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Received September 17, 1999

We report the synthesis of block and alternating thiophene/phenylene co-oligomers that is based either on the Suzuki coupling reaction or on the Grignard reaction. These reaction schemes enable us to obtain the target compounds at reasonably high yields. The resulting materials have been fully characterized through the solid-state ^{13}C nmr and Fourier-transform ir as well as the ^1H nmr. Of these, the solid-state ^{13}C nmr and ir are particularly useful in characterizing the materials of higher molecular weight, since those materials are difficult to dissolve in organic solvents.

J. Heterocyclic Chem., **37**, 281 (2000).

Introduction.

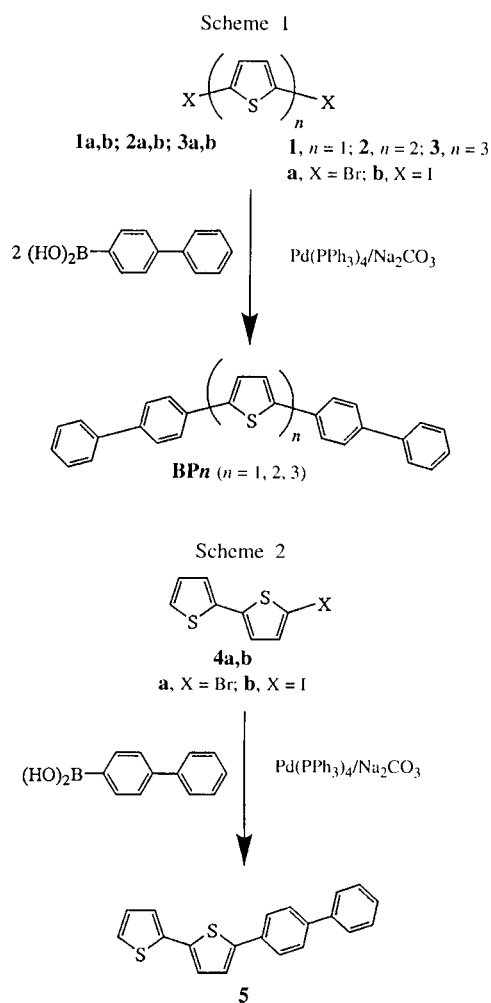
Thiophene/phenylene co-oligomers (*i.e.* the hybridized oligomers comprising thiophenes and phenylenes) have been synthesized and developed as a novel class of organic semiconductors [2,3]. One of the major advantages of these compounds is that extension of the π -conjugation can be tuned as desired by changing the total ring number of the thiophenes and phenylenes and their mutual arrangement in the molecule. In particular, those co-oligomers can be good candidates as light-emitting materials [2,3].

In the previous article, we reported among the thiophene/phenylene co-oligomers the syntheses of a series of phenyl-capped oligothiophenes [1]. These co-oligomers exhibit different molecular alignments in thin films either parallel or perpendicular to the substrate plane, depending on the different chemical species [2]. In the present article we show the syntheses of other sorts of co-oligomers, *i.e.* block and alternating co-oligomers. These compounds add realistic diversity to the family of thiophene/phenylene co-oligomers.

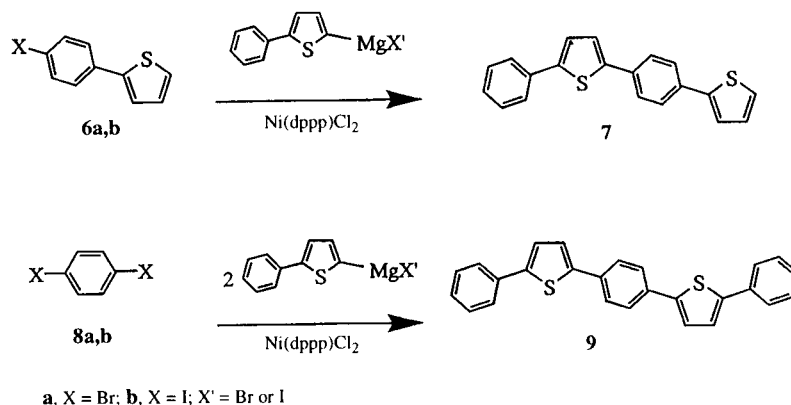
Preparation of the Materials.

Schemes 1 and 2 show synthetic routes of the block co-oligomers. These compounds were synthesized at reasonably high yields *via* the Suzuki coupling reaction [4], in which the use of 4-biphenylboronic acid has been found effective. Meanwhile, the alternating co-oligomers were prepared through the Grignard reaction [5] (Scheme 3).

