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Synthesis and Characterization of π-Conjugated Polymers with a 2,5-Substituted Phosphole Skeleton

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Summary

Novel π-conjugated polymers **10a-c** having the phosphole ring were prepared by $PdCl_2(PPh_3)_2$/CuI catalyzed coupling of 1-phenyl-2,5-bis(*p*-bromophenyl)phosphole **8** with fluorine-substituted diethynylbenzene **9a-c**. The obtained polymers **10a-c** were regio-regulated with the 2,5-substituted phosphole ring in the polymer main chain, and characterized by ^1H, ^{31}P NMR, and FTIR. Polymers **10a-c** were found to be an extended π-conjugated system according to the results of UV-Vis absorption spectra. In the fluorescence emission spectra of **10a-c**, moderate emission peaks were observed in the visible blue to green region.

Introduction

Novel π-conjugated polymers for optoelectronic applications, such as organic light-emitting diodes (OLED) [1], thin-film transistors [2], and chemical sensors [3], have attracted increasing attention over several decades. Among various types of π-conjugated polymers, those bearing the heterocyclopentadiene moiety as the π-electron system, such as thiophene, pyrrole, and silole, have been synthesized, and their conductive and photochemical behaviors have been extensively investigated [4]. On the other hand, phosphacyclopentadiene (phosphole) has received little attention as a building block for extended π-conjugated systems [5–7], despite its numerous applications in organic and metal coordination chemistry [8]. After Wittig and Geissle described the synthesis of a fused phosphole in 1953 [9], the first practically applicable synthesis was reported in 1959 by two independent groups [10]. The first successful synthesis of phosphole-containing π-conjugated polymers was reported by Tilley and coworkers [11]. Zirconocene-mediated oxidative cyclization of dialkyne and the subsequent reaction of the zirconacyclopentadiene-containing polymer with $PhPCl_2$ by the polymer reaction gave both 2,4- and 2,5-substituted phosphole-containing polymers, which exhibited bluish-green emission with a large Stokes shift. Réau and coworkers also prepared phosphole-containing polymers through the electrolytic polymerization by using cyclic voltammetry [7b,c]. In our previous studies, we synthesized and characterized π-conjugated polymers consisting of the regio-regulated phosphole unit, and their photochemical and electrochemical behaviors were investigated [12]. Recently, Réau and coworkers reported the construction of phosphole-containing π-conjugated systems and demonstrated the possibility of applying them to optoelectronic devices [13]. In view of the increasing importance of phosphole-containing conjugated systems, studies on the synthesis and properties of novel conjugated polymers having a phosphole unit in the main chain are considered to be worthy of investigation. In this study, we synthesized a new 2,5-substituted phosphole monomer as a building block of the conjugated polymer; by the similar synthetic approach, we then prepared novel π-conjugated polymers **10a-c** having alternate phosphole- and fluorine-substituted benzene in the main chain.

Experimental

General

NMR spectra were recorded on JEOL JNM-EX270 spectrometer or JEOL EX400 spectrometer. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard (^1H and ^{13}C) or H_3PO_4 as an external standard (^{31}P). UV-Vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI 8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. All experiments were performed under dry argon. Column chromatography was performed with Wakogel C-300 silica gel. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen. Triethylamine was distilled from potassium hydroxide under nitrogen. 1,4-Bromoiodobenzene **1**, 1,6-heptadiyne **2**, zirconocene dichloride **4**, 1,4-dibromotetrafluorobenzene, 1,4-dibromo-2,5-difluorobenzene, 1,4-dibromo-2-fluorobenzene, trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, *n*-BuLi, CuCl, and $PhPCl_2$ were obtained commercially, and used without further purification. 1,4-Diethynyl-polyfluorobenzenes **9a-c** were prepared as described in the literature [14].

