

論 文 の 要 旨

題 目 Synthesis of new thiazole-condensed germoles and their derivatives with enhanced electron-deficient properties

(電子欠損特性が向上した新規チアゾール縮環ゲルモールおよびその誘導体の合成)

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Organic π -conjugated materials have received much attention in the past decade owing to their application to organic electronic devices, such as organic solar cells (OSCs), organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs), which exhibit several advantages including low weight, low cost, high flexibility and adjustable electronic states in comparison with inorganic material-based devices. The development of high-performance organic semiconductors in devices, which relies on the synthesis of π -conjugated blocks with proper electronic states, is required for the progress of organic electronics.

In Chapter 1 presented motivation and background of this thesis. The introduction of a heteroatom bridge to aromatic units such as thiophene, pyridine, furan, selenophene, and benzene is a promising method to tune the electronic state. Heteroatom bridges can modify the electronic state not only by electronic effects of the heteroatom but also by steric effects enhancing coplanarity of the aromatic units. However, their polymers are usually p-type semiconductors (hole-transporting). In contrast to p-type polymers, which exhibit impressive device performances with high hole mobilities exceeding $10 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, n-type (electron-transporting) polymers have been limited due to the presence of minority electron-deficient groups and because the synthesis process is complicated; these disadvantages have impeded the development of n-type semiconductor materials. In addition, n-type polymers show relatively low device stability because of their relatively high sensitivity to moisture in the photoexcited and carrier-doped states, and this issue has hindered their application in devices. Clearly, the development and design of new n-type organic semiconductors is imperative.

Several thiazole-containing compounds have been reported, such as cyclopentadithiazole (CDTz), indacenodithiazole (IDTz), 4,7-di(thiazol-2-yl)-2,1,3-benzothiadiazole (DTzBT), bithiazole imide (BTzI), and dithiazolythienothiophene bisimide (TzBI). Polymers with these thiazole-containing units have been studied as semiconductors in OFETs with enhanced electron-withdrawing properties. For example, IDT- and IDTz-ladder-type monomers were copolymerized with 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole (DTBT) or DTzBT units to obtain ambipolar polymers PIDT-DTBT, PIDT-DTzBT, and PIDTz-DTBT. Notably, these thiazole-based polymers showed improved electron-transporting properties compared with that of thiophene congeners, indicating that introducing weak donor units in D-A polymers is beneficial to generate efficient electron-transporting materials.

In Chapter 2, new thiazole-condensed single and double germole derivatives (DTzG and GIDTz) were prepared as weak donor units by the reactions of respective lithiated thiazole compounds with

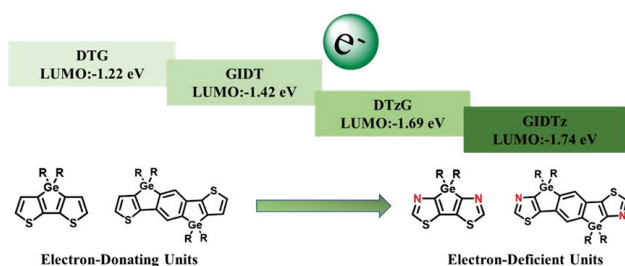


Figure 1. Schematic diagram of the structures and HOMOs/LUMOs of germoles compounds.

derivatives possess enhanced electron deficiency compared with thiophene-based germole congeners reported previously. This is supported by density functional theory (DFT) calculations that reveal lower-lying HOMO and LUMO for the thiazole-condensed germoles than the thiophene-condensed congeners, as shown in Figure 1.

