Synthesis of Thiophene/Phenylene Co-oligomers. V [1]. Functionalization at Molecular Terminals toward Optoelectronic Device Applications

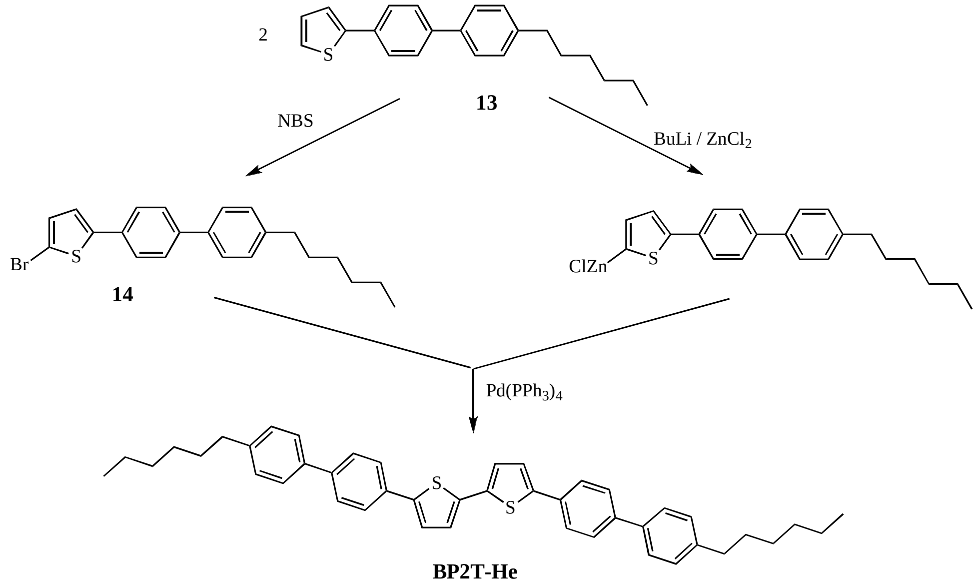
Toshifumi Katagiri

Sumitomo Seika Chemicals Co., Ltd.
Fine Chemicals Research Laboratory
346-1 Miyanishi, Harima-cho, Kako-Gun, Hyogo 675-0145, Japan

Satoshi Ota, Takayuki Ohira, Takeshi Yamao, Shu Hotta*

Kyoto Institute of Technology
Department of Macromolecular Science and Engineering
Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

Received August 10, 2006



We report the synthesis of various thiophene/phenylene co-oligomers with a total number of thiophene and benzene (phenylene) rings of 5 and 6 with various terminal groups. Those terminal groups have been chosen from among alkyl groups, methoxy groups, trifluoromethyl groups, and cyano groups. The molecular backbone of these compounds comprises phenyl- or biphenylyl-capped thiophene (or oligothiophene) or an alternating co-oligomer. The synthesis is based on either the Suzuki coupling reaction or the Negishi coupling reaction. These reaction schemes enabled us to obtain the target compounds in high quality. In particular, the latter coupling method turned out to produce the compounds at a high yield. The terminal groups are expected to produce various functionalities based upon their electron donating character (alkyl groups and methoxy groups) or electron withdrawing character (trifluoromethyl groups and cyano groups). Additionally some of these groups bring about enhanced solubility. This will lead to the production of a diversity of modified compounds of thiophene/phenylene co-oligomers. To give an example that demonstrates usefulness of the target compounds, we present optoelectronic data that are associated with their device applications.

J. Heterocyclic Chem., **44**, 853 (2007).

INTRODUCTION

Thiophene/phenylene co-oligomers are characterized as hybridized oligomers comprising thiophene and benzene (phenylene) rings and are currently attracting much attention as a novel class of organic semiconductors [2,3]. These co-oligomers exhibit interesting light-emitting and charge transport characteristics [2,3]. In previous articles, we reported among thiophene/phenylene co-oligomers the syntheses of a variety of phenyl-capped oligothiophenes, thienyl-capped oligophenylenes, as well as block and alternating co-oligomers [1,4–6] whose total number of thiophene and benzene rings is 3 to 8

One of the major advantages of these compounds is that extension of the π-conjugation can be tuned as desired by changing the total number of the thiophene and benzene rings and their mutual arrangement in the molecule. More importantly the electronic structure and properties may further be tuned by appropriately introducing substituent groups. To this end, in the present studies, we have modified the thiophene/phenylene co-oligomers by substituting various functional groups at the molecular terminals. These functional groups have been chosen from among alkyl groups, methoxy groups, trifluoromethyl groups, and cyano groups. Electron donative character (alkyl groups and methoxy groups) and electron attractive character (trifluoromethyl groups and cyano groups) will very likely produce various electronic functionalities. Some of these groups are responsible for enhanced solubility of the resulting compounds relative to ones without them. The good solubility is advantageous to industrial applications.

RESULTS AND DISCUSSION

Preparation of the Materials and Their Spectroscopic Characterization. The overall synthetic strategy is shown in Figure 1, where (a) three blocks or (b) two blocks are joined to synthesize the target compounds. The synthesis of these compounds is based either on the Suzuki coupling reaction [7] or on the Negishi coupling reaction [8]. In particular, the latter coupling method produces the target compounds in high yields. This coupling scheme has also been applied to the synthesis of symmetric thiophene/phenylene co-oligomer molecules with an even total number of thiophene and benzene rings (Schemes V, VI, and VII). In these cases even though self coupling occurs among the thienylzinc chloride intermediates, such a side reaction leads to the production of the aimed compounds as well. All the synthetic routes for the target co-oligomer compounds are summarized in Schemes I to VII. Scheme VIII depicts the synthetic scheme of intermediates of 4-bromo-4'-butylbiphenyl (**1a**) and 4-bromo-4'-hexylbiphenyl (**1b**) that are to be used for the synthesis of **BP1T-Bu** and **BP2T-He**.

