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We report the synthesis of phenyl-capped oligothiophenes *via* improved synthetic schemes. These schemes are based on the Grignard coupling reaction and enable us to obtain the target compounds at high yields. The resulting materials have been fully characterized through nmr and ir spectroscopies. The ir analysis is particularly useful in characterizing the materials of higher molecular weight, since those materials are difficult to dissolve in organic solvent. We also show an improvement on preparation of halogenated (oligo)thiophenes that are used as intermediates for synthesizing the target compounds. An alternative synthetic route to the phenyl-capped oligothiophenes that utilizes the Suzuki coupling reaction is presented as well.

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Introduction.

Various oligothiophenes and oligophenylenes have been synthesized and developed, since these materials are potentially useful as electroactive and/or photoactive organic semiconductors. Using the former materials, for instance, field-effect transistors have been proposed and fabricated [1,2]; the latter have been studied on the electro-luminescent devices [3,4].

In view of such promising aspects and making a further step forward, Hotta and Lee [5] have pointed out that thiophene/phenylene co-oligomers (*i.e.*, the hybridized oligomers comprising thiophenes and phenylenes) can be good candidates as light-emitting materials. One of the advantages of this novel class of organic semiconductors is that the extension of π -conjugation can be tuned as desired by changing the total ring number of the thiophenes and phenylenes and their mutual arrangement in the molecule.

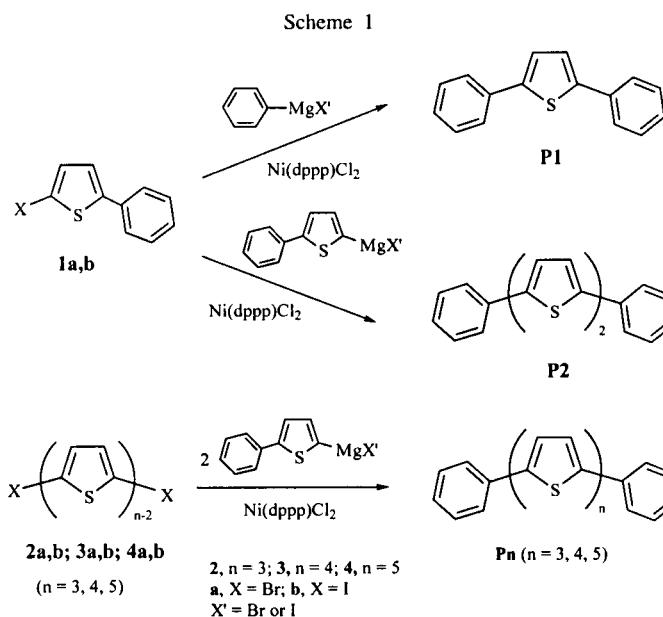
In this article we report syntheses of a series of phenyl-capped oligothiophenes **P_n** (see molecular structure in Scheme 1), a specific class of the thiophene/phenylene co-oligomers. Their syntheses could sparingly be found in previous work. For example, Steinkopf *et al.* [6] synthesized **P2** *via* the Grignard coupling using 2-iodo-5-phenylthiophene (**1b**) as a starting material the reported yield of **P2** [6] was at most 8%; this seems due partly to the incomplete generation of the Grignard reagent [6]. Steinkopf *et al.* [7] proposed a different synthetic procedure for **P3** and **P4**, but the yields were even lower (less than 1%) [7]. Another attempt at preparing **P2** was made by Peters *et al.* [8] *via* palladium-catalyzed coupling reaction of a stannyl compound. The authors, however, stated that the yield was low (~2.5%). To overcome those drawbacks, Graf *et al.* [9] proposed an improved synthetic scheme in which they used the Grignard reagent phenylmagnesium bromide instead of compound **1**. The Grignard reagent was coupled with

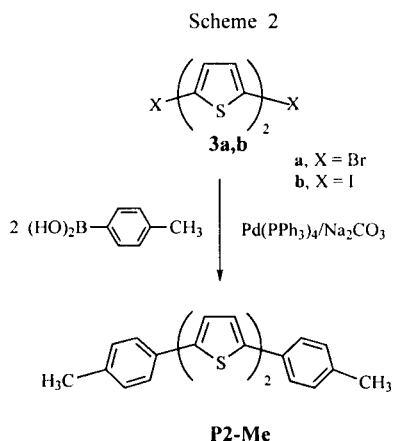
5,5''-dibromo-2,2':5',2''-terthiophene (**4a**) to produce **P3**. Its yield was reportedly 55% [9], but the value was still low.