In Scheme 1 monohalides generated by an equimolar reaction between **1a,b** (or **2a,b** or **3a,b**) and 4-biphenyl-



Scheme 3



boronic acid become less soluble with increasing n . Therefore, appropriately good solvents were selected so that quantitative generation of the aimed compounds **BP n** ($n = 1-3$) can be ensured through complete dissolution of the monohalides. For that purpose we used as the reaction solvents benzene, chlorobenzene, and 1,2,4-trichlorobenzene for synthesizing **BP n** ($n = 1, 2$, and 3), respectively. Thus, all these compounds were synthesized almost in a quantitative manner (94–100%). After purifying the resulting materials their overall yields were reasonably high (> 46%).

The alternating co-oligomers were synthesized by the Grignard coupling reaction (Scheme 3). In this scheme we used the Grignard reagent derived from 2-bromo-5-phenylthiophene or 2-iodo-5-phenylthiophene [1]. The quantitative generation of the alternating co-oligomers was also confirmed; yields of **7** and **9** were 100% and 91%, respectively. The overall yields of about 60% were reached for these compounds after purification of the materials. For the synthesis of **7**, we used intermediates of 2-(4-halogenophenyl)thiophene (**6a,b**). Of these intermediates, **6a** was effectively formed *via* the Suzuki coupling between 2-iodothiophene and 4-bromobenzeneboronic acid. In other words, **6a** was preferentially generated by this reaction, with the self-coupling of 4-bromobenzeneboronic acid of secondary importance. As a result roughly a 30% yield was attained for the synthesis of **6a**.

Amongst the compounds synthesized in the present studies, to the best of our knowledge, no literature has yet been reported regarding the syntheses of **BP n** ($n = 2$ and 3), **5**, **7**, or **9**.

Spectroscopic Characterization of the Materials.

The compounds **BP n** ($n = 1-3$) together with **9** are quite sparingly soluble at room temperature in any common organic solvents. Their nmr characterization in solution will therefore be a formidable task. Under such circumstances the high-resolution ^{13}C nmr spectroscopy and

Fourier-transform ir spectroscopy in the solid state are very useful in characterizing the materials. Regarding **5** and **7**, on the other hand, their molecular structure can readily be determined by the ^1H nmr in solution (see EXPERIMENTAL).

From the point of view of assigning the ^{13}C nmr lines of **BP n** ($n = 1-3$) and **9** we remark that these compounds have four kinds of specific carbons that are directly bonded to a thiophene or phenylene (or phenyl). These carbons are categorized as follows: (A) the thiophene carbon directly bonding to a thiophene, (B) the thiophene carbon directly bonding to a phenylene, (C) the phenylene carbon directly bonding to a thiophene, and (D) the phenylene carbon directly bonding to a phenylene. These ^{13}C nmr peaks usually arise in the low magnetic-field region in the spectra.

For the purpose of assigning the relevant lines, we benefit from the coexistence of the *S-syn* and *anti* conformers [6] in **BP2**. This compound exhibits two pairs of split lines. One is split at 141.4 and 140.1 ppm; the other at 138.4 and 137.0 ppm. Amongst the A–D carbons, the nmr line positions of the thiophene-associated A and B carbons should be most largely influenced by the *syn/anti* interconversion, according as the local chemical environment around those carbons changes most largely by this interconversion [6]. Consequently, the two pairs of split lines must be due to A and B carbons.

Since the A carbon in 2,2':5',2''-terthiophene is peaked either at 137.6 ppm or at 136.3 ppm [7], the pair of split lines located at related positions of 138.4 and 137.0 ppm for **BP2** is most likely attributed to the A carbon as well. It follows, therefore, that the other pair of split lines at 141.4 and 140.1 ppm is assigned to the B carbon. We note here that 5,5'-diphenyl-2,2'-bithiophene [1] also indicates in a similar region a line splitting related to the case of **BP2**. The former compound shows two pairs of split lines at 140.7 and 140.0 ppm as well as 137.4 and 136.7 ppm. Following the above arguments the pair located in the

higher magnetic field is due to the A carbon, whereas that in the lower field is assigned to the B carbon.

