

# Synthesis of $\pi$ -Conjugated Polymers Containing Phosphole Units in the Main Chain by Reaction of an Organometallic Polymer Having a Titanacyclopentadiene Unit<sup>†</sup>

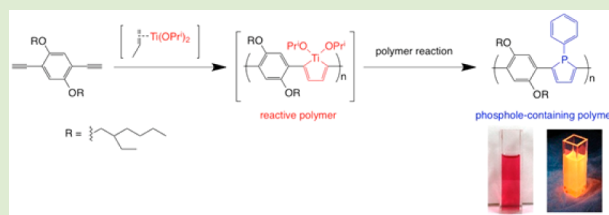
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## Supporting Information

**ABSTRACT:** A regioregular organometallic polymer possessing titanacyclopentadiene units in the main chain, which was obtained by the reaction of terminal diyne and a low-valent titanium complex, was subjected to the reaction with dichlorophosphines to give  $\pi$ -conjugated polymers with phosphole or phosphole oxide units in the main chain. For example, a phenylphosphole-containing polymer was obtained in 76% yield by the reaction with dichlorophenylphosphine, whose number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) were estimated to be 6100 and 1.9, respectively, by GPC. The polymer was found to have an extended  $\pi$ -conjugated system, and its lowest unoccupied molecular orbital (LUMO) energy level was remarkably low ( $-3.28$  eV) as supported by its UV-vis absorption spectrum and cyclic voltammetric (CV) analysis. Also, the polymer exhibits orange photoluminescence with an emission maximum ( $E_{max}$ ) of 595 nm and a quantum yield ( $\Phi$ ) of 0.10.



$\pi$ -Conjugated polymers are applicable to various functional materials such as organic light-emitting diodes (OLEDs), organic solar cells (OSCs), organic field effect transistors (OFETs), and chemosensors.<sup>2</sup> Among them, those possessing heteroatoms are expected to exhibit unique features originated from the nature of the heteroatoms. For example, polymers containing heteroles of the group 16 elements such as thiophene and selenophene are known to serve as electron-rich (electron-donor) materials. In cases of those containing the group 15 elements, quite a few examples of pyrrole-containing polymers have been reported which likewise exhibit electron-rich properties. Accordingly, these polymers are also applicable to p-type semiconducting materials for the electronic applications. Although polymers containing heteroles with the heavier group 15 elements such as phosphole are expected to exhibit electron-accepting properties due to the  $\sigma^*-\pi^*$  orbital interactions between the group 15 elements and butadiene unit in each heterole unit,<sup>3</sup> only a few synthetic studies on phosphole-containing polymers have been reported.

Tilley et al. first reported the synthesis of a phosphole-containing polymer by the reaction of a zirconacyclopentadiene-containing organometallic polymer with dichlorophenylphosphine.<sup>4</sup> However, the resulting phosphole-containing polymer did not exhibit sufficient  $\pi$ -conjugated properties due to the lack of the regioregularity of the precursor polymer. Chujo et al. reported the synthesis of regioregular  $\pi$ -conjugated phosphole-containing polymers by the Sonogashira-Hagihara coupling of an aromatic diyne and phosphole-containing aryl

dihalides that were prepared by the transformation of regioregular zirconacyclopentadiene intermediates.<sup>5</sup> Likewise, Imahori et al. described the synthesis of phosphole- or phosphole oxide-containing  $\pi$ -conjugated polymers by use of the Stille coupling technique.<sup>6</sup> The electrochemical polymerization of a phosphole-containing monomer was also described by Réau et al.<sup>7</sup> The polymers obtained by these methods exhibited the effective extension of the  $\pi$ -conjugated system. From the synthetic viewpoint, however, these methods seem to limit the structure of the monomers to the 3,4-fused bicyclic systems due to the requirements from the organometallic intermediates. They also require the multiple synthetic procedures for monomers and polymers. The catalysts and the active species applicable to the polymerization would also be limited due to the high coordination ability and the reactivity of the phosphole units. Thus, the development of an alternative synthetic approach is very important for both the synthetic viewpoint and the progress of phosphole-containing materials.