Thus, the systematic syntheses of **P_n** have not yet been well-established. In addition, the previously reported synthetic schemes required somewhat tedious and/or vigorous reaction conditions. Bearing these in mind, we have improved the synthetic schemes of **P_n** ($n = 1-5$) and have been successful in preparing the materials of high quality under mild reaction conditions. Moreover to the best of our knowledge, no literature has been accessible so far regarding the synthesis of **P5**.

Preparation of the Materials.

Scheme 1 shows synthetic routes of **P_n** ($n = 1-5$) based on the Grignard coupling reaction. Of **P_n**, **P1-P3** were





synthesized in diethyl ether. As for **P4** and **P5**, on the other hand, anisole was used as solvent. This is because the starting materials 5,5'-dihalo-2,2'-bithiophene (**3**) and 5,5''-dihalo-2,2':5',2''-terthiophene (**4**) are both barely soluble in diethyl ether, but can readily be dissolved in anisole. Thus, **1** was first quantitatively transformed into the corresponding Grignard reagent in diethyl ether. Then, diethyl ether was evaporated and replaced with anisole [10] and the Grignard reagent was coupled with **3** or **4**.

To prepare **P2-P5**, the reaction vessel containing the solid intermediate **1** together with magnesium was evacuated beforehand under mild heat to ensure a rigorously moisture- and oxygen-free environment. This contributes toward the quantitative formation of the Grignard reagent of **1** and enables us to synthesize the target compounds at a high yield. In particular, **P2** and **P3** were produced in excellent yields (97% for **P2** and 94% for **P3**). After recrystallizing the resulting materials of **P2** and **P3** from suitable solvent such as toluene, their overall yields exceeded 60%.

Although **P4** was not obtained in a quantitative manner, its yield (*ca.* 40%; see experimental) was by far higher than that implied in the literature [7]. The quantitative formation was not achieved for **P5**, either. The reason for this would be that a monohalide generated from the equimolar coupling reaction between **4** and the Grignard reagent derived from **1** partly precipitates and wouldn't react further with the Grignard reagent of **1**. Nevertheless, the said monohalide can easily be removed by the Soxhlet extraction with dichloromethane, in which the monohalide is soluble but **P5** is insoluble. Pure **P5** can be obtained through recrystallizing the non-extracted material from 1,2,4-trichlorobenzene. Thus, a yield of *ca.* 30% was obtained.

As an alternative synthetic route for **Pn**, we utilized the Suzuki coupling reaction [11]. An example is illustrated in Scheme 2 where *p*-tolylboronic acid reacts with **3** to form 5,5'-bis(*p*-tolyl)-2,2'-bithiophene (**P2-Me**), which is a methyl derivative of phenyl-capped bithiophene.

We also made an improvement upon the syntheses of **1**, **3**, and **4**. Kellogg *et al.* [12,13] showed that acid-catalyzed

bromination of thiophenes and bithiophenes with *N*-bromo-succinimide (NBS) readily takes place to form the corresponding α -bromo derivatives in a 50:50 (v/v) mixture of chloroform and glacial acetic acid. In the meanwhile, iodination of **5**, **6**, and **7** was reported to progress in the presence of iodine and mercury(II) oxide to form the corresponding iodide compounds **1b**, **3b**, and **4b**, respectively [14-18].

On the basis of those precedents, we have found out that the bromination of thiophenes and oligothiophenes with NBS proceeds effectively either in methanol or in dichloromethane even in the absence of glacial acetic acid. This is particularly useful for the bromination of **7** when dichloromethane is used as solvent. This is because **7** is difficult to dissolve in the 50:50 (v/v) mixture of chloroform and glacial acetic acid, but is readily dissolved in dichloromethane.