For a further precise assignment we can usefully invoke the results of 5,5'-diphenyl-2,2'-bithiophene [1] and 5,5"-diphenyl-2,2':5',2"-terthiophene [1]. As in 5,5'-diphenyl-2,2'-bithiophene the line of the C carbon occurs at 133.8 ppm, the corresponding C carbon of **BP2** exhibits a line at a related position of 133.4 ppm. As a consequence, the line at 135.5 ppm for **BP2** is attributed to the D carbon. The remainder occurring in the higher field (~125–130 ppm) are assigned to the carbons that are bonded to a hydrogen.

The ^{13}C nmr lines for the other compounds were assigned along the case of **BP2**. Notice that the A carbons are absent in **BP1**. In **BP1**, furthermore, the lines for C and D carbons were overlapped. Meantime, the conformers coexistence was observed for neither **BP1** nor **BP3**. In the case of **9** the lowest magnetic-field line (142.2 ppm) is again attributed to the B carbons. Since **9** has two kinds of C carbons, the associated lines should be resolved in the spectrum. Of these, the 134.3-ppm line is expected to be due to the C carbon in the terminal phenyl group, because 5,5"-diphenyl-2,2':5',2"-terthiophene exhibits the corresponding line of the C carbon at 134.2 ppm. Accordingly, the 132.6-ppm line of **9** is ascribable to the C carbon of the central phenylene. The aforementioned assignments are summarized in Table 1.

Table 1

^{13}C nmr Band Positions (ppm) and Their Assignments of Various Thiophene/phenylene Co-oligomers.

Compound	A carbon	B carbon	C carbon	D carbon	Others
BP1	--	143.0	135.4**	135.4**	125.4-129.9
BP2	138.4*, 137.0*	141.4*, 140.1*	133.4	135.5	125.1-129.3
BP3	136.7	140.6	133.6	135.2	125.2-129.8
9	--	142.2	134.3, 132.6	--	125.1-129.3

* Split lines

** An overlapped line

The definition of the A-D carbons can be seen in the text.

To further confirm the above assignments of the ^{13}C nmr lines we complementarily utilize the results of the Fourier-transform ir spectroscopy. Here the most reliable clue lies in close inspection of the ir region around 1400–1500 cm^{-1} and 700–800 cm^{-1} [8]. Since the materials in the present studies comprise solely aromatic rings of thiophenes and phenylenes, these materials display intense ring stretching vibrations and CH out-of-plane deformation vibrations in the 1400–1500 cm^{-1} and 700–800 cm^{-1} regions, respectively. Furthermore, the

location of these vibrations unambiguously determines the substitution modes of the thiophenes and phenylenes [8,9].

In practice, **BP n** ($n = 1-3$) exhibit closely related ir profiles including the above-mentioned regions. The relevant characteristic frequencies as well as those associated with the CH stretching modes are collected in Table 2. Regarding these **BP n** , sharply resolved peaks occurring around 1445 and 795 cm^{-1} are assigned to the ring stretching and CH out-of-plane deformation modes of the 2,5-disubstituted thiophene ring, respectively [9]. Meanwhile, two intense bands around 1480 and 1410 cm^{-1} are due to the ring stretching mode of the 4-biphenyl group. Two sharp peaks arising around 760 and 690 cm^{-1} are attributed to the CH out-of-plane deformation mode of the monosubstituted benzene ring in the 4-biphenyl group; another sharp peak around 835 cm^{-1} is due to the 1,4-disubstituted benzene ring in the same group [8].

Table 2

Infrared Band Positions (cm^{-1}) and Their Assignment of Various Thiophene/phenylene Co-oligomers

Compound	CH stretching	Ring stretching		CH out-of-plane deformation	
		Thiophene	Phenyl(ene)	Thiophene	Phenyl(ene)
BP1	3052	1446	1485, 1409	801	839, 760, 687
BP2	3055	1443	1480, 1406	794	831, 758, 688
BP3	3052	1442	1484, 1408	793	835, 761, 689
5	3063	1447, 1425	1484, 1406	798	835, 761, 684
7	3070	1451, 1425	1488	798	817, 750, 684
9	3052	1452	1485	799	829, 747, 683

The assignments of the other compounds were carried out similarly. Both **5** and **7** exhibit an additional peak at 1425 cm^{-1} in the ring stretching region because of the presence of the 2-monosubstituted thiophene ring [10]. For **7**, however, a peak around 1410 cm^{-1} is absent according to the absence of the 4-biphenyl group. Regarding **9**, there are only two major bands in the ring stretching region, because neither the 2-monosubstituted thiophene ring nor the 4-biphenyl group is present in this compound.