Synthesis

*1,7-Bis(4-bromophenyl)hepta-1,6-diyne **3***

A 200 mL flask was charged with 1-bromo-4-iodobenzene **1** (14.7 g, 50 mmol), 1,7-heptadiyne **2** (2.4 g, 25 mmol), $PdCl_2(PPh_3)_2$ (0.88 g, 1.25 mmol), CuI (0.25 g, 1.25 mmol), 100 mL of anhydrous THF, and 30 mL of dry NEt_3. The reaction was carried out at 0°C for 12 h with stirring. The reaction mixture was filtered to eliminate ammonium salts. Solvent was evaporated and then purified by column chromatography (SiO_2, hexane). Recrystallization from methanol provided a white solid (4.5 g, 11 mmol, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (quin, J = 7.0 Hz, 2H), 2.57 (t, J = 7.0 Hz, 4H), 7.26 (d, J = 8.1 Hz, 4H), 7.40 (d, J = 8.1 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.7, 27.7, 80.3, 90.3, 121.7, 122.7, 131.4, 133.0; HRMS (FAB) calcd for $C_{19}H_{14}{}^{79}Br_2$ M^+: 399.9462, found 399.9466; IR (film) 2236 cm^{-1}. Anal. Calcd for $C_{19}H_{14}Br_2$: C, 56.75; H, 3.51; Br, 39.74%. Found: C, 56.81; H, 3.44; Br, 39.71%.

*1-Phenyl-2,5-bis(p-bromophenyl)phosphole **8***

A 100 mL flask was charged with Cp_2ZrCl_2 **4** (0.73 g, 2.5 mmol) and 20 mL anhydrous THF under argon. This solution was cooled to -78°C and *n*-BuLi (3.2 mL of 1.6 M hexane solution, 5.0 mmol) was added dropwise. The resulting solution was stirred at -78°C for 30 min. Compound **3** (1.0 g, 2.5 mmol) in 30 mL THF was added slowly. The resulting solution was warmed to room temperature and stirred for an additional 6 h. The mixture was cooled to 0°C, and then CuCl (0.49 g, 5.0 mmol) was added directly under a flow of argon. The color of the solution changed from light red to dark green. After stirring for 30 min, $PhPCl_2$ (0.44 g, 2.5 mmol) was added slowly by a syringe. The reaction mixture was stirred overnight, and the solvent was removed under reduced pressure. The crude residue was dissolved in degassed $CHCl_3$ and washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$. Solution was plugged through basic alumina column to remove Zirconium species. Solvent was evaporated and the residue was subjected to column chromatography (silica gel, degassed hexane/$CHCl_3$ under argon) to give the pure product **8** (0.42 g, 0.82 mmol, 33%) as a bright yellow solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.33 (m, 1H), 2.42 (m, 1H), 2.71 (m, 2H), 2.92 (m, 2H), 7.16 (m, 2H), 7.31-7.39 (m, 11H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 29.1, 30.1, 118.5, 120.2, 128.8, 129.5, 131.6, 133.2, 134.2, 134.9, 136.6, 155.3; $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +35.6 ppm; HRMS (FAB) calcd for $C_{25}H_{19}{}^{79}Br_2P$ M^+: 507.9591, found 507.9585.

Polymerization

A typical procedure is as follows [15]. A mixture of **8** (0.77 g, 1.50 mmol), **9a** (0.30 g, 1.50 mmol), $PdCl_2(PPh_3)_2$ (52.6 mg, 0.075 mmol), CuI (14.3 mg, 0.075 mmol), NEt_3 (10 mL), and THF (30 mL) was placed in a 100 mL flask under an argon atmosphere. The reaction was refluxed for 48 h with stirring. After the reaction, precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated and poured into degassed MeOH (50 mL) to precipitate the polymer. All work-up procedures were done under an argon atmosphere. The resulting polymer **10a** was filtered, washed with MeOH, and dried in vacuo to give 0.28 g (0.51 mmol, 34%) as a yellow powder.

10a. Yield: 34%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.36 (br, 2H), 2.70 (br, 2H), 2.86 (br, 2H), 7.0-7.6 (m, 13H); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +27.3 ppm. IR (film) 2210 cm^{-1}.