We have been working on the synthesis and reactions of organometallic polymers possessing reactive metallacyclic systems such as cobaltacyclopentadiene, titanacyclobutene, and titanacyclopentadiene units.<sup>8</sup> Among them, the polymers containing titanacyclopentadiene-2,5-diyl units, obtainable by the regiospecific metallacyclization of terminal alkynes with a

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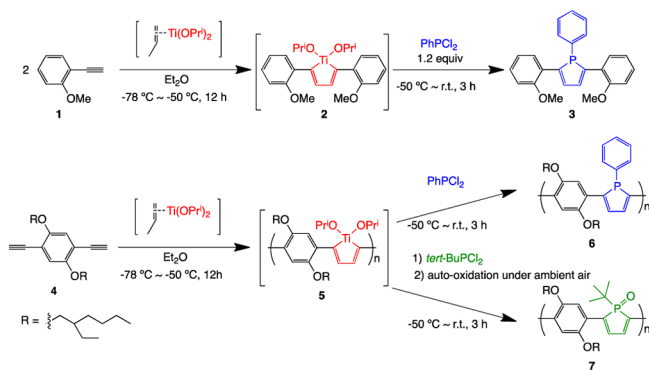
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low-valent titanium complex,<sup>9</sup> proved to be powerful synthetic precursors for functional  $\pi$ -conjugated polymers possessing versatile functional groups and heteroatoms. Namely,  $\pi$ -conjugated polymers containing 1,3-butadiene, phenylene, 1,4-bismercapto-substituted 1,3-diene, thiophene, and selenophene units have been obtained from the regioregular organotitanium polymers.<sup>10</sup> As a new synthetic approach of the phosphole-containing  $\pi$ -conjugated polymers, we describe herein the reaction of a regioregular organometallic polymer having a titanacyclopentadiene moiety in the main chain with organophosphorous reagents. The optoelectronic properties of the obtained phosphole-containing  $\pi$ -conjugated polymers are also described.

On the basis of the facts that reactions of metalacyclopentadienes such as titanacyclopentadienes and zirconacyclopentadienes can be transformed into functional molecules by reactions with various electrophilic reagents under mild conditions,<sup>11</sup> we first looked into the possibility of the conversion of the titanacyclopentadiene building blocks into phospholes by use of dihalophosphines. As a model reaction of the polymer reaction, a titanacyclopentadiene derivative (**2**), prepared *in situ* from 2-methoxyphenylacetylene (**1**) with a low-valent titanium(II) complex, was subjected to the reaction with  $\text{PhPCl}_2$  (1.2 equiv) from  $-50^\circ\text{C}$  to ambient temperature without isolating the titanacyclopentadiene intermediate (Scheme 1). As a result, the objective 1-phenylphosphole

### Scheme 1. Synthesis of Model Compound and Polymers



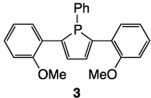
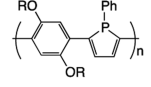
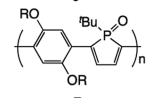
derivative (**3**) was obtained in 88% yield as yellow oil. Reflecting upon the regiospecific metallacyclization process, a 2,5-substituted phosphole was obtained as a single regioisomer, whose  $^{31}\text{P}$  NMR spectrum exhibits a singlet peak at 14.9 ppm.<sup>3b</sup>

The regioregular titanacyclopentadiene-containing polymer (**5**) was likewise subjected to the reaction with  $\text{PhPCl}_2$ . That is, the organotitanium polymer (**5**), prepared by the reaction of 1,4-diethynyl-2,5-di(2-ethylhexyloxy)benzene (**4**) with a low-valent titanium(II) complex, generated *in situ* from  $\text{Ti}(\text{OPr})_4$  and  $\text{Pr}^i\text{MgCl}$  from  $-78$  to  $-50^\circ\text{C}$  was subjected to the transformation into a 1-phenylphosphole-containing polymer (**6**) by the addition of  $\text{PhPCl}_2$  without isolation. Consequently, the phosphole-containing polymer (**6**) was obtained in 76% yield by precipitation with hexane as a dark red solid, which is soluble in common organic solvents such as tetrahydrofuran (THF), toluene, dichloromethane, and chloroform. The number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of **6** were estimated to be 6100 and 1.9, respectively, by GPC.

