# Chapter 3
# Element-Blocks π-Conjugated Polymers by Post-element-Transformation Technique

**Ikuyoshi Tomita**

**Abstract** The synthesis of a new class of π-conjugated polymers possessing versatile element-blocks is described. That is, regioregular organotitanium polymers having titanacyclopentadiene-2,5-diyl units, which are obtained from a low-valent titanium complex and diynes, are subjected to the polymer reactions with elements-containing electrophiles to produce π-conjugated polymers possessing unique element-blocks. Optoelectronic features of the resulting element-blocks π-conjugated polymers are also described.

**Keywords** Polymer reactions · π-Conjugated polymers · Organometallic polymers · Heteroles · Chemosensors

## 3.1 Introduction

The precision control of electronic features of π-conjugated polymers is an important subject for many applications such as field-effect transistors, dyes for solar cells, and organic light-emitting devices [1–4]. In accordance with the idea that incorporation of appropriate element-blocks into polymers is effective to build up advanced functional materials [5], it has also been proposed that the addition of heteroatoms into the π-electronic systems is quite effective to tune up their electronic properties such as HOMO and LUMO energy levels and their bandgaps based on the theoretical calculations [6]. Further, the theoretical studies suggest that the incorporation of plural elements often affects dramatically on their electronic properties [7]. Nevertheless, the elements that have successfully been introduced into π-conjugated polymers are still limited so far, and many elements-containing π-conjugated polymers (i.e., element-blocks π-conjugated polymers) still remained untouched.

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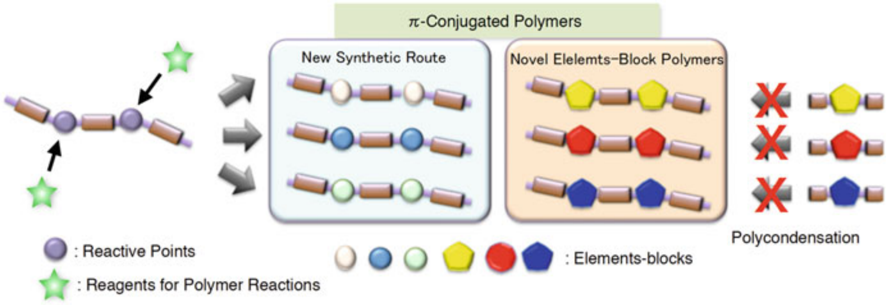


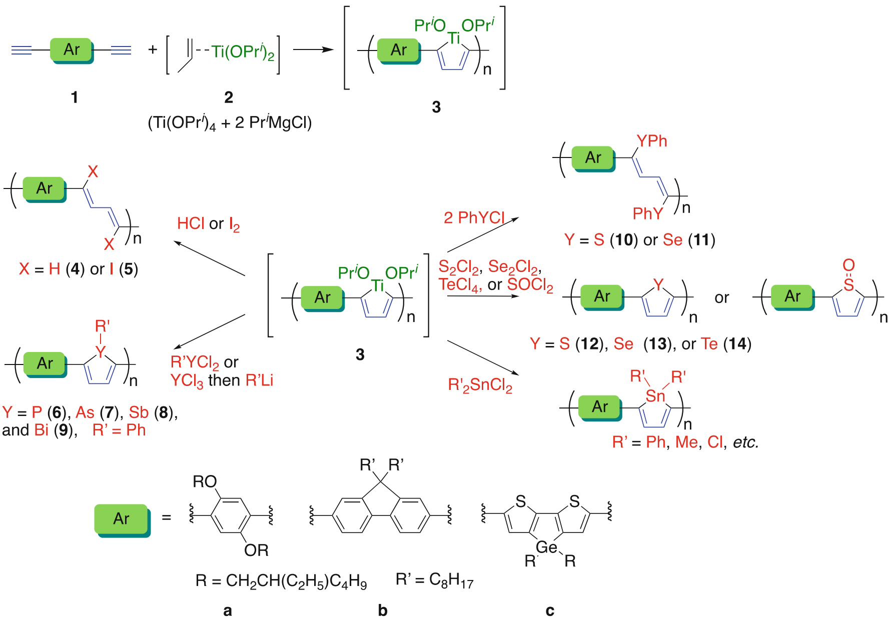
**Fig. 3.1** Synthesis of versatile element-blocks π-conjugated polymers by means of polymer reactions accompanying transformation of main chain structures