We have also observed that the iodination of thiophenes and oligothiophenes with *N*-iodosuccinimide (NIS) occurs smoothly in the presence of glacial acetic acid *equimolar* to NIS, allowing us to avoid using a highly toxic reagent of mercury(II) oxide. The iodination can be carried out in methanol or dichloromethane as in the case of the bromination. Practically, the presence of the above small amount of acetic acid does not reduce the solubility of the oligothiophenes at all (see experimental). The synthetic processes pertinent to the iodination are summarized in Scheme 3. Bromination can be done analogously. Note that the halogenation of **5** takes place preferentially at the α -position of thiophene [12,14,15].

Spectroscopic Characterization of the Materials.

The molecular structures of **P1**, **P2**, **P2-Me**, and other intermediates can reasonably be determined by the ^1H nmr (see experimental). Compounds **P3-P5** with higher molecular weight, however, are extremely difficult to dissolve at room temperature in any common organic solvents. Their nmr characterization in solution will therefore be a formidable task. Under such circumstances ir spectroscopy is a powerful tool for characterizing the materials. The most reliable clue lies in close inspection of the ir region around 700-800 cm^{-1} [19]. Since the materials in the present studies

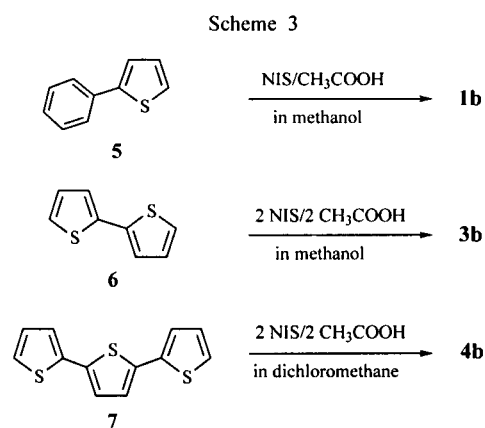


Table 1

Infrared Band Positions (cm⁻¹) and Their Assignment of Various Phenyl-capped Oligothiophenes

Compound	CH stretching		Ring stretching		CH out-of-plane deformation	
	Aromatic	Aliphatic	Thiophene	Phenyl	Thiophene	Phenyl
P1	3055	–	1454	1488	802	750, 688
P2	3055	–	1443	1484	794	750, 684
P3	3055	–	1440	1484	791	750, 684
P4	3055	–	1440	1488	791	747, 684
P5	3060	–	1441	1488	791	750, 686
P2-Me	3067	2912	1448	1499	798	818

comprise solely aromatic rings of thiophenes and phenylenes, these materials display intense CH out-of-plane deformation vibrations in the aforementioned region. Furthermore, the location of these vibrations unambiguously determines the substitution modes of the thiophenes and phenylenes [19,20].

In practice, **P_n** (n = 1-5) exhibit closely related ir profiles including the ~700-800 cm⁻¹ region. The relevant characteristic frequencies as well as those associated with the CH stretching and ring stretching modes are summarized in Table 1. Regarding these **P_n**, a sharply resolved peak around 795 cm⁻¹ is assigned to the CH out-of-plane deformation mode of the 2,5-disubstituted thiophene ring [20]; two intense bands around 750 and 685 cm⁻¹ are due to the same mode of the monosubstituted benzene ring [19]. If one compares these spectra with that of **P2-Me**, the assignment is more decisive. Besides a dominant peak at 798 cm⁻¹ due to the CH out-of-plane mode of the 2,5-disubstituted thiophene ring, the latter spectrum displays a single major peak at 818 cm⁻¹ in the ~700-800 cm⁻¹ region (see Table 1). This peak replaces the two bands around 750 and 685 cm⁻¹ observed for **P_n**, obviously reflecting the presence of the 1,4-disubstituted benzene ring [19].

On the basis of those spectroscopic characteristics, we conclude that all **P_n** (n = 1-5) possess the oligothiophene skeleton in the center of the molecule with the phenyl groups located at both the molecular terminals, as immediately inferred from Scheme 1.

Conclusion.