10b. Yield: 33%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.28 (br, 2H), 2.76 (m, 2H), 2.85 (br, 2H), 7.0-7.8 (m, 17H); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +27.8 ppm. IR (film) 2209 cm^{-1}.

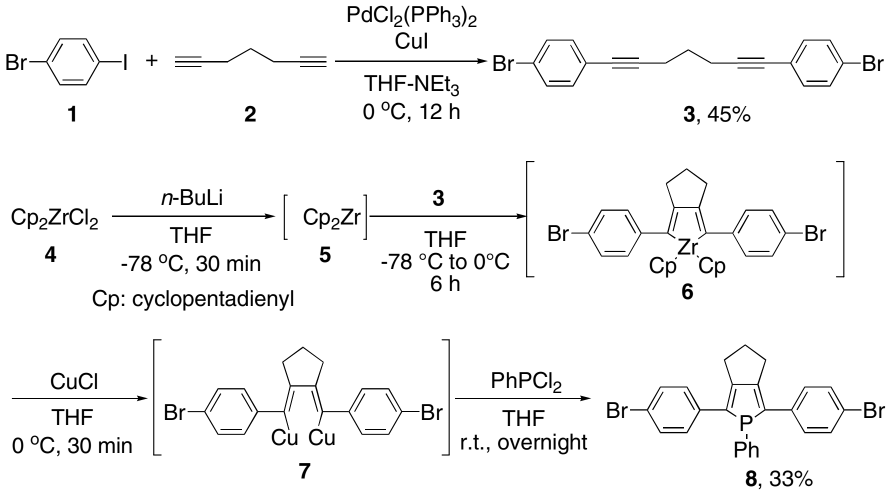
10c. Yield: 28%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.25 (br, 2H), 2.50 (m, 2H), 2.70 (br, 2H), 7.0-7.8 (m, 16H); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +27.9 ppm. IR (film) 2209 cm^{-1}.

Results and Discussion

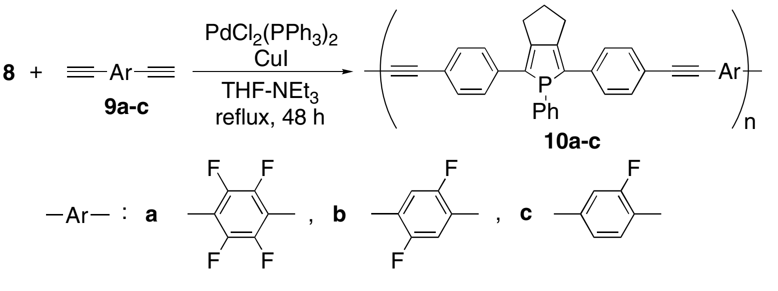
The synthetic route of the phosphole monomer **8** is summarized in Scheme 1. The chemoselective $PdCl_2(PPh_3)_2$/CuI catalyzed cross-coupling reaction of 1,4-bromoiodobenzene **1** with 1,6-heptadiyne **2** gave 1,7-bis(4-bromophenyl)hepta-1,6-diyne **3** in 45% yield. The reaction of **3** with zirconocene **5**, formed by the reaction of zirconocene dichloride **4** with *n*-BuLi, gave a red solution of the corresponding zirconacyclopentadiene **6** [15], which was used in situ for the next step. After **6** was converted into **7** using 2 equivalent CuCl [17], the addition of $PhPCl_2$ to the solution of **7** gave the desired phosphole monomer **8** in 33% yield on the basis of **3**. The structure of the monomer **8** was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectra, as well as by HRMS. From the ^{31}P NMR spectrum of **8**, a single peak derived from the phosphorus atom of the phosphole ring was observed at +35.6 ppm. Although the solution of **8** is unstable in air, a peak at approximately +57.5 ppm derived from phosphole(V) oxide was not observed within the NMR measurement period. Fluorine-substituted diethynylbenzenes **9a-c** were prepared as described in the literature procedure [14].

