdots\text{O}$  substances were involved in attractive noncovalent interactions that contributed to self-planarization and rigidification of the crystal. QTAIM analysis identified BCPs between  $\text{Bi}\cdots\text{O}$ ,  $\text{Sb}\cdots\text{O}$ , and  $\text{As}\cdots\text{O}$ , corresponding to van der Waals interactions as revealed by the interaction region indicator.

In Chapter 2, A triazolgermole ring condensed with a benzene or thiophene ring was synthesized. The thienotriazolgermole was subjected to bromination to produce the corresponding bromide, which was then transformed using the palladium-catalyzed Stille coupling reaction to yield thienotriazolegermole substituted with triphenylamine, resulting in an enhanced extension of conjugation. A combination of optical measurements, electrochemical calculations, and density functional theory are used to examine the electronic states of these triazolgermole derivatives. In photoluminescence measurements, thienotriazolegermole substituted with triphenylamine demonstrated clear solvatochromic properties. This indicates intramolecular charge transfer. This underscores the utility of the triazolgermole unit as an acceptor in donor–acceptor compounds. Furthermore, the author explored potential applications of thienotriazolegermole substituted with triphenylamine as a sensing material. (Figure 2)

Dithieno[3,2-b:4,5-c']germole was prepared as a new unsymmetrically condensed gemole. Benzo[4,5]thieno[2,3-c]germole was also prepared as the benzene-condensed analogue. The optical and electrochemical measurements were employed to analyze the electronic states and properties of these germoles, which are unsymmetrically condensed. This analysis was further supported by quantum chemical calculations on simplified model compounds. Stille cross coupling reactions of bromodithieno[3,2-b:4,5-c']germole with di(stannylthienyl)- and di(stannylthiazolyl)benzothiadiazole provided conjugated donor-acceptor oligomers, which exhibited clear solvatochromic behaviors with respect to the photoluminescence spectra, indicating potential applications of the dithieno[3,2-b:4,5-c']germole unit as an electron donor of donor-acceptor systems