In general, π-conjugated polymers are prepared by the polycondensation of the monomers possessing the corresponding building blocks, and the transition metal-catalyzed coupling reactions are often employed for the polycondensation processes. However, π-conjugated polymers possessing the corresponding units are hardly accessible by the conventional polycondensation approach, because most of the elements-carbon and/or inter-element bonds in the elements-containing monomers are unstable under the polymerization conditions. Accordingly, new synthetic methods are required to produce the element-blocks π-conjugated polymers.

This chapter deals with a new synthetic approach based on the polymer reactions that enable the synthesis of versatile element-blocks π-conjugated polymers by means of the transformation of the transition metals in the main chain into various elements (Fig. 3.1). That is, regioregular organotitanium polymers having titanacyclopentadiene-2,5-diyl units were prepared from a low-valent titanium complex and diynes, and their polymer reactions with elements-containing electrophiles were carried out as new synthetic methods to produce π-conjugated polymers possessing unique element-blocks. Optoelectronic features of the resulting element-block π-conjugated polymers are also described.

## 3.2 Synthesis of Element-Blocks π-Conjugated Polymers via Organotitanium Polymers

Based on the regioregular metallacyclization of a low-valent titanium (**2**) and terminal alkynes established by Sato and his coworkers [8, 9], organotitanium polymers having titanacyclopentadiene-2,5-diyl units (**3**) were prepared from aromatic terminal diynes (**1**) [10]. The organotitanium polymers (**3**) are air-unstable and thermally unstable. However, they exhibit excellent reactivity toward many electrophilic reagents. For example, the treatment of the polymers (**3**) with hydrochloric acid and iodine gave polymers having 1,3-butadiene-1,4-diyl and 1,4-diiodo-1,3-butadiene-1,4-diyl units (**4** and **5**), respectively (Scheme 3.1).

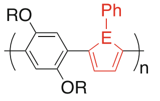


**Scheme 3.1** Synthesis of element-blocks π-conjugated polymers by post-element-transformation processes

Likewise, reactions of the organotitanium polymers (**3**) with electrophiles possessing the group 14, 15, and 16 elements were performed to produce π-conjugated polymers possessing heteroles of the group 14, 15, and 16 elements. For example, the reaction of the organotitanium polymer (**3a**) with dichlorophenylphosphine produced a red-colored phosphole-containing π-conjugated polymer (**6a**) [11]. Compared to that of the corresponding polymer with thiophene moieties (**12a**, vide infra), the phosphole-containing polymer thus obtained (**6a**) proved to have low-lying LUMO energy level due to the $\sigma^*$-$\pi^*$ orbital interaction, [12] while the HOMO energy levels for both the polymers were comparably high, as predicted from the theoretical calculations [6] and also from the preceding report of the analogous phosphole-containing polymers [13–15]. The phosphole-containing π-conjugated polymer (**6a**) exhibits yellow and orange photoluminescence in solution and in film, respectively.

From the theoretical calculations of the heteroles of the group 15 elements, it was supposed that the stibole has the lowest LUMO energy level and the LUMO decreases in the order of P ~ As > Bi > Sb. In accordance with the calculations, a stibole-containing polymer (**8a**), which could be prepared by the transformation reaction of **3a**, was found to have the narrowest bandgap as a result of the lowering of the LUMO energy level (Table 3.1). An arsole-containing polymer (**7a**) could successfully be obtained by the collaborative research with Naka and his coworkers by the use of diiodophenylarsine generated in situ from a less volatile and safer arsenic precursor [16, 17]. The optical and electronic properties (i.e., HOMO and

**Table 3.1** Optical properties and bandgap of **6a**–**9a**

| | Polymer | E | $\lambda_{max}$ (nm)[a] | $\lambda_{onset}$ (nm)[a] | Bandgap (eV)[b] |
|---|---|---|---|---|---|
|  <br>R = $CH_2CH(C_2H_5)C_4H_9$ | **6a** | **P** | 510 | 622 | 1.99 |
| | **7a** | **As** | 517 | 612 | 2.03 |
| | **8a** | **Sb** | 550 | 685 | 1.81 |
| | **9a** | **Bi** | 517 | 648 | 1.93 |