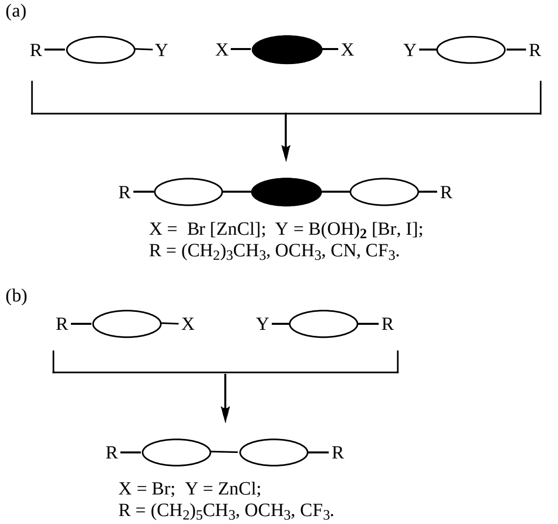
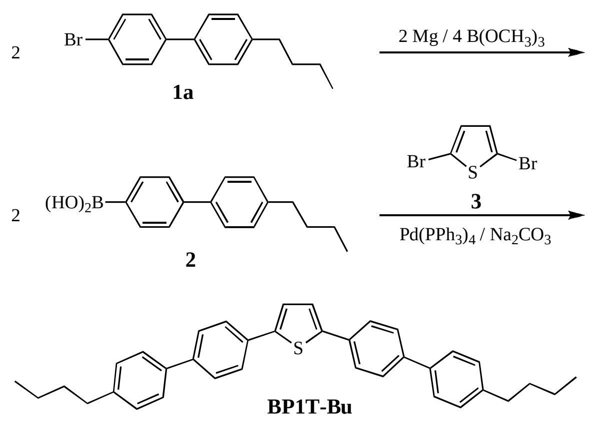
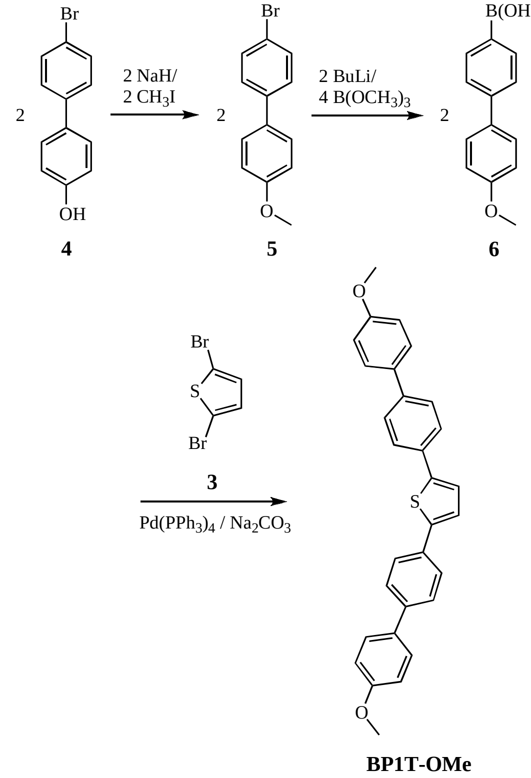


Figure 1. Synthetic Strategy of (a) 3-Block Coupling and (b) 2-Block Coupling.