The structure of the polymer (**6**) could be supported by its  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra. In the  $^1\text{H}$  NMR spectrum of **6**,

peaks attributable to the alkoxy and aromatic protons are observable at 3.13–3.98 ppm and at 6.77–7.95 ppm, respectively, whose peak intensity ratio (4.2:9.0) was in good accordance with that for the expected structure (**4**:**9**). In the  $^{31}\text{P}$  NMR spectrum of **6**, a singlet peak attributable to the phosphole unit was detected at 12.0 ppm, which was in good accordance with that for the model compound (**3**: 14.9 ppm) (Table 1). By the reaction of **5** with  $^t\text{BuPCl}_2$ , a polymer (**7**) was

**Table 1. Synthesis of 3, 6, and 7**

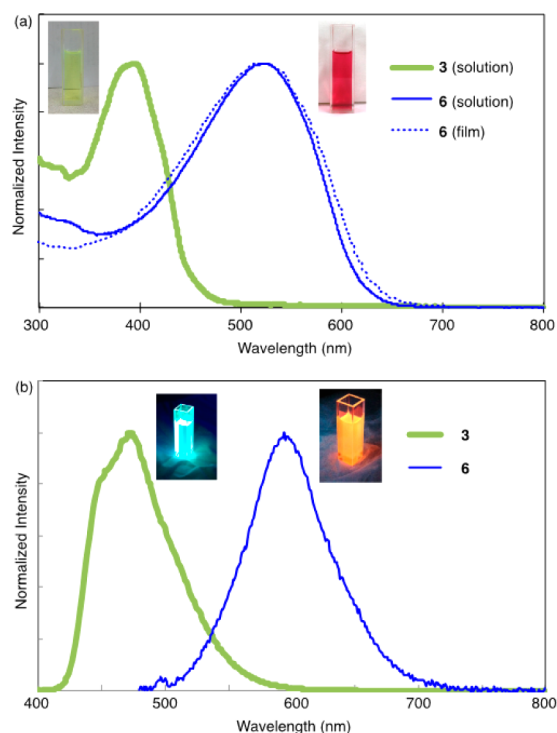
compounds	yield (%)	$M_n$ ( $M_w/M_n$ ) <sup>d</sup>	$^{31}\text{P}$ NMR ( $\delta$ , ppm) <sup>e</sup>
	88 <sup>a</sup>	-	14.9
	76 <sup>b</sup>	6100 (1.9)	12.0
	58 <sup>c</sup>	5300 (1.7)	37.2

<sup>a</sup>Isolated yield after alumina column chromatography. <sup>b</sup>Isolated yield after precipitation into hexane. <sup>c</sup>Isolated yield after precipitation into MeOH. <sup>d</sup>GPC ( $\text{CHCl}_3$ , polystyrene Std). <sup>e</sup>Measured in  $\text{CDCl}_3$ .

also obtained in 58% yield as a red solid by precipitation with MeOH, whose  $M_n$  and  $M_w/M_n$  of **7** were estimated to be 5300 and 1.7, respectively, by GPC. From the  $^{31}\text{P}$  NMR spectrum of **7**, however, the product was found to contain only 1-*tert*-butylphosphole oxide units as a result of auto-oxidation of the phosphorus atom during the workup procedure.<sup>3b</sup>

In the UV–vis absorption spectrum of **6** taken in  $\text{CHCl}_3$ , the absorption maximum ( $\lambda_{\text{max}}$ ) was observed at 522 nm, which is red-shifted by 126 nm and by 214 nm compared to those of the model compound (**3**:  $\lambda_{\text{max}} = 396$  nm) and the preceding regioregular phosphole-containing wholly aromatic polymer<sup>4</sup> ( $\lambda_{\text{max}} = 308$  nm), respectively (Figure 1). These clear bathochromic shifts support the extension of the effective  $\pi$ -conjugation along the polymer backbone. It was found that the UV–vis absorption spectrum of **6** measured in film was almost comparable to that taken in  $\text{CHCl}_3$ , indicating the absence of the intermolecular interaction or the conformational change of the  $\pi$ -conjugated backbone. The photoluminescence (PL) spectra were obtained in  $\text{CHCl}_3$  by excitation at the wavelength of its absorption maximum (522 nm). The phosphole-containing polymer (**6**) exhibits the orange fluorescence with an emission maximum at 594 nm, and the quantum yield was determined to be 0.10 (Table 2).