[a] Measured in THF
[b] Optical bandgap, estimated from their $\lambda_{onset}$

LUMO energy levels, UV-vis absorptions, and photoluminescence spectra) of the arsole-containing polymer (**7a**) were found to be very close to those of the phosphole-containing polymer (**6a**). However, the arsole-containing polymer (**7a**) exhibits remarkably higher oxidation-tolerant nature compared to that of the phosphole-containing polymer (**6a**), which readily undergoes oxidation to produce a phosphole oxide-containing polymer.

π-Conjugated polymers having 1,4-phenylthio-1,3-butadiene-1,4-diyl and 1,4-phenylseleno-1,3-butadiene-1,4-diyl units (**10** and **11**) were prepared by the reactions with PhSCl and PhSeCl, respectively [18]. The transformation of the organotitanium polymers (**3**) into π-conjugated polymers having heteroles of the group 16 elements was likewise attainable by the use of appropriate electrophilic reagents. That is, thiophene-, selenophene-, and tellurophene-containing π-conjugated polymers (**12**, **13**, and **14**) were obtained by the reactions of **3** with sulfur monochloride, selenium monochloride, and tellurium tetrachloride, respectively [19]. The π-conjugated polymers having the group 16 elements thus prepared were found to have high HOMO and LUMO energy levels, where the LUMO energy levels tend to decrease by the use of heavier elements, resulting in the bathochromic shift of the UV-vis spectra.

As an electrophilic reagent, thionyl chloride works effectively to give thiophene-1-oxide-containing polymers (**15**) from **3**. The UV-vis spectrum of the **15a** exhibited a significant bathochromic shift compared to that of the corresponding thiophene-containing polymer (**12a**), which indicated the excellent effect of the plural elements on the optical and electronic properties of the π-conjugated materials.

Concerning the transformation of **3** into π-conjugated polymers having heteroles of the group 14 elements, the reaction with organotin dichloride or tin tetrachloride takes place smoothly to produce stannole-containing π-conjugated polymers (**16**), while the reactions with germanium halides or silicon halides did not proceed sufficiently under analogous conditions.

As indicated above, π-conjugated polymers having the group 14–16 elements (**6**–**16**) were synthesized by the polymer reactions of the organotitanium intermediates (**3**). Their electronic and optical properties were found to be affected largely by the nature of the element-blocks. As shown in Fig. 3.2, the UV-vis absorptions of the π-conjugated polymers varied in a wide range. Some of the polymers are photoluminescence-active, and the color of the emission also altered in a wide range, depending on the elements incorporated in the π-conjugated system.