Scheme I

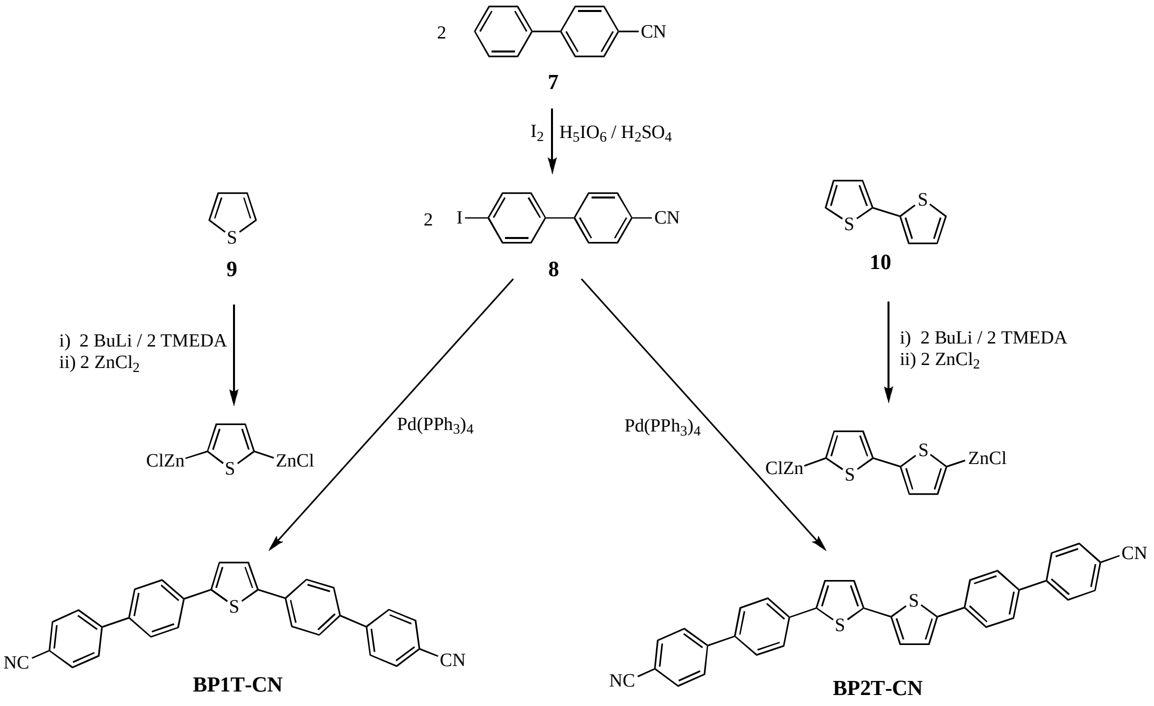


Scheme II

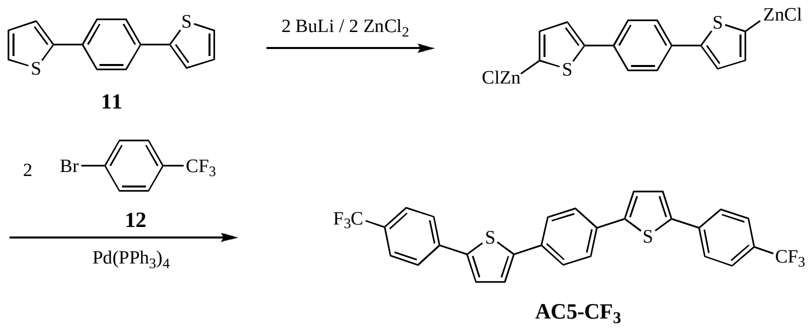


As mentioned previously [1], co-oligomer compounds of the total ring number of 5 or larger than this are very sparingly soluble at room temperature in any common organic solvent, if those compounds lack terminal substituents. This made it difficult to identify

Scheme III



Scheme IV



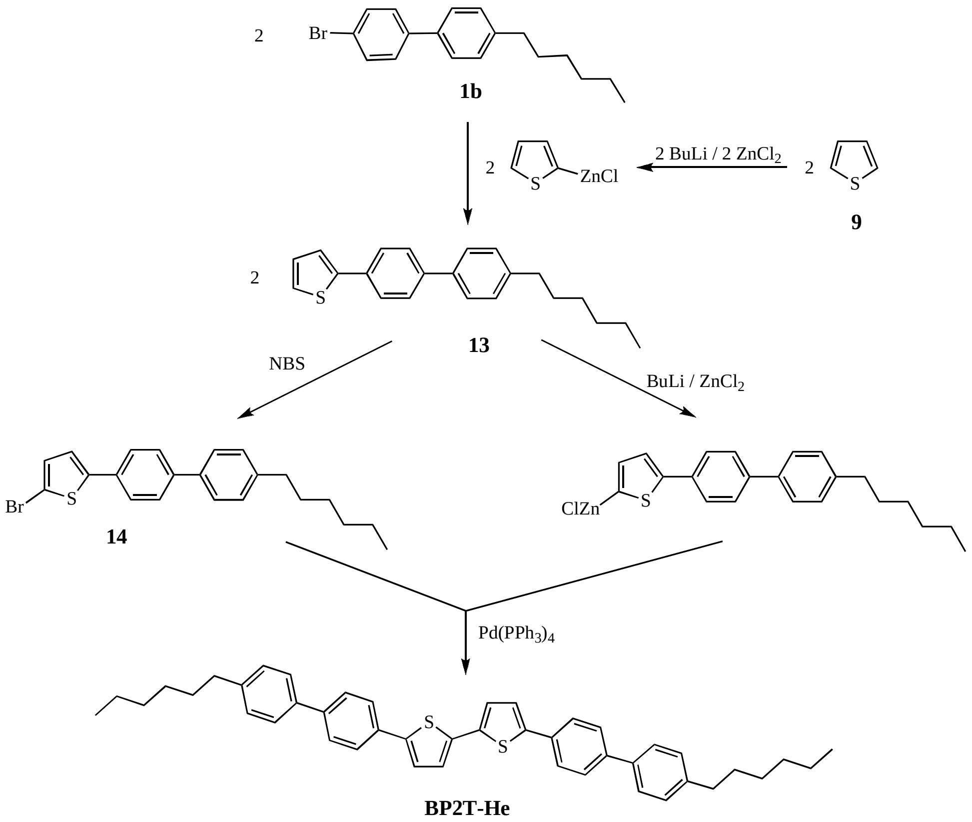
them by usual ^1H nmr spectroscopy. However, the compounds with the terminal substituents have better solubility. In particular, **BP1T-Bu**, **AC5-CF$_3$**, and **P4T-CF$_3$** are soluble enough to identify them by ^1H nmr (in deuteriotetrahydrofuran). Even in cases where nmr identification was not possible, Fourier-transform (FT) ir spectroscopy in the solid state provides a firm basis for structural assignments. In particular, the spectral lines around 1400–1500 cm^{-1} (aromatic ring CC stretching modes) and 700–800 cm^{-1} (CH out-of-plane deformation vibration modes) enable us to determine the molecular structure unambiguously. The location of these bands helps determine the substitution modes of the thiophene and benzene rings [9,10].