Polymers **10a-c** were obtained as yellow solids by the Sonogashira reaction [15], as shown in Scheme 2. The results of the polymerizations under optimum conditions are

Scheme 1



Scheme 2



listed in Table 1. For example, the polymerization of **8** with **9a**, in the presence of a catalytic amount of $PdCl_2(PPh_3)_2/CuI$ in THF-Et_3N at reflux temperature for 48 h under an argon atmosphere, proceeded smoothly to give the corresponding polymer **10a** in 34% isolated yield as a yellow powder (Table 1).

Table 1. Synthesis of Polymers **10a-c**

Polymer	Yield[a] / %	M_w[b]	M_n[b]	M_w/M_n[b]
10a	34	7000	6800	1.03
10b	33	3900	2000	1.96
10c	28	2100	1400	1.50

[a]Isolated yield after reprecipitation from MeOH. [b]GPC ($CHCl_3$), polystyrene standards.

The structures of polymers **10a-c** were confirmed by the ^1H, ^{31}P NMR, and FTIR spectra. ^1H and ^{31}P NMR spectra are shown in Figure 1. The ^{31}P NMR spectrum of **10a** showed only one signal at +27.3 ppm derived from the phosphorus atom of the phosphole unit in the conjugated polymer main chain (Figure 1b). The phosphorus peak of polymer **10a** was shifted upfield compared with that of monomer **8** (δ +35.6 ppm). The phosphorus atom was strongly influenced by the environment of the phosphole moiety. On the other hand, in the ^{31}P NMR spectra of the obtained polymers **10a-c**, the signal for the phosphorus atom of the phosphole ring appeared at around +27 ppm, regardless of the number of substituted fluorine atoms of the co-monomer unit. We confirmed that there were no signals of phosphines coordinated to the palladium center. These ^{31}P NMR chemical shifts of the phosphorus atom incorporated into the phosphole skeleton imply that the lone pair of the phosphorus atom slightly participates in the conjugation system.

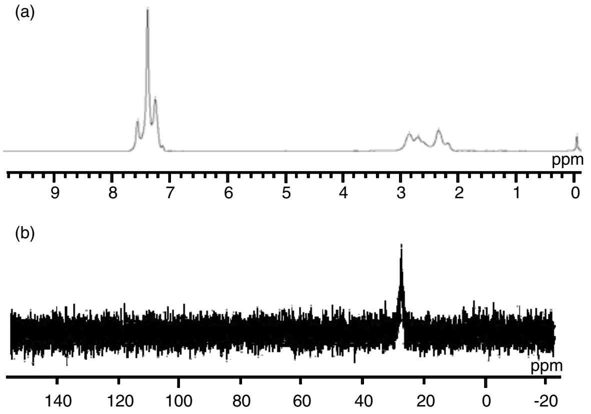


Figure 1. (a) ^1H NMR and (b) ^{31}P NMR spectra of the polymer **10a** in $CDCl_3$.

Measurements of molecular weight were performed by gel permeation chromatography (GPC) in a $CHCl_3$ eluent using a calibration curve of polystyrene standards (Table 1). Polymer **10a** had a number-average molecular weight (M_n) of 6800, which corresponds to a degree of polymerization of 13 with M_w/M_n of 1.03. All polymers **10a-c** were soluble in common solvents such as THF and $CHCl_3$. This relatively good solubility is probably due to the fused carbocyclic framework as well as the phenyl substituent at the phosphorus atom. In the solid state, these polymers were stable in air, whereas they were gradually oxidized in a homogeneous solution.

The optical properties of polymers **10a-c** are summarized in Table 2. The absorption and emission spectra of all polymers were recorded in a dilute chloroform solution at room temperature. The absorption spectrum of polymer **10a** is shown in Figure 2 along with the absorption spectrum of monomer **8**. Polymer **10a** exhibited a strong UV absorption maximum at approximately 395 nm, attributed to the π-π* transition, which was red-shifted with respect to that of monomer **8** (λ_{max} = 378 nm). This result indicates the effective expansion of the π-conjugated system in the polymer backbone. The shapes of the absorption spectra of polymers **10a-c** were almost identical and independent of the number of fluorine atoms of the co-monomer unit.