The electrochemical properties of the polymer (**6**) were evaluated from the cyclic voltammetric (CV) analysis in the film state (Figure S5, Supporting Information). From the onset oxidation potential ( $E_{\text{ox}}$ ) and the reduction potential ( $E_{\text{red}}$ ) observed in the CV measurement, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of **6** were estimated to be  $-5.35$  and  $-3.28$  eV, respectively. It is of note that the LUMO energy level of the polymer (**6**) is significantly lower than those of the thiophene-containing polymer obtained via the same organotitanium polymer (LUMO =  $-2.9$  eV).<sup>10d</sup> The low LUMO energy level of the phosphole-containing polymer is most probably due to the  $\sigma^*-\pi^*$  orbital interaction in the

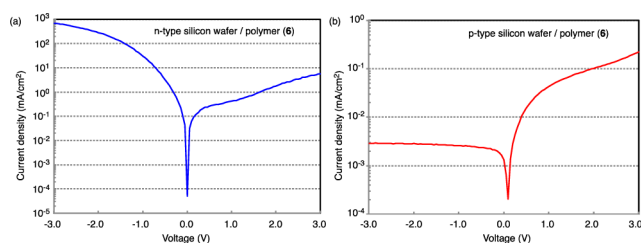


**Figure 1.** UV-vis absorption (a) and photoluminescence (b) spectra of the polymer (**6**) and the model compound (**3**) in  $\text{CHCl}_3$  solution or film.

phosphole unit. Besides, it was found that the HOMO energy level of the polymer (**6**) was almost comparable to that of the thiophene-containing polymer (HOMO =  $-5.3$  eV). Accordingly, the phosphole-containing polymer would be applicable to both electron-deficient and electron-rich  $\pi$ -conjugated materials.

In order to demonstrate the rectifying properties of **6**, simple diode circuits were prepared by spin coating a THF solution of **6** onto p-type and n-type silicon wafers. The aluminum electrode was deposited on the thin layer of the polymer under vacuum, and their  $I$ - $V$  profiles were evaluated in the range of  $-3$  to  $3$  V (Figure 2). As a result, rectification properties were observed in both circuits. That is, the diode circuit composed of n-type silicon and **6** exhibits the electric current in the negative electric field, while that composed of p-type silicon and **6** shows the electric current only in the positive electric field. These results can be taken to mean that the phosphole-containing polymer (**6**) is applicable to both n-type and p-type  $\pi$ -conjugated materials.

In summary, the  $\pi$ -conjugated polymers containing phosphole or phosphole oxide moieties were prepared by the reactions of a regioregular organometallic polymer having a titanacyclopentadiene moiety in the main chain. The extension of the  $\pi$ -conjugation along the polymer backbone was supported from its UV-vis absorption spectrum. The phosphole



**Figure 2.**  $I$ - $V$  profiles measured in the simple diode circuits composed of **6** and n-type silicon (a) and **6** and p-type silicon (b).

hole-containing polymer exhibits orange photoluminescence with an emission maximum of 594 nm. The LUMO energy level of this polymer proved to be lower than that of the analogous thiophene-containing polymer, reflecting upon the electron-accepting nature of the phosphole unit. The polymer is applicable to both n-type and p-type materials due to its high HOMO and low LUMO energy levels.

Within the knowledge of the authors, this is the first example of the polymer reaction route that can provide phosphole- and phosphole oxide-containing fully  $\pi$ -conjugated polymers. We believe that the present method is quite suitable for the versatile macromolecular design of phosphole-containing  $\pi$ -conjugated polymers from very simple starting materials (i.e., terminal diynes and dihalophosphines). On the basis of these synthetic advantages and the unique electronic features of the phosphole- and phosphole oxide-containing polymers, their applications to organic devices such as OSCs and OLEDs are in progress.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental procedures and all characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

<sup>†</sup>This work was partly presented.<sup>1</sup>

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## ■ REFERENCES

- (1) Tomita, I. *ACS Polym. Prepr.* **2004**, *45*, 415–416.
- (2) For reviews, see: (a) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091. (b) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*,

**Table 2.** Optical Properties of **3** and **6**

compounds	$\lambda_{\text{sol,max}}^a$ (nm)	$\lambda_{\text{sol,onset}}^a$ (nm)	$\lambda_{\text{film,max}}^b$ (nm)	$\lambda_{\text{film,onset}}^b$ (nm)	$E_{\text{max,sol}}^c$ (nm)	$\Phi^d$	$E_{\text{g(opt)}}^e$ (eV)
<b>3</b>	396	448	<sup>b</sup>	<sup>b</sup>	477	0.57	2.77
<b>6</b>	522	620	525	630	594	0.10	2.00