The relevant characteristic frequencies as well as those associated with the CH stretching modes are collected in Table 1. Their assignments have been carried out as described in our previously published work [1,4–6] dealing with the synthesis of other co-oligomers and in relevant literature [11,12]. The characteristic frequencies from the substituent groups are definitive as well. These results are consistent with those of nmr.

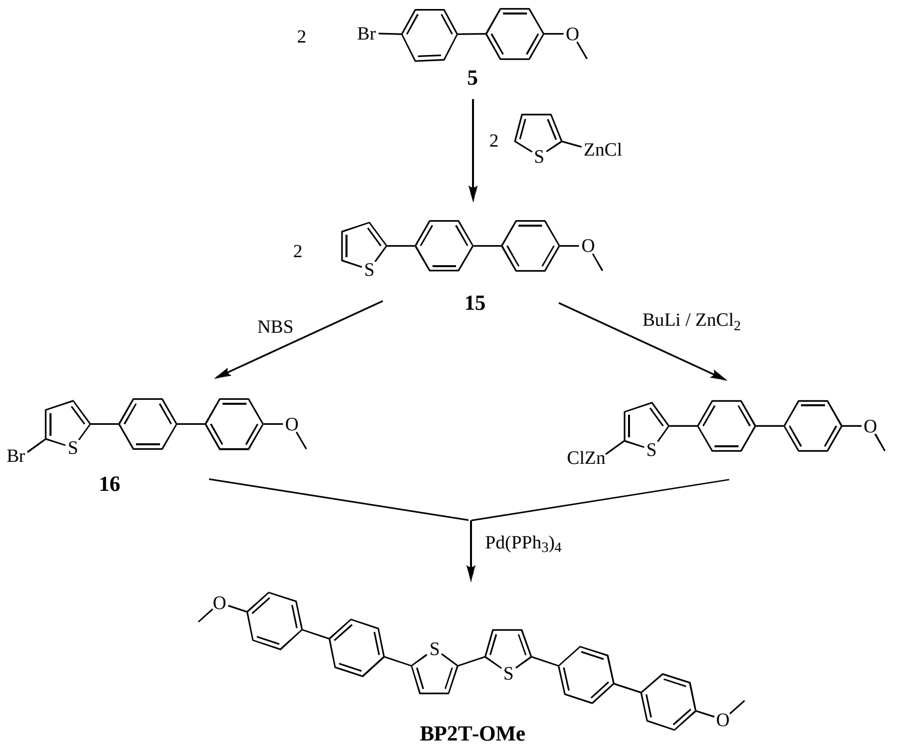
Thus, on the basis of these spectroscopic features we conclude that the co-oligomers in the present studies possess the molecular structures shown in Schemes I–VII.

Optoelectronic Properties. In relation to the optoelectronic device applications we present the results of **BP1T-OMe**. Figure 2 shows an action characteristic diagram of a field-effect transistor (FET) fabricated with a

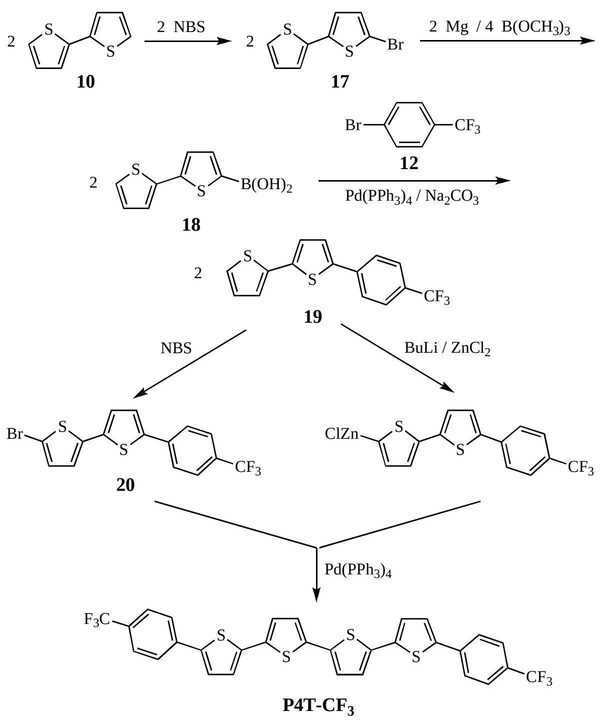
Scheme V



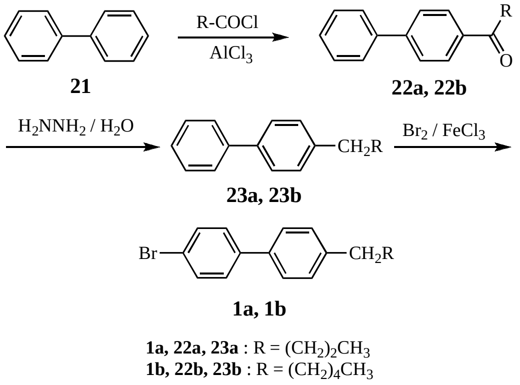
Scheme VI



Scheme VII



Scheme VIII



single crystal of **BP1T-OMe**. A threshold voltage was around 15 V above which normal device feature is clearly noted. The mobility was estimated to be 7.6 x 10^{-3} cm^2/Vs in the saturation regime and 3.1 x 10^{-3} cm^2/Vs in the linear regime. The mobility was higher than that of **BP1T** [5], a parent compound of **BP1T-OMe** (without the methoxy groups). The mobility of **BP1T** was 1.2 x 10^{-3} cm^2/Vs in the saturation regime and 2.9 x 10^{-4} cm^2/Vs in the linear regime.