The ^1H nmr spectral characteristics of **5** and **7** are worthy of being noted. The local chemical environments in the vicinity of the two hydrogen atoms on the β -carbons of the inner thiophene are more closely related to each other in the compound **7** than in **5**. This is also the case with the hydrogens on the 2-, 3-, 5-, and 6-carbons of the inner phenylene. What is anticipated from this situation is that the ^1H nmr lines of those hydrogens for **7** may well coalesce [6]. This is actually true of the said hydrogens of the inner phenylene (see EXPERIMENTAL). As for **5**, on the other hand, the corresponding lines do not coalesce.

This feature is useful in distinguishing these two compounds spectroscopically, seeing that the two compounds display somewhat related spectral profiles in the ir.

Thus, on the basis of the above-mentioned spectroscopic characteristics we conclude that all the co-oligomers in the present studies possess the well-defined molecular structure, as immediately inferred from Schemes 1–3.

Conclusion.

We have described the systematic synthetic methods of the block and alternating thiophene/phenylene co-oligomers that are based upon the Suzuki coupling reaction and the Grignard reaction. The block co-oligomers were synthesized at reasonably high yields *via* the Suzuki coupling reaction in which 4-biphenylboronic acid was effectively used. The alternating co-oligomers were prepared through the Grignard reaction. To the best of our knowledge, well-characterized **BP n** ($n = 2$ and 3), **5**, **7**, and **9** have been synthesized successfully for the first time.

All the materials prepared above have been satisfactorily characterized by the nmr and ir spectroscopy. To identify **BP n** ($n = 1$ – 3) and **9**, in particular, we made the most of the high-resolution ^{13}C nmr spectroscopy in the solid state.

EXPERIMENTAL

Melting points were measured on a Seiko Instruments SSC5000 thermal analysis system. The solid-state ^{13}C CP-MAS nmr measurements were performed on a Bruker DSX-300 spectrometer equipped with a CP-MAS accessory and operating at 75.48 MHz. The ^{13}C chemical shifts were calibrated indirectly with an external standard of adamantane (29.5 ppm relative to tetramethylsilane). The experimental errors of the ^{13}C chemical shift values were estimated to be less than ± 0.2 ppm. The ^1H nmr spectra were recorded on a Varian Gemini 300BB spectrometer in deuteriochloroform solutions and chemical shifts are reported in ppm (δ) relative to tetramethylsilane as an internal standard. As an exception the ^1H nmr spectrum of **6a** was measured in a deuteriobenzene solution to obtain good resolution. 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 CEInstruments EA 1110 CHNS-O apparatus.

Dehydrated diethyl ether was purchased from Wako Pure Chemical and 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-Bis(4-biphenyl)thiophene (**BP1**).

2,5-Diiodothiophene **1b** (336 mg, 1.00 mmole) and 4-biphenylboronic acid (792 mg, 4.00 mmoles) as well as tetrakis(tri-

phenylphosphine)palladium(0) [abbreviated as $\text{Pd}(\text{PPh}_3)_4$ in Schemes 1 and 2; 139 mg, 0.12 mmole] were dissolved in benzene (80 ml) and nitrogen was bubbled through this reaction solution 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 mmoles), and then the solution was refluxed for 6 hours under nitrogen environment. The resulting solution was then cooled with an ice/water bath and oxidized with 1 ml of an aqueous solution of hydrogen peroxide (30%), yielding precipitates. These precipitates were collected by filtration, washed with methanol, and recrystallized from 1,2,4-trichlorobenzene to give bright yellow solid **BP1**, yield 68%, mp 329°, lit [11] mp 337°.

Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{S}$: C, 86.56; H, 5.19; S, 8.25. Found: C, 86.00; H, 5.11; S, 8.27.

5,5'-Bis(4-biphenyl)-2,2'-bithiophene (**BP2**).

We applied the same procedure as the case of the **BP1** synthesis, except for using 5,5'-diiodo-2,2'-bithiophene **2b** [1] (418 mg, 1.00 mmole) and chlorobenzene in place of **1b** and benzene, respectively. The reaction mixture was heated at 100° for 6 hours. The precipitates generated after the course of reaction were collected by filtration and washed by turns with acetone and methanol. These precipitates were recrystallized from 1,2,4-trichlorobenzene to give shiny yellow solid **BP2**, yield 57%, mp 358°.