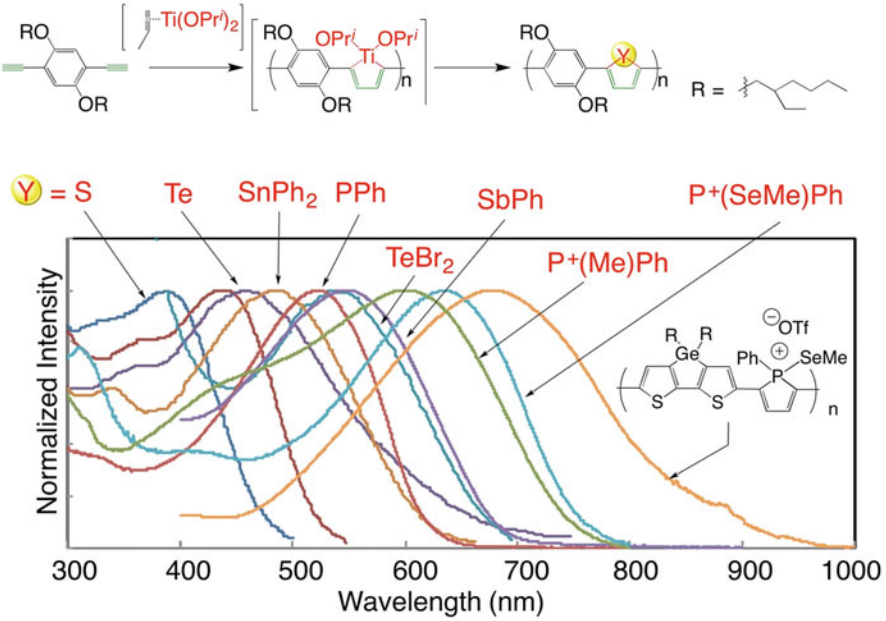
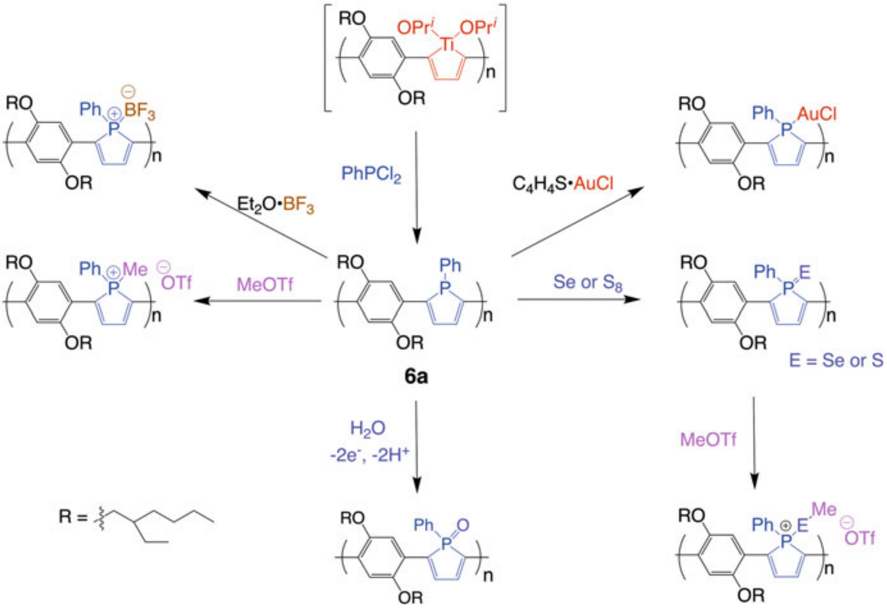


**Fig. 3.2** UV-vis spectra of **12a**, **14a**, **16a**, **6a**, $Br_2$ adduct of **14a**, onium salts of **6a** and **6c**

## 3.3 Synthesis of π-Conjugated Polymers Possessing Plural Elements by Further Reactions of Element-Blocks π-Conjugated Polymers

Some of the elements on the π-conjugated polymers thus obtained can be modified or transformed into other elements by the further polymer reactions. For example, the phosphole-containing π-conjugated polymer (**6a**) was subjected to oxidation with sulfur and selenium to produce polymers having pentavalent phosphorous atoms (Scheme 3.2). The sulfur and selenium atoms can be alkylated further to give the corresponding phosphonium salt-containing polymers. The reactions of **6a** by the alkylation and complexation with boron trifluoride and gold(I) also produced the corresponding phosphorous-containing π-conjugated polymers. All the transformation processes proceed quantitatively as monitored by the $^{31}$P NMR spectra. Through these chemical modifications, the color of the polymers turned from red to blue or purple, and the UV-vis absorption spectra exhibited remarkable bathochromic shift (Fig. 3.3). For example, the $\lambda_{max}$ of the polymer shifted to longer wavelength by 130 nm after the selenation followed by the alkylation. Chemical modifications of the arsole-containing π-conjugated polymer (**7a**) can also be performed which also resulted in the change of the optical and electronic properties. From the theoretical studies performed by Tanaka, the lowering of the energy level of the $\sigma^*$ orbital in the arsine-carbon or arsine-elements bond effectively lowered the LUMO energy level through the $\sigma^*$-$\pi^*$ molecular orbital interaction [17].