Figure 3 shows an emission spectrum of another single crystal of **BP1T-OMe**. The spectrum is characterized by the narrowed emission line when it is excited with a strong laser beam. The spectrum was taken with an excitation energy of 587 $\mu J/cm^2$ (per laser pulse). The sharply resolved line is located at 507 nm with a shoulder at 514 nm and the full width at half maximum (FWHM) of the 507-nm line was ~7 nm. This small FWHM is due to the amplified spontaneous emission [3b] and may well be associated with the laser oscillation [13]. The positions of these lines are significantly red-shifted relative to the corresponding lines at 465 and 495 nm for **BP1T** [3b].

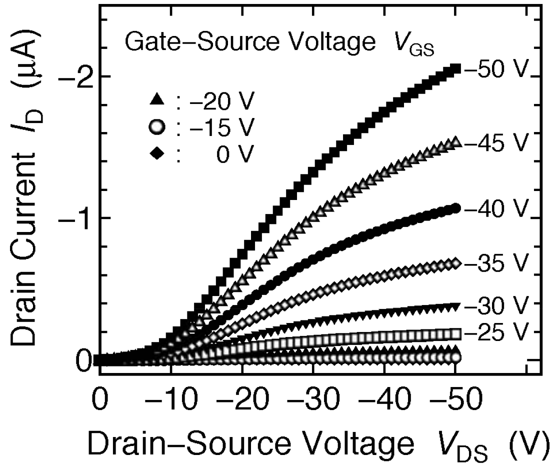


Figure 2. Action characteristic diagram of an FET fabricated with a single crystal of **BP1T-OMe**.

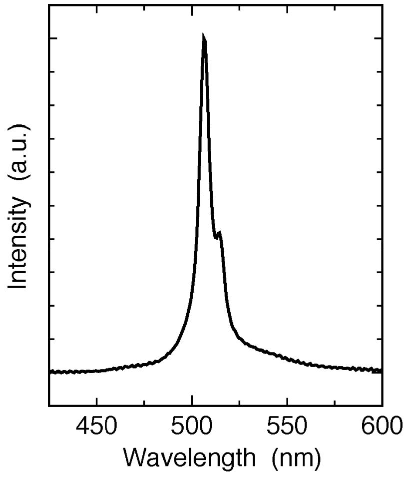


Figure 3. Emission spectrum of a single crystal of **BP1T-OMe**.

The enhanced mobility and red-shift in the emission line for **BP1T-OMe** in comparison with **BP1T** can be interpreted by the extension of the π-conjugated system produced by the methoxy groups. This is consistent with the results of the molecular orbital calculations. Both the decrement in the ionization potential (*i.e.* the rise in the HOMO level) and increment in the electron affinity (*i.e.* the fall in the LUMO level) are expected to be responsible. A similar effect can be recognized for the alkyl substituted oligothiophenes [14]. Table 2 summarizes and compares the relevant results of **BP1T** and **BP1T-OMe**.

Table 1

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

Compound	CH Stretching		CN	Ring CC Stretching		CF	COC	CH out-of-plane deformation	
	Aromatic	Aliphatic	Stretching	Phenylene	Thienylene	Stretching	Stretching	Phenylene	Thienylene
BP1T-Bu	3026	2958-2855	-	1492	1450	-	-	817	799
BP1T-He	3025	2955-2850	-	1491	1445	-	-	813	795
BP1T-CN	3028	-	2225	1489	1450	-	-	820	793
BP2T-CN	3064	-	2224	1487	1443	-	-	823	796
BP1T-OMe	3039	2956-2839	-	1491	1441	-	1255, 1038	825	798
BP2T-OMe	3062	2958-2838	-	1489	1441	-	1254, 1037	822	794
AC5-CF$_3$	3074	-	-	1498	1451	1329, 1132	-	841	799
P4T-CF$_3$	3062	-	-	1450	1489	1327, 1130	-	839	792

Table 2

Comparison of Physical Properties of **BP1T-OMe** and **BP1T** [a]

Compound	Field-effect mobility (cm^2/Vs)		Emission line position (nm)		HOMO (eV)	LUMO (eV)
BP1T-OMe	7.6 x 10^{-3} (saturation regime)	3.1 x 10^{-3} (linear regime)	507	514	–6.88	–0.35
BP1T	1.2 x 10^{-3} (saturation regime)	2.9 x 10^{-4} (linear regime)	465 [b]	495 [b]	–7.44	0.41

[a] lit [5]. [b] lit [3b].

EXPERIMENTAL

Device Fabrication and Optoelectronic Measurements. The method of the single crystal growth can be seen elsewhere [15]. An FET was fabricated by mounting a single crystal of **BP1T-OMe** on a silicone wafer covered with silicone oxide of 300 nm in thickness. The flat crystal plane was made in close contact with the silicon wafer substrate. Au source and drain contacts were deposited on top of the **BP1T-OMe** crystal with homemade vacuum deposition equipment. The back of the SiO$_2$/Si wafer substrate was used as the gate contact and silicon dioxide layer was used for the gate insulator. The action characteristics of the FET devices were measured using an Agilent Technologies 4156B precision semiconductor parameter analyzer. The measurements were carried out at room temperature in ambient air.