Anal. Calcd. for $\text{C}_{32}\text{H}_{22}\text{S}_2$: C, 81.66; H, 4.71; S, 13.63. Found: C, 80.48; H, 4.62; S, 13.75.

5,5"-Bis(4-biphenyl)-2,2':5',2"-terthiophene (**BP3**).

We applied the same procedure as the case of the **BP1** synthesis, except for using 5,5"-diiodo-2,2':5',2"-terthiophene **3b** [1] (500 mg, 1.00 mmole) and 1,2,4-trichlorobenzene in place of **1b** and benzene, respectively. The reaction mixture was heated at 100° overnight. The precipitates generated after the course of reaction were collected by filtration and washed by turns with acetone and dichloromethane. These precipitates underwent Soxhlet extraction with dichloromethane and the non-extracted material was recrystallized from 1,2,4-trichlorobenzene to give yellow solid with golden luster of **BP3**, yield 46%, mp 386°.

Anal. Calcd. for $\text{C}_{36}\text{H}_{24}\text{S}_3$: C, 78.22; H, 4.38; S, 17.40. Found: C, 77.50; H, 4.38; S, 17.68.

5-(4-Biphenyl)-2,2'-bithiophene (**5**).

2,2'-Bithiophene (Aldrich; 4.16 g, 25 mmoles) and *N*-iodosuccinimide (5.62 g, 25 mmoles) each were dissolved in methanol (40 ml) and both the solutions were mixed together. To this mixed solution was put acetic acid (1.43 ml, 25 mmoles), soon yielding precipitation. The reaction mixture was put into a refrigerator to ensure generation of the precipitates, which were removed by filtration. To the resulting filtrate were added 80 ml water and 120 ml diethyl ether, the reaction products obtained above being transferred to the diethyl ether layer in a separating funnel. This layer was separated from the water layer and washed successively with water, 10% aqueous solution of potassium hydroxide (two times), and water. The resulting diethyl ether solution was dried with anhydrous calcium chloride and diethyl ether was removed with a rotary evaporator to give 3.7 g of an oily compound. This compound was found to comprise 5-iodo-2,2'-bithiophene (**4b**) [12] and unreacted 2,2'-bithiophene from tlc, which gave R_f (hexane) of 0.62 and 0.56, respectively.

Meanwhile, the aforementioned precipitates removed were identified as 5,5'-diiodo-2,2'-bithiophene (**2b**) [1], which had R_f (hexane) of 0.66.

Of the above oily compound, was taken 1.92 g without further purification. This portion together with 4-biphenylboronic acid (1.80 g, 9.10 mmoles) and tetrakis(triphenylphosphine)palladium(0) (456 mg, 0.39 mmole) was dissolved in benzene (80 ml). After this the reaction mixture was treated similarly to the case of the **BP1**. The precipitates generated were collected by filtration and thoroughly washed by turns with water and methanol. These precipitates further underwent Soxhlet extraction with dichloromethane. The extracted material (that precipitated in the bottom flask of the Soxhlet apparatus) was then collected by filtration to give 0.76 g of a crude material. This was recrystallized successively from hexane and 2-butanone to give yellow solid **5**, mp 226°; ^1H nmr: δ 7.04 (dd, 1H, a thienyl proton, $J = 5.1$, 3.6 Hz), 7.17 (d, 1H, a thienylene proton, $J = 3.6$ Hz), 7.22 (dd, 1H, a thienyl proton, $J = 3.6$, 1.2 Hz), 7.25 (dd, 1H, a thienyl proton, $J = 5.1$, 1.2 Hz), 7.28 (d, 1H, a thienylene proton, $J = 3.6$ Hz), 7.63 (d, 2H, phenylene protons, $J = 8.6$ Hz), 7.69 (d, 2H, phenylene protons, $J = 8.6$ Hz), 7.34–7.67 ppm (m, 5H, phenyl protons).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{S}_2$: C, 75.43; H, 4.43; S, 20.14. Found: C, 75.69; H, 4.42; S, 19.33.

1-(2-Thienyl)-4-(5-phenylthiophene-2-yl)benzene (**7**).