**Scheme 3.2** Chemical modifications of **6a**

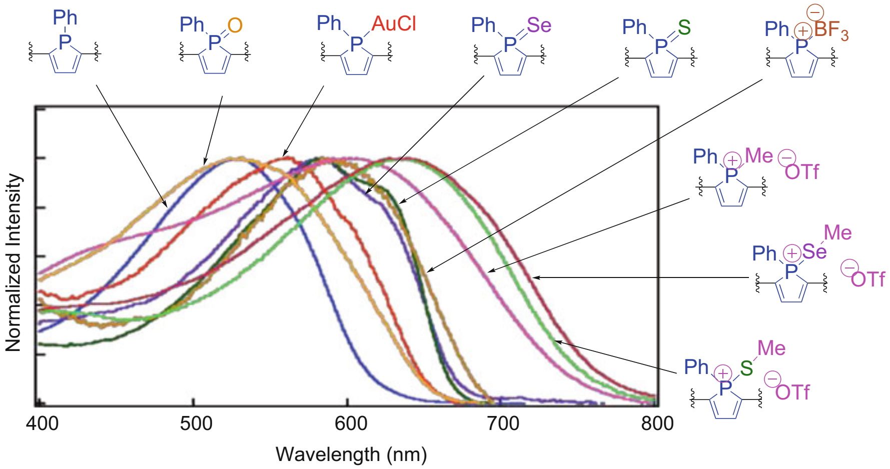
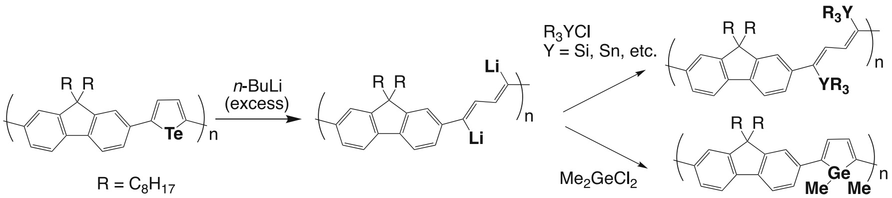
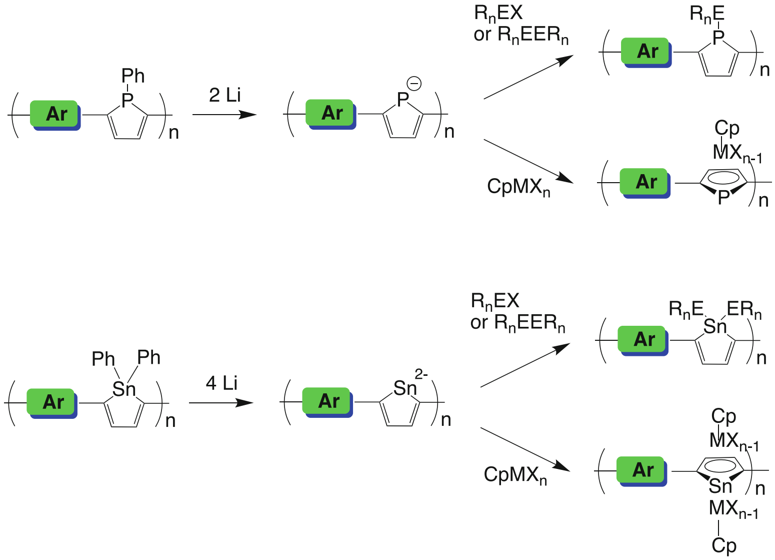


**Fig. 3.3** UV-vis spectra of polymers derived from **6a**

As mentioned above, the phosphole-containing π-conjugated polymers (**6**) exhibit yellow and orange photoluminescence in solution and in film, respectively. It was found that the photoluminescence was totally quenched through these chemical modifications, which may suggest the application of the polymers as the turnoff photoluminescence chemosensors.



**Scheme 3.3** Synthesis of element-blocks π-conjugated polymers via the lithiation of the tellurophene-containing polymer (**14b**)



**Scheme 3.4** Transformation of phosphole- and stannole-containing polymers

The tellurophene-containing polymers **(14)** can also be reacted further to produce π-conjugated polymers that have not been prepared by the direct transformation of the organotitanium intermediates (**3**). That is, the tellurophene-containing π-conjugated polymer (**14b**) was treated with *n*-butyllithium to generate a highly reactive lithiated polymer. Through the lithiated form, reagents having lower electrophilicity such as germanium halides, silicon halides, and others can be reacted smoothly to produce the corresponding element-blocks π-conjugated polymers (Scheme 3.3).