To measure the emission spectra, the excitation laser light was irradiated perpendicular to the flat crystal plane. The laser beam with various energies was focused on the crystal plane for the whole crystal to be irradiated. The emission from the crystal was detected parallel to its plane. The third harmonic generation of Nd:YAG laser (LOTIS TII, Nd:YAG LASER SYSTEM LS-2137) was used as the excitation light, which provided 18-ns pulses at 355 nm with a 10 Hz repetition rate. The emissions from the crystal were detected with a photonic multichannel analyzer (HAMAMATSU PHOTONICS, PMA11/C7473-36) after passing through a UV-cut filter.

The quantum chemical calculations at semiempirical levels were carried out on WinMOPAC3.9 in a manner similar to that described in lit [16].

Organic Synthesis and Characterization. Tetrahydrofuran, hexane, *N*,*N*-dimethylformamide, and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine were purchased from Kishida Reagents and dehydrated over Molecular Sieves 4A 1/8 (Wako Pure Chemical) prior to use. Other chemical reagents were purchased from standard sources and used as received unless otherwise specified.

Melting points were determined either on a Seiko Instruments SSC5200 thermal analysis system or a METTLER Thermosystem FP800HT. The ^{1}H nmr spectra were recorded on a Varian Mercury-400BB spectrometer (400 MHz) in a solution of either in deuteriochloroform, deuteriodichloromethane, or in deuteriotetrahydrofuran and chemical shifts are reported in ppm (δ) relative to tetramethylsilane as an internal standard. The ir spectra were taken on a JEOL JIR-6500 FT-IR spectrophotometer with finely pulverized samples dispersed and embedded in a potassium bromide matrix. Elemental analyses (for carbon, hydrogen, and nitrogen) were carried out on a Yanaco CHN CORDER MT-5 at Center for Organic Elemental Microanalysis of Kyoto University. Sulfur and fluorine were analyzed with a standard oxygen-flask combustion method.

The molecular structure of the intermediates **1a**, **2**, **6**, **8**, **1b**, **14**, **16**, **20** just prior to the final coupling reaction toward the aimed compounds has definitively been determined by the ^{1}H nmr. This also confirms that the aimed compounds have a unique molecular structure.

2,5-Bis(4'-butylbiphenyl-4-yl)thiophene (BP1T-Bu). 4-Bromo-4'-butylbiphenyl (**1a**) (52.6 g, 182 mmoles) dissolved at room temperature in anhydrous tetrahydrofuran (210 mL) was added dropwise to a suspension of magnesium (4.65 g, 191 mmoles) in anhydrous tetrahydrofuran (20 mL) under a dry nitrogen environment. After most of the magnesium disappeared, the reaction solution was cooled at -65 °C. To this solution was added trimethyl borate (37.9 g, 365 mmoles) dissolved in anhydrous tetrahydrofuran (78 mL) under -60 °C. After being stirred for 1 hour at -65 °C and another 1 hour at room temperature, the reaction mixture was cooled over an ice/water bath. To the resulting solution was successively added under 25 °C 10% sulfuric acid (111 g), water (202 g), and ethylacetate

(200 mL). The ethylacetate layer was separated from the water layer in a separating funnel. The water layer was once again extracted with ethyl acetate (200 mL) and the combined ethyl acetate layers were washed with saturated aqueous sodium chloride solution and dried with anhydrous magnesium sulfate. After ethyl acetate was partly removed with a rotary evaporator, the remaining ethyl acetate solution was cooled over an ice/water bath to give 4'-butyl-4-biphenylboronic acid (**2**) after filtration. The Hexane (100 mL) was added to the filtrated solution to precipitate and recover from that solution 4'-butyl-4-biphenylboronic acid (**2**). We obtained in total the crystals of 27.3 g (59%) of 4'-butyl-4-biphenylboronic acid (**2**), mp 157 °C; ^{1}H nmr (deuteriotetrahydrofuran): δ 0.94 (t, 3H, methyl protons, J = 7.6 Hz), 1.38 (sextuplet, 2H, methylene protons, J = 7.6 Hz), 1.63 (quintuplet, 2H, methylene protons, J = 7.6 Hz), 2.64 (t, 2H, methylene protons, J = 7.6 Hz), 7.12 (s, 2H, hydroxyl protons), 7.23 (d, 2H, phenylene protons, J = 8.0 Hz), 7.54 (d, 2H, phenylene protons), 7.56 (d, 2H, phenylene protons), 7.83 ppm (d, 2H, phenylene protons, J = 8.0 Hz).