A flask containing equimolar amounts of 2-iodo-5-phenylthiophene (286 mg, 1.00 mmole) and magnesium (24.3 mg, 1.00 mmole) was evacuated under mild heat. To this solid mixture was added dry diethyl ether (10 ml) to prepare a Grignard reagent. After making sure that all amounts of magnesium disappeared, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride [abbreviated as Ni(dppp) Cl_2 in Scheme 3; 10 mg, 0.018 mmole] and 2-(4-bromophenyl)thiophene **6a** (120 mg, 0.50 mmole) were added successively, soon causing precipitation. After being stirred overnight at room temperature the reaction mixture was refluxed for 6 hours. The reaction mixture was then cooled over an ice/water bath and subsequently hydrolyzed with 2 *N* hydrochloric acid (0.5 ml). The resulting precipitates were collected by filtration and washed with methanol. These precipitates further underwent Soxhlet extraction with dichloromethane as in the case of the synthesis of **5**. The extracted material was again collected by filtration to give 80 mg of a crude material. This was recrystallized from acetone to give yellow solid **7**, yield 58%, mp 221°; ^1H nmr: δ 7.10 (dd, 1H, a thienyl proton, $J = 5.0$, 3.9 Hz), 7.30 (dd, 1H, a thienyl proton, $J = 5.0$, 1.2 Hz), 7.31 (d, 1H, a thienylene proton, $J = 3.9$ Hz), 7.33 (d, 1H, a thienylene proton, $J = 3.9$ Hz), 7.36 (dd, 1H, a thienyl proton, $J = 3.9$, 1.2 Hz), 7.65 (s, 4H, phenylene protons), 7.27–7.67 ppm (m, 5H, phenyl protons).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{S}_2$: C, 75.43; H, 4.43; S, 20.14. Found: C, 75.50; H, 4.46; S, 19.82.

1,4-Bis(5-phenylthiophene-2-yl)benzene (**9**).

The Grignard reagent of 1.00 mmole was prepared through the same procedure as described for the synthesis of **7**. After making sure that all amounts of magnesium disappeared, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (10 mg, 0.018 mmole) and 1,4-diiodobenzene **8b** (83 mg, 0.25 mmole) were added successively, soon causing precipitation. The reaction mixture was then treated similarly to the case of the synthe-

sis of **7**. The resulting precipitates (obtained through the Grignard coupling reaction) were collected by filtration and washed with acetone. These precipitates were recrystallized from 1,2,4-trichlorobenzene to give deep yellow solid **9**, yield 60%, mp 304°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{S}_2$: C, 79.15; H, 4.60; S, 16.25. Found: C, 78.57; H, 4.47; S, 16.25.

2-(4-Bromophenyl)thiophene (**6a**).

2-Iodothiophene (0.84 g, 4.00 mmoles) and 4-bromobenzenboronic acid (1.00 g, 5.00 mmoles) as well as tetrakis(triphenylphosphine)palladium(0) (173 mg, 0.15 mmole) were dissolved in benzene (80 ml) and nitrogen was bubbled through this reaction solution for 30 minutes to remove dissolved oxygen. To the reaction solution was added 10 ml of an aqueous solution of sodium carbonate (1.06 g, 10.0 mmoles), and then the solution was heated at 60° overnight under nitrogen environment. The resulting reaction mixture was then cooled with an ice/water bath and oxidized with 1 ml of an aqueous solution of hydrogen peroxide (30%), yielding precipitates. These precipitates were collected by filtration and washed with a great deal of an equivolume mixture of water and methanol. These precipitates were dried and recrystallized from a mixture solvent methanol:water (4:1, v/v) to obtain colorless crystals **6a** [13], yield 29%; ^1H nmr: δ 6.72 (dd, 1H, a thienyl proton, $J = 5.4$, 3.6 Hz), 6.81 (dd, 1H, a thienyl proton, $J = 5.4$, 1.1 Hz), 6.90 (dd, 1H, a thienyl proton, $J = 3.6$, 1.1 Hz), 7.08 (dd, 2H, phenylene protons, $J = 8.6$, 1.8 Hz), 7.18 ppm (dd, 2H, phenylene protons, $J = 8.6$, 2.3 Hz).

Acknowledgements.

We thank Dr. F. Nakanishi, National Institute of Materials and Chemical Research (NIMC), and Dr. H. Fukushima, JRCHMM, for their helpful discussions and suggestions. Thanks are also due to Dr. K. Okita, Japan Chemical Innovation Institute, for rendering the ^{13}C nmr apparatus available to the present work. This work was supported by NEDO for the Harmonized Molecular Materials theme funded through the project on Technology for Novel High-Functional Materials (AIST). S. A. L. thanks Japan Science and Technology Corporation (JSTC) for its financial aid.

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