We have described the systematic synthetic methods of the phenyl-capped oligothiophenes (**P_n**) that are based mostly upon the Grignard coupling reaction, partly utilizing the Suzuki coupling reaction. In the case of the Grignard coupling, we have made the most of the reagents 2-halo-5-phenylthiophene (**1**). Among **P_n**, in particular, we obtained **P2** and **P3** in a quantitative manner. Although in the case of **P4** and **P5** we could not obtain them quantitatively, the yield of **P4** was by far higher than that implied in the previously reported literature. Moreover to the best of our knowledge, well-characterized **P5** has been synthesized successfully for the first time.

We have improved the preparation methods of the intermediates **1**, **3**, and **4** such that their formation *via* halogenation with NBS or NIS readily progresses without using excess of acetic acid or a toxic reagent. Additionally, the Suzuki coupling reaction turned out to be useful as an alternative way of the synthesis of **P_n**.

All the materials prepared above have been satisfactorily characterized by the nmr and ir spectroscopies.

EXPERIMENTAL

Melting points were measured on a Seiko Instruments SSC5000 thermal analysis system. The ¹H nmr spectra were recorded on a Varian Gemini 300BB spectrometer in deuteriochloroform solution and chemical shifts are reported in ppm (δ) relative to tetramethylsilane as an internal standard. The ir spectra were taken on a Perkin-Elmer System 2000 FT-IR spectrophotometer with finely pulverized particles dispersed and embedded in a potassium bromide matrix. Elemental analyses (for carbon, hydrogen, and sulfur) were carried out on a CE Instruments EA 1110 CHNS-O apparatus. Quantitative analyses of halogens (bromine and iodine) were performed in a Hamada-rika FHO-A flask-type combustion apparatus.

Dehydrated diethyl ether and anhydrous anisole were purchased from Wako Pure Chemical and from Aldrich, respectively, and these were used without further purification or desiccation. Other chemical reagents were purchased from standard sources and used as received unless otherwise specified. The formation of the Grignard reagents and the subsequent Grignard coupling reaction were carried out in dry glassware and the reaction system was kept under dry nitrogen throughout.

2,5-Diphenylthiophene (**P1**).

Equimolar amounts of distilled bromobenzene (596 mg, 3.80 mmoles) and magnesium (92.3 mg, 3.80 mmoles) were mixed in anhydrous diethyl ether (15 ml) to prepare a Grignard reagent. To the resulting Grignard reagent were added [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl₂; 40 mg, 0.074 mmole) and **1a** (454 mg, 1.90 mmoles) successively. After stirring overnight at room temperature, the reaction mixture was refluxed for 6 hours. When cooled over an ice/water bath and subsequently hydrolyzed with 2 N hydrochloric acid (2 ml), the reaction mixture produced precipitates, which were collected by filtration and washed with cold methanol. The precipitates were recrystallized from methanol to give pale yellow solid **P1**, yield 35%, mp 155°, lit [21] mp 153-154°; ¹H nmr: δ 7.25-7.65 (m, 10H, phenyl protons), 7.29 ppm (s, 2H, thiophene protons).

Anal. Calcd. for C₁₆H₁₂S: C, 81.31; H, 5.12; S, 13.57. Found: C, 80.95; H, 5.11; S, 13.05.

5,5'-Diphenyl-2,2'-bithiophene (**P2**).

A flask containing equimolar amounts of **1a** (478 mg, 2.00 mmoles) and magnesium (48.6 mg, 2.00 mmoles) was evacuated under mild heat. To this solid mixture was added anhydrous diethyl ether (15 ml) to prepare a Grignard reagent. After all magnesium disappeared, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (20 mg, 0.037 mmole) and an additional 383 mg of **1a** (1.60 mmoles) were added successively. Precipitation occurred immediately. The reaction mixture was then treated

similarly to the case of **P1** synthesis. The resulting precipitates were recrystallized from toluene to give bright yellow solid **P2**, yield 69%, mp 238°, lit [6] mp 237°; ¹H nmr: δ 7.18 (d, J = 3.9 Hz, 2H, thienylene protons), 7.25 (d, J = 3.9 Hz, 2H, thienylene protons), 7.27-7.63 ppm (m, 10H, phenyl protons).

