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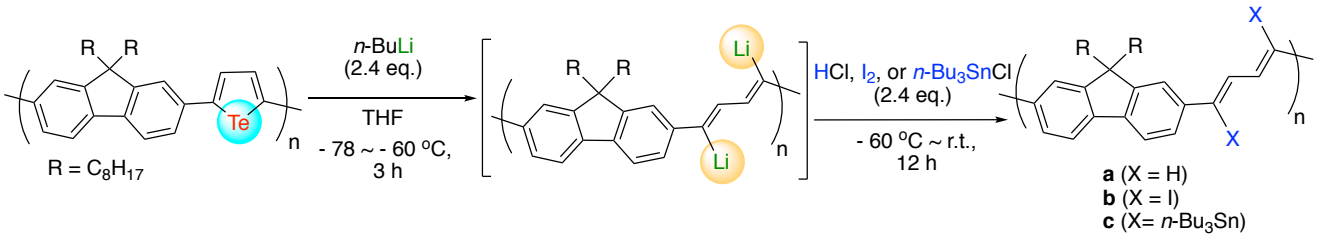
論文題目

“Chemical Modifications of Group 14-16 Element-containing π-Conjugated Polymers”

This thesis has dealt with new approaches to produce π-conjugated polymers containing group 14-16 heavier elements by facile chemical modifications of π-conjugated polymers containing heteroles such as tellurophene, phosphole, and stannole and unique features of the resulting π-conjugated polymers.

In *Chapter 1*, the research backgrounds related to π-conjugated materials, element-block-containing materials, main-chain reactive polymers, and chemical modification of heteroatom-containing π-conjugated polymers are described.

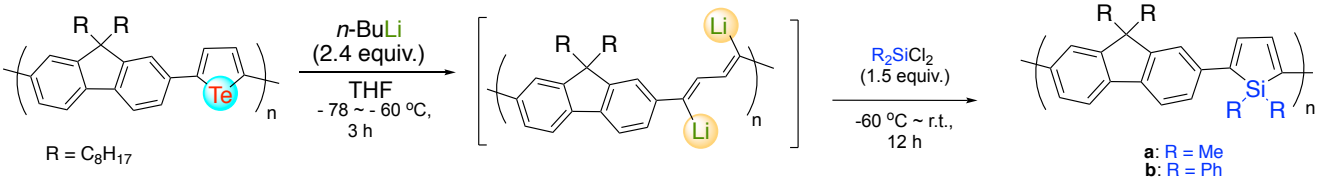
In *Chapter 2*, on the basis of the facts that tellurophene-containing π-conjugated polymers are obtainable from organotitanium polymers and that the tellurium atoms in the tellurophene derivatives can be transformed into lithium atoms, the synthesis of reactive lithiated polymer precursor and its transformations into some functionalized π-conjugated polymers are described (Scheme 1). For example, the lithiated polymer prepared is subjected to the reaction with tri-*n*-butyltin chloride to demonstrate its high reactivity.



Scheme 1

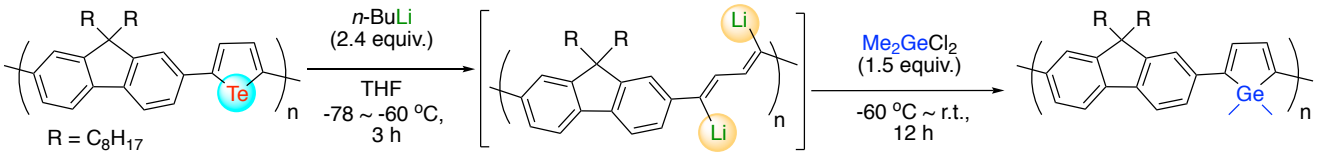
In *Chapter 3*, the reactions of reactive lithiated polymer precursor to produce π-conjugated polymers containing heteroles of group 14 elements are described.