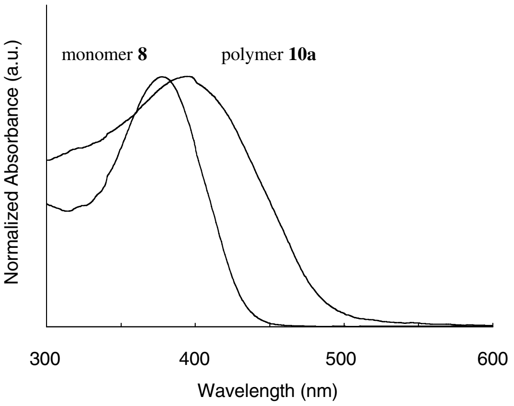


Figure 2. Absorption spectra of polymer **10a** and monomer **8** in $CHCl_3$ solution.

Table 2. Optical Properties of Polymers **10a-c**

Polymer	UV $\lambda_{max}{}^{a}$ / nm	log ε^{a}	PL $\lambda_{max}{}^{a,b}$ / nm	Φ^{c}
10a	395	4.00	470	0.18
10b	388	4.20	461	0.30
10c	396	4.09	502	0.21

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [b] Excited at 390 nm. [c] The quantum yield (Φ) was calculated in $CHCl_3$ at room temperature by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard.

The fluorescence emission spectrum of polymer **10a** is shown in Figure 3, as a representative example. In the fluorescence emission spectrum of the solution of **10a** in chloroform, which was obtained at room temperature using an excitation wavelength of 390 nm, the emission peak of **10a** was observed at 470 nm in the visible bluish-green region. The absorption and emission spectra of polymer **10a** have a moderate Stokes shift ($\Delta\lambda$ = 75 nm). Polymers **10a-c** exhibited low quantum efficiencies in chloroform solution (Table 2); using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard [18], these polymers typically have values higher than 0.2.

In conclusion, we have synthesized a new 2,5-substituted phosphole monomer with a five-membered fused carbocycle as a building block, we have also prepared three

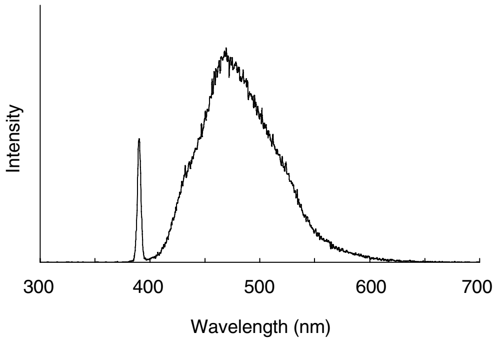


Figure 3. Photoluminescence spectrum of polymer **10a** in $CHCl_3$ solution.

types of novel π-conjugated polymers having 2,5-substituted phosphole and fluorine-substituted diethynylbenzene as repeating units in the main chain. The extension of π-conjugation through the polymer backbone was observed. By changing the co-monomer, the optical properties of the phosphole-containing polymer can be readily tuned. In this study, we showed that 2,5-substituted phosphole moieties are attractive building blocks for the preparation of a novel π-conjugated polymer system.

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18. The absorbance of each sample was below 0.05 at the excitation wavelength at 350 nm, in the measurement of the fluorescence quantum yield. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{\mathrm{unk}} = \Phi_{\mathrm{std}}[A_{\mathrm{std}}F_{\mathrm{unk}}/A_{\mathrm{unk}}F_{\mathrm{std}}][n_{\mathrm{D,unk}}/n_{\mathrm{D,std}}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_{D} is the refractive index [CH_2Cl_2 ($n_{\mathrm{D}} = 1.424$) and $CHCl_3$ ($n_{\mathrm{D}} = 1.446$) were used].