Anal. Calcd. for C₂₀H₁₄S₂: C, 75.43; H, 4.43; S, 20.14. Found: C, 75.15; H, 4.42; S, 19.74.

5,5''-Diphenyl-2,2':5',2''-terthiophene (**P3**).

In a manner similar to the synthesis of **P2**, the Grignard reagent was prepared by using **1b** (572 mg, 2.00 mmol) in place of **1a**. After completion of the Grignard reagent formation, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (20 mg, 0.037 mmol) and 2,5-diiodothiophene **2b** (Aldrich; 269 mg, 0.80 mmol) were added successively. Precipitation occurred immediately. The reaction mixture was then treated similarly to the case of **P1** synthesis. The resulting precipitates were recrystallized from toluene to give yellow solid **P3**, yield 64%, mp 279°, lit [7] mp 273°.

Anal. Calcd. for C₂₄H₁₆S₃: C, 71.96; H, 4.03; S, 24.01. Found: C, 71.57; H, 3.79; S, 23.37.

5,5'''-Diphenyl-2,2':5',2''':5'',2'''-quaterthiophene (**P4**).

The Grignard reagent was prepared from equimolar amounts of **1b** (544 mg, 1.90 mmol) and magnesium (46.2 mg, 1.90 mmol) following the same manner as described for the **P3** synthesis. After the completion of the Grignard reagent formation, diethyl ether was evaporated with a dry nitrogen blow and subsequently replaced with anisole (6 ml) [10]. To this reaction mixture were successively added [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (10 mg, 0.018 mmol) and **3b** (334 mg, 0.80 mmol) dissolved in anisole (4 ml). Precipitation occurred immediately. The resulting reaction mixture was stirred overnight at room temperature and then heated at 100° for 6 hours. The reaction mixture was cooled over an ice/water bath and subsequently hydrolyzed with 2 *N* hydrochloric acid (1 ml). The resulting precipitates were collected by filtration and washed by turns with acetone and dichloromethane. The precipitates were recrystallized from 1,2,4-trichlorobenzene to give orange solid **P4**, yield 41%, mp 336°, lit [7] mp 317°.

Anal. Calcd. for C₂₈H₁₈S₄: C, 69.67; H, 3.76; S, 26.57. Found: C, 69.02; H, 3.70; S, 26.26.

5,5''''-Diphenyl-2,2':5',2''':5'',2''':5''''-quinquethiophene (**P5**).

The same procedure as described for the **P4** synthesis was applied, except for using **4b** in place of **3b**. The resulting precipitates underwent Soxhlet extraction with dichloromethane and the non-extracted material was recrystallized from 1,2,4-trichlorobenzene to give brownish solid with coppery luster of **P5**, yield 33%, mp 350°.

Anal. Calcd. for C₃₂H₂₀S₅: C, 68.05; H, 3.57; S, 28.38. Found: C, 66.82; H, 3.39; S, 28.65.

5,5'-Bis(*p*-tolyl)-2,2'-bithiophene (**P2-Me**).

Compound **3b** (418 mg, 1.00 mmol) and *p*-tolylboronic acid (544 mg, 4.00 mmol) as well as tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄; 139 mg, 0.12 mmol) were dissolved in benzene (80 ml) and this reaction solution was purged with nitrogen for 30 minutes to remove dissolved oxygen. To the reaction solution was added 5 ml of an aqueous solution of sodium carbonate (848 mg, 8.00 mmol). The solution was

stirred for two days and nights at room temperature under a nitrogen atmosphere. The resulting solution was then cooled with an ice/water bath and oxidized with 1 ml of an aqueous solution of hydrogen peroxide (30%), to yield precipitates. These precipitates, which were collected by filtration and washed with methanol, further underwent Soxhlet extraction with dichloromethane. The extracted material precipitated in the bottom flask of the Soxhlet apparatus was collected by filtration and recrystallized from chloroform to give bright yellow solid **P2-Me**, yield 38%, mp 252°; ¹H nmr: δ 2.37 (s, 6H, methyl protons), 7.15 (d, J = 3.8 Hz, 2H, thienylene protons), 7.20 (d, J = 3.8 Hz, 2H, thienylene protons), 7.20 (dd, J = 8.0, 2.1 Hz, 4H, phenylene protons), 7.50 ppm (dd, J = 8.0, 2.1 Hz, 4H, phenylene protons).