Compound **2** (27.3 g, 107 mmoles) and 2,5-dibromothiophene (**3**) (8.65 g, 36 mmoles) as well as tetrakis(triphenylphosphine)-palladium(0) [abbreviated as $Pd(PPh_3)_4$ in the Schemes; 7.7 g, 6.7 mmoles] were dispersed and dissolved in a mixture of 1,2,4-trichlorobenzene (1.15 L) and aqueous sodium carbonate (22.7 g, 214 mmoles in 532 mL of water). After being warmed at 85 °C for 8 hours, the reaction solution was cooled to 25 °C and filtrated. The resulting precipitates were washed successively with water (500 mL) and acetone (500 mL). These precipitates were recrystallized from 1,2,4-trichlorobenzene to give 14.9 g (84%) of **BP1T-Bu** as yellow crystals, mp 307 °C, lit [17] mp 321 °C; ^{1}H nmr (deuteriotetrahydrofuran): δ 0.95 (t, 6H, methyl protons, J = 7.6 Hz), 1.39 (sextuplet, 4H, methylene protons, J = 7.6 Hz), 1.64 (quintuplet, 4H, methylene protons, J = 7.6 Hz), 2.65 (t, 4H, methylene protons, J = 7.6 Hz), 7.26 (d, 4H, phenylene protons, J = 8.0 Hz), 7.44 (s, 2H, thienylene protons), 7.58 (d, 4H, phenylene protons, J = 8.0 Hz), 7.66 (d, 4H, phenylene protons, J = 8.0 Hz), 7.74 ppm (d, 4H, phenylene protons, J = 8.0 Hz). Anal. Calcd. for $C_{36}H_{36}S$: C, 86.35; H, 7.25; S, 6.40. Found: C, 86.12; H, 7.10; S, 6.14.

2,5-Bis(4'-methoxybiphenyl-4-yl)thiophene (BP1T-OMe). 4-Bromo-4'-hydroxybiphenyl (**4**) (151.4 g, 608 mmoles) was dissolved in anhydrous *N,N*-dimethylformamide (1.5 L) and the reaction solution was cooled at 5 °C. To this solution was added sodium hydride (60%), and the reaction mixture was kept at 25 °C for 1 hour and at 50 °C for another hour. After the solution was cooled at 30 °C, iodomethane (111.6 g, 786 mmoles) was added dropwise to this solution. After being kept at that temperature for 2 hours, the resulting solution was poured into ice water (4.5 L) for crystallization to yield 157.9 g (99%) of 4-bromo-4'-methoxybiphenyl (**5**), mp 143–144 °C, lit [18] mp 144.5 °C.

Compound (**5**) (53.0 g, 201 mmoles) was dissolved in anhydrous tetrahydrofuran (1.55 L) with *N,N,N',N'*-tetramethylethylenediamine (abbreviated as TMEDA in the Schemes; 23.1 g, 199 mmoles) and cooled at -65 °C. To this solution was added dropwise 86 mL (224 mmoles) of 2.6 *M n*-butyllithium and trimethyl borate (41.7 g, 401 mmoles) dissolved in anhydrous tetrahydrofuran (120 mL) successively. The reaction mixture was stirred at room temperature for 1 hour. The resulting solution was successively treated with (i) 10% sulfuric acid (111 g), (ii) washed with saturated aqueous sodium chloride solution, (iii) extracted with ethyl acetate, and (iv) dried with anhydrous magnesium sulfate as in the case of the synthesis of **BP1T-Bu**. This solution was concentrated by evaporation of ethyl acetate and successively cooled at 5 °C for crystallization after addition of chloroform. The crystals generated was collected and dried to give 36.7 g (80%) of (4'-methoxybiphenyl-4-yl)boronic acid (**6**), mp 189–195 °C; ^{1}H nmr (deuteriotetrahydrofuran): δ 3.80 (s, 3H, methyl protons), 6.96 (d, 2H, phenylene protons, J = 8.8 Hz), 7.10 (s, 2H, hydroxyl protons), 7.53 (d, 2H, phenylene protons, J = 8.4 Hz), 7.56 (d, 2H, phenylene protons, J = 8.8 Hz), 7.81 ppm (d, 2H, phenylene protons, J = 8.4 Hz).

Compound **6** (43.8 g, 192 mmoles) and 2,5-dibromothiophene (15.6 g, 64 mmoles) as well as tetrakis(triphenylphosphine)-palladium(0) (9.4 g, 8.1 mmoles) were dispersed and dissolved in a mixture of 1,2,4-trichlorobenzene (2.9 L) and aqueous sodium carbonate (56.5 g, 533 mmoles in 330 mL of water). This reaction mixture was treated similarly as in the case of the synthesis of **BP1T-Bu**. The resulting precipitates were recrystallized from 1,2,4-trichlorobenzene to give 14.3 g (50%) of **BP1T-OMe** as yellow crystals, mp 359 °C. Anal. Calcd. for $C_{30}H_{24}O_2S$: C, 80.33; H, 5.39; S, 7.15. Found: C, 80.55; H, 5.39; S, 7.15.

2,5-Bis(4'-cyanobiphenyl-4-yl)thiophene (BP1T-CN). 4-Biphenylcarbonitrile (**7**) (50.0 g, 279 mmoles) was mixed with acetic acid (137 mL), water (28 mL), and 97% sulfuric acid (4.2 mL). To this reaction mixture were added iodine (36.4 g, 143 mmoles) and periodic acid (14.0 g, 61 mmoles), and the reaction solution was warmed to 70 °C for 24 hours to yield precipitates. The precipitates were washed with water and methanol alternately and dissolved with chloroform (1 L). This solution was washed with saturated aqueous sodium chloride solution and dried with anhydrous magnesium sulfate. After chloroform was evaporated, the remaining solid was dissolved in hot ethyl acetate (500 mL). To the solution was added methanol (250 mL) and cooled to 5 °C for crystallization. The precipitates generated was filtrated and dried to give pale yellow crystals of 56.6 g (67%) of 4'-iodo-biphenyl-4-carbonitrile (**8**), mp 178 °C, lit [19] mp 166 °C; ^{1}H nmr (deuteriochloroform): δ 7.32 (d, 2H, phenylene protons, J = 8.0 Hz), 7.65 (d, 2H, phenylene protons, J = 8.4 Hz), 7.73 (d, 2H, phenylene protons, J = 8.4 Hz), 7.82 ppm (d, 2H, phenylene protons, J = 8.0 Hz).