In Chapter 3, distannylated DTzG and GIDTz were copolymerized with dibrominated 2,1,3-benzothiadiazole and 4,7-di(thiazol-2-yl)-2,1,3-benzothiadiazole to produce four new donor-acceptor conjugated copolymers, as shown in Figure 2. The optical, electrochemical, and thermal properties of the copolymers were characterized, and intramolecular charge transfer was evaluated

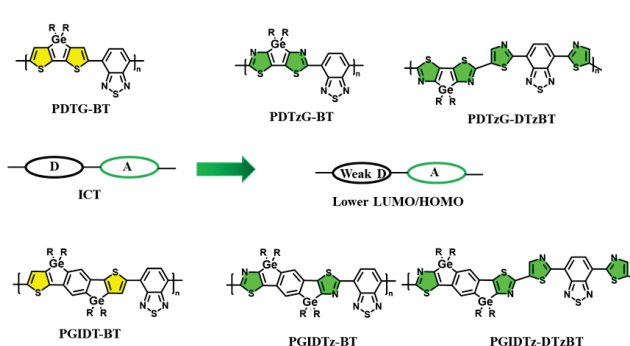


Figure 2. Schematic diagram of the structures of copolymers.

on the basis of solvatochromic behavior in the photoluminescence spectra. DFT calculations revealed that these thiazole-containing copolymers exhibited lower HOMO and LUMO energy levels than those of thiophene-based congeners PDTG-BT and PGIDT-BT, and this finding agreed with the experimental results. The intramolecular noncovalent S–N and N–H bond interactions and the effects of the bridging atom (C or Ge) on the HOMO and LUMO energy levels were also suggested by the DFT calculations.

In Chapter 4, dicyanovinyl-capped dithiazologermoles (DTzG-DCV and GIDTz-DCV) were synthesized, and their optical and electrochemical properties were investigated. Both DTzG-DCV and GIDTz-DCV showed solvatochromism, exhibiting red shifts of the photoluminescence (PL) bands

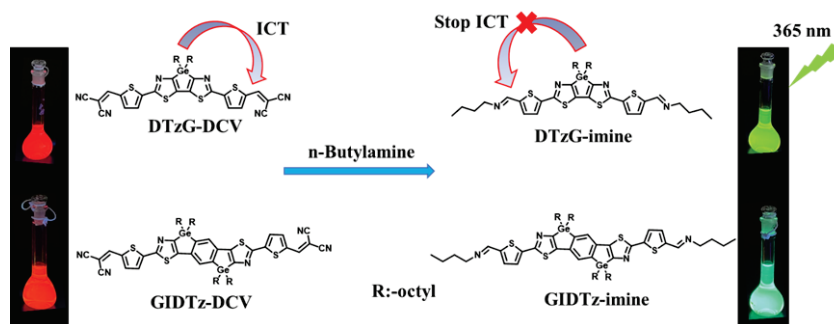


Figure 3. Schematic diagram of the reaction of stopping ICT.

dichlorodioctylgermane. The compound structures were verified by ^1H NMR, ^{13}C NMR, and mass spectral measurements. The single-crystal structure of brominated GIDTz shows high planarity of the fused ring system. The optical and electrochemical properties of DTzG and GIDTz derivatives indicate that the

with increasing solvent polarity from toluene to DMF, likely due to intramolecular donor-acceptor interaction. Moreover, they served as selective PL sensors, with spectral changes in the presence of amines and

fluoride and iodide ions, but not other halogen ions, in solution. DTzG-DCV and GIDTz-DCV

underwent a quick and high-yield reaction with n-butylamine to give imine derivatives, accompanied by PL color changes, as shown in Figure 3. Similar color changes were observed even in the solid state with n-butylamine and n-hexylamine. In contrast, reactions with secondary and tertiary alkylamines caused no obvious changes in PL color. The color changes are visible to the naked eye under irradiation with a portable UV lamp at 365 nm, and thus DTzG-DCV and GIDTz-DCV can be used for the quick and selective sensing of primary amines.

On the basis of the abovementioned results, the author developed strategies to enhance the electron-withdrawing properties of germales-based compounds by the introduction of thiazole units appropriately. The resultant compounds all showed lower LUMO energy levels than previously reported thiophene-based congeners. These are expected as weak donors for the construction of optoelectronic materials with weak donor-acceptor interaction for enhancing the n-type semiconducting properties and tuning the fluorescent behaviors.