Anal. Calcd. for C₂₂H₁₈S₂: C, 76.26; H, 5.23; S, 18.51. Found: C, 76.34; H, 5.06; S, 17.84.

2-Bromo-5-phenylthiophene (**1a**).

2-Phenylthiophene (**5**) was synthesized following the literature method [21]. Compound **5** (3.20 g, 20 mmol) was dissolved in 20 ml of methanol, and to this solution was added another methanol solution (40 ml) containing *N*-bromosuccinimide (3.92 g, 22 mmol). White precipitate formed immediately. The reaction mixture was put into a refrigerator to ensure generation of the precipitation. The precipitate was collected by filtration and washed with a large amount of an equivolume mixture of water and methanol. The resulting precipitate was dried and recrystallized from a mixture of methanol:water (5:1, v/v) to obtain colorless crystals **1a**, yield 32%; ¹H nmr: δ 7.03 (d, J = 3.8 Hz, 1H, a thienylene proton), 7.06 (d, J = 3.8 Hz, 1H, a thienylene proton), 7.27-7.53 ppm (m, 5H, phenyl protons).

Anal. Calcd. for C₁₀H₇SBr: C, 50.23; H, 2.95; S, 13.41; Br, 33.41. Found: C, 50.00; H, 2.87; S, 13.21; Br, 33.54.

2-Iodo-5-phenylthiophene (**1b**).

Compound **5** (8.01 g, 50 mmol) and *N*-iodosuccinimide (16.87 g, 75 mmol) were dissolved in methanol (50 ml). To this solution acetic acid (4.29 ml, 75 mmol) was added and soon white precipitate formed. The reaction mixture was then treated in a manner similar to that described for the **1a** synthesis. The resulting precipitate was recrystallized from a mixture of methanol:water (20:3, v/v) to obtain colorless crystals **1b**, yield 68%; ¹H nmr: δ 6.98 (d, 1H, a thienylene proton, J = 3.8 Hz), 7.22 (d, 1H, a thienylene proton, J = 3.8 Hz), 7.27-7.54 ppm (m, 5H, phenyl protons).

Anal. Calcd. for C₁₀H₇SI: C, 41.98; H, 2.46; S, 11.21; I, 44.35. Found: C, 41.83; H, 2.39; S, 11.02; I, 44.40.

5,5'-Diiodo-2,2'-bithiophene (**3b**).

2,2'-Bithiophene **6** (Aldrich; 831 mg, 5.00 mmol) and *N*-iodosuccinimide (2.81 g, 12.5 mmol) were dissolved in methanol (75 ml). To this solution acetic acid (0.72 ml, 12.5 mmol) was added and soon precipitate formed. The reaction mixture was then treated in a manner similar to that described for the **1a** synthesis. The resulting precipitate was successively washed with methanol, dried, and recrystallized from acetone to give colorless crystals **3b**, yield 48%; ¹H nmr: δ 6.79 (d, J = 3.9 Hz, 2H, thienylene protons), 7.15 ppm (d, J = 3.9 Hz, 2H, thienylene protons).

5,5''-Diiodo-2,2':5',2''-terthiophene (**4b**).

2,2':5',2''-Terthiophene **7** (Aldrich; 994 mg, 4.00 mmol) and *N*-iodosuccinimide (1.98 g, 8.80 mmol) were dissolved in dichloromethane (60 ml). To this solution acetic acid (0.50 ml,

8.8 mmoles) was added and soon precipitate formed. The reaction mixture was then magnetically stirred for 2 hours over an ice/water bath. The resulting precipitate was washed with methanol and recrystallized from 2-butanone to give yellow solid **4b**, yield 63%; ^1H nmr: δ 6.84 (d, $J = 3.9$ Hz, 2H, side thienylene protons), 7.01 (s, 2H, central thienylene protons), 7.17 ppm (d, $J = 3.9$ Hz, 2H, side thienylene protons).

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