<sup>a</sup>Measured in  $\text{CHCl}_3$ . <sup>b</sup>Not measured. <sup>c</sup>Emission maxima, irradiated at their  $\lambda_{\text{max}}$  (nm). <sup>d</sup>The quantum yields ( $\Phi$ ) were estimated at ambient temperature using quinine in 0.50 M sulfuric acid aqueous solution as a standard. <sup>e</sup>Estimated from  $\lambda_{\text{onset}}$ .

1324–1338. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574. (d) Kularatne, R. S.; Magurudeniya, H. D.; Sista, P.; Biewer, M. C.; Stefan, M. C. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 743–768.

(3) (a) Hay, C.; Fischmeister, C.; Hissler, M.; Réau, R. *Angew. Chem., Int. Ed. Engl.* **2000**, *10*, 1812–1815. (b) Hay, C.; Hissler, M.; Fischmeister, C.; Berthelot, J. R.; Toupet, L.; Nyulaszi, L.; Réau, R. *Chem.—Eur. J.* **2001**, *7*, 4222–4236. (c) Fave, C.; Hissler, M.; Sénéchal, K.; Ledoux, I.; Zyss, J.; Réau, R. *Chem. Commun.* **2002**, *16*, 1674–1675. (d) Fave, C.; Cho, T. Y.; Hissler, M.; Chen, C. W.; Luh, T. Y.; Wu, C. C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254–9255. (e) Crassous, J.; Réau, R. *Dalton Trans.* **2008**, *48*, 6865–6876. (f) Hobbs, M. G.; Baumgartner, T. *Eur. J. Inorg. Chem.* **2007**, *23*, 3611–3628. (g) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681–4727.

(4) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566–5569.

(5) (a) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594–2597. (b) Na, H. S.; Morisaki, Y.; Aiki, Y.; Chujo, Y. *Polym. Bull.* **2007**, *58*, 645–652.

(6) Saito, A.; Matano, Y.; Imahori, H. *Org. Lett.* **2010**, *12*, 2675–2677.

(7) Talancé, V. L.; Hissler, M.; Zhang, L. Z.; Kárpáti, T.; Nyulászi, L.; Quintero, D. C.; Bäuerle, P.; Réau, R. *Chem. Commun.* **2008**, 2200–2202.

(8) (a) Tomita, I.; Nishio, A.; Endo, T. *Polym. Bull.* **1993**, *30*, 179–186. (b) Tomita, I.; Nishio, A.; Endo, T. *Macromolecules* **1994**, *27*, 7009–7010. (c) Tomita, I.; Nishio, A.; Endo, T. *Macromolecules* **1995**, *28*, 3042–3047. (d) Rozhanskii, I.; Tomita, I.; Endo, T. *Macromolecules* **1996**, *29*, 1934–1938. (e) Lee, J. C.; Nishio, A.; Tomita, I.; Endo, T. *Macromolecules* **1997**, *30*, 5205–5212. (f) Tomita, I.; Nishio, A.; Endo, T. *Appl. Organometal. Chem.* **1998**, *12*, 735–742. (g) Tomita, I.; Lee, J. C.; Endo, T. *J. Organomet. Chem.* **2000**, *611*, 570–576. (h) Zhou, W. M.; Tomita, I. *Polym. Bull.* **2008**, *61*, 603–609. (i) Tomita, I.; Ueda, M. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 511–518.

(9) (a) Yamaguchi, S.; Jin, R. Z.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060–10062. (b) Hamada, T.; Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 7342–7344.

(10) (a) Atami, K.; Kino, T.; Zhou, W. M.; Nishiyama, H.; Tomita, I. *Synth. Met.* **2009**, *159*, 949–951. (b) Kino, T.; Nishiyama, H.; Tomita, I. *Appl. Organometal. Chem.* **2010**, *24*, 558–562. (c) Nishiyama, H.; Tomita, I. *Macromol. Chem. Phys.* **2010**, *20*, 2248–2253. (d) Nishiyama, H.; Kino, T.; Tomita, I. *Macromol. Rapid Commun.* **2012**, *33*, 545–549.

(11) (a) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835–2886. (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310–2312.