In Section 1, the synthesis of silole-containing π-conjugated polymers is described. The lithiated polymer prepared is subjected to reactions with dimethylsilyl dichloride and diphenylsilyl dichloride to produce dimethylsilole- and diphenylsilole-containing π-conjugated polymers, respectively (Scheme 2). The low-lying LUMO level and optical property of silole-containing polymer are also described.



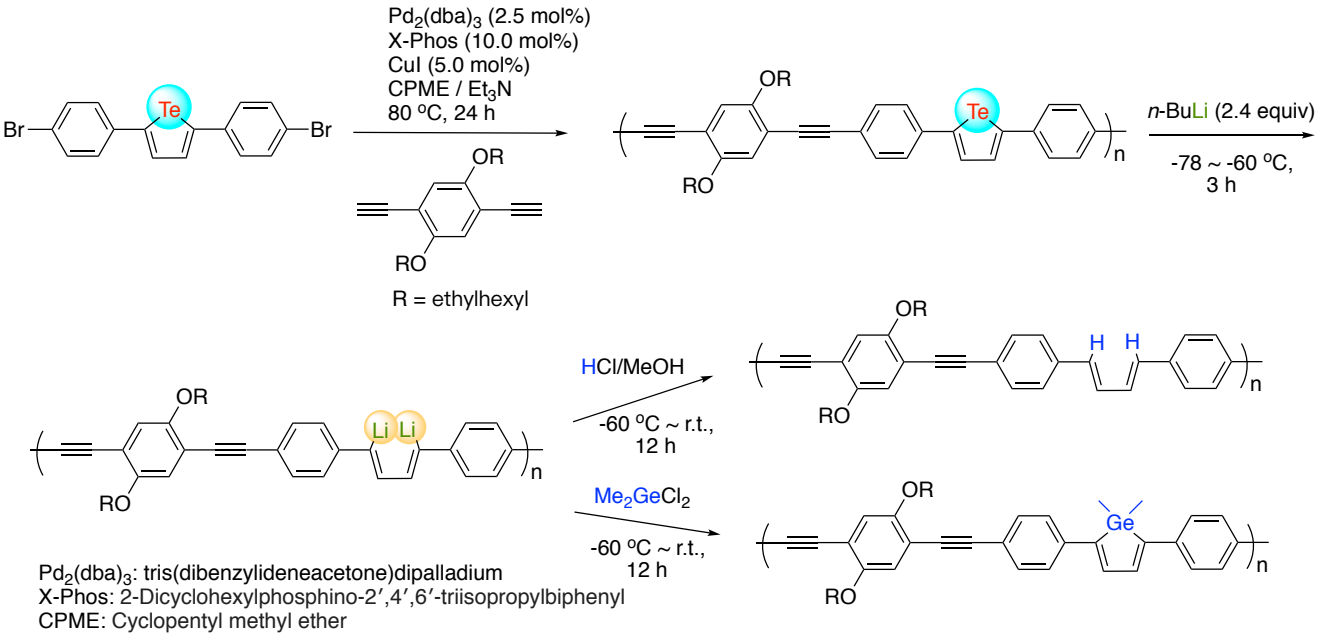
Scheme 2

In Section 2, the synthesis of germole-containing π-conjugated polymers is described. The lithiated polymer prepared is subjected to the reaction with dimethylgermyl dichloride to produce a dimethylgermole-containing π-conjugated polymer (Scheme 3). The low-lying LUMO level and unique optical property of the germole-containing polymer are also described. In addition, the presence of chemical interaction of the polymer with fluoride was demonstrated by the changes observed in the UV-vis absorption spectra.