Reduction of the phosphole- and stannole-containing polymers (**6** and **16**) takes place quantitatively to give phospholyl anion-containing and stannole dianion-containing polymers, respectively. These intermediates not only enable the exchange reactions of the substituents on the phosphorus and tin elements but also provide the chances to prepare polymers having unique heterocyclopentadienyl transition metal complexes (Scheme 3.4).

## 3.4 Potential Applications of Element-Blocks π-Conjugated Materials

The unique optical and electronic features of the element-blocks π-conjugated polymers are attractive for many applications. As mentioned above, the fluorescent chemosensors can be constructed based on the specific interaction of elements attached to the π-conjugated polymers. Not only the phosphole-containing polymers but also arsole-, thiophene-, selenophene-, tellurophene, stannole-, and 1,4-dithio-1,3-butadiene-containing polymers exhibit stimuli-responsive luminescence and/or UV-vis absorption changes which may also be attractive for chemosensor applications.

On the basis of their low LUMO and high HOMO energy levels, the phosphole-containing polymers serve as both n- and p-type semiconductors, depending on the nature of the silicon substrate in the fabricated diode device (Fig. 3.4) [11].

Because the polymer reaction routes involving the post-element-transformation processes are suitable to carry out the parallel synthesis of a series of π-conjugated polymers, it is possible to perform the rational approach to obtain functional materials having desired features. For example, photoluminescent polymers with various colors can be designed by the use of a designed diyne (**1c**) [20].

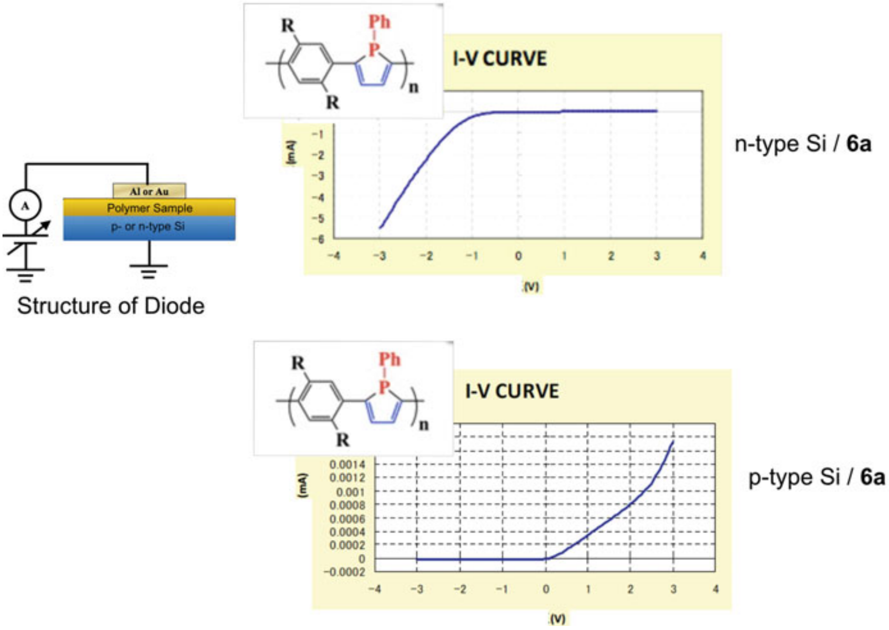


**Fig. 3.4** Semiconducting properties of **6a**

Low-bandgap intramolecular charge transfer π-conjugated polymers with varied LUMO energy levels such as **6d** and its derivatives can also be designed by using a diyne having a high HOMO energy level (**1d**) through collaborative research with Ohshita and his coworkers.

## 3.5 Summary

By the progress of the synthetic methods for π-conjugated polymers possessing versatile element-blocks, unprecedented materials with unique optical and electronic features could be created which potentially exhibit excellent functions for optical and electronic devices and chemosensors. The great potential of the element-blocks to control the electronic state of π-electron systems of organic molecules and macromolecules could be convinced at least in part by the present studies. The author strongly wishes the further progress of the related synthetic researches as well as the applications of the new materials.

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