Scheme 3

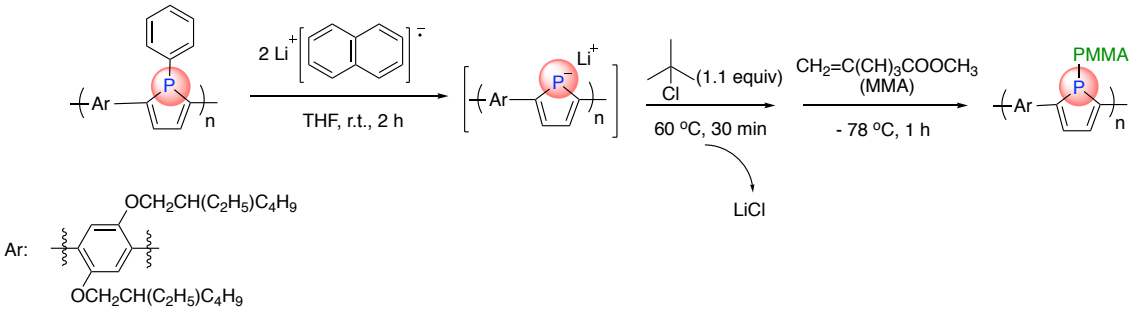
In *Chapter 4*, a π-conjugated tellurophene-containing polymer is prepared alternatively by the Sonogashira-Hagihara cross-coupling polymerization of 1,4-bis(2-ethylhexyloxy)-2,5-diethynyl-benzene and 2,5-di(4-bromophenyl)tellurophene, and was subjected to the reaction with *n*-butyllithium followed by dimethylgermyl dichloride to produce a dimethylgermole-containing π-conjugated polymer (Scheme 4). The present polymer reaction route that involves the transmetallation from tellurium to lithium followed by that from lithium to other elements may provide a new promising synthetic method of versatile heteroatom-containing π-conjugated polymers that cannot be produced by the polycondensation processes.



Scheme 4

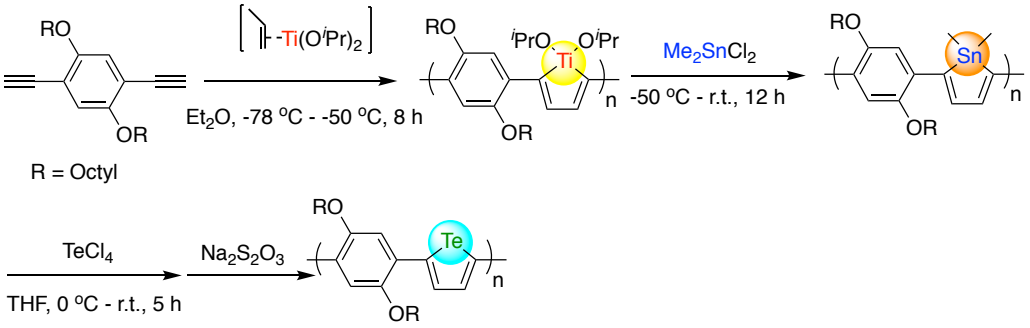
In *Chapter 5*, the synthesis of phosphole-containing π-conjugated polymers having grafted chains

by the anionic graft copolymerization of (meth)acrylates initiated from the phospholyl anion-containing polymer intermediate is described to facilitate the well-dispersion of the π-conjugated polymers in insulating commodity polymeric materials such as poly(methyl methacrylate) (PMMA) (Scheme 5). As a consequence, the PMMA-grafted phosphole-containing polymer exhibits the orange fluorescence both in bulk and in solutions, whose fluorescence quantum yields are comparable both in bulk and in solutions presumably due to the restrictions of the intermolecular π-π interactions by the grafted PMMA chains.



Scheme 5

In *Chapter 6*, a 1,1-dimethylstannole-2,5-diyl-containing polymer, which was obtained from an organotitanium polymer with Me_2SnCl_2, was subjected to the reaction with $TeCl_4$ followed by the treatment with aqueous $Na_2S_2O_3$ to give a tellurophene-2,5-diyl-containing polymer (Scheme 6). The high efficiency transformation can be supported by the ^1H NMR and UV-vis absorption spectra.



Scheme 6

In *Chapter 7*, the summary of this thesis and future perspectives are described.