Thiophene (**9**) (2.39 g, 28 mmoles) was dissolved in dehydrated hexane (35 mL) with *N,N,N',N'*-tetramethylethylenediamine (6.78 g, 58 mmoles). To this solution was added dropwise at 0 °C 25 mL (65 mmoles) of 2.6 *M n*-butyllithium, and the reaction mixture was refluxed for 30 min and successively cooled to -10 °C. To the resulting solution was further added dropwise anhydrous zinc chloride (8.52 g, 63 mmoles) dispersed in anhydrous tetrahydrofuran (100 mL), and the solution was kept at 25 °C for 2 hours. To this solution were added tetrakis(triphenylphosphine)-palladium(0) (1.0 g, 0.87 mmole) and subsequently 4'-iodo-biphenyl-4-carbonitrile (**8**) (20.9 g, 68 mmoles) dissolved in anhydrous tetrahydrofuran (200 mL). The reaction mixture was warmed to 50 °C for 16 hours and then cooled to 20 °C, yielding precipitates. These precipitates were successively washed with tetrahydrofuran (100 mL), water (500 mL), a drop of 35% hydrochloric acid, water (500 mL), and acetone (200 mL). These precipitates were recrystallized from 1,2,4-trichlorobenzene to give 8.1 g (65%) of **BP1T-CN** as yellow crystals, mp 300 °C. Anal. Calcd. for $C_{30}H_{18}N_2S$: C, 82.16; H, 4.14; N, 6.39; S, 7.31. Found: C, 82.39; H, 4.17; N, 6.27; S, 7.46.

5,5'-Bis(4'-cyanobiphenyl-4-yl)-2,2'-bithiophene (BP2T-CN). Bithiophene (**10**) (16.5 g, 99 mmoles) was dissolved in anhydrous tetrahydrofuran (823 mL) with *N,N,N',N'*-tetramethylethylenediamine (24.1 g, 207 mmoles). To this solution was added dropwise at 0 °C 91 mL (237 mmoles) of 2.6 *M n*-butyllithium, and the reaction mixture was warmed and stirred at room temperature for 3 hours and successively cooled to 15 °C. To the resulting solution was further added dropwise anhydrous zinc chloride (30.8 g, 226 mmoles) dispersed in anhydrous tetrahydrofuran (360 mL). Afterward the resulting solution was treated similarly as in the case of the synthesis of **BP1T-CN**. After addition of tetrakis(triphenylphosphine)palladium(0) (3.54 g, 3.1 mmoles), 4'-iodo-biphenyl-4-carbonitrile (**8**) (73.8 g, 242 mmoles) dissolved in anhydrous tetrahydrofuran (710 mL) was added dropwise and kept at 50 °C for 12 hours to yield precipitates. These precipitates were successively washed with tetrahydrofuran, water, 35% hydrochloric acid, water, and acetone. These precipitates were recrystallized from 1,2,4-trichlorobenzene to give 22.1 g (43%) of **BP2T-CN** as yellowish orange crystals, mp 316 °C. Anal. Calcd. for $C_{34}H_{20}N_2S_2$: C, 78.43; H, 3.87; N, 5.38; S, 12.32. Found: C, 78.26; H, 3.74; N, 5.24; S, 12.56.

1,4-Bis{5-[4-(trifluoromethyl)phenyl]thiophene-2-yl}benzene (AC5-CF_3). 1,4-Bis(2-thienyl)benzene (**11**) was synthesized following the methods described in lit [4]. Compound **11** (17.7 g, 73 mmoles) was dissolved in anhydrous tetrahydrofuran (1.1 L) and cooled to -10 °C. To this solution was added dropwise at that temperature 73 mL (190 mmoles) of 2.6 *M n*-butyllithium, and the reaction mixture was warmed and stirred at room temperature for 3 hours and successively cooled to -10 °C again. To the resulting solution was further added dropwise anhydrous zinc chloride (25.9 g, 190 mmoles), and the reaction mixture was warmed to 25 °C and kept at that temperature for 3 hours. To this solution was further added 1-bromo-4-(trifluoromethyl)-benzene (**12**) (53.5 g, 238 mmoles) and tetrakis(triphenylphosphine)palladium(0) (3.7 g, 3.2 mmoles), and the reaction mixture was warmed to 50 °C and kept at that temperature for 17 hours, yielding precipitates. The precipitates were washed successively with tetrahydrofuran, water, 35% hydrochloric acid, and acetone. These precipitates were recrystallized from 1,2,4-trichlorobenzene to give 15.1 g (39%) of **AC5-CF_3** as yellow crystals, mp 277 °C; ^{1}H nmr (deuteriotetrahydrofuran): δ 7.52 (d, 2H, thienylene protons, J = 4.0 Hz), 7.58 (d, 2H, thienylene protons, J = 4.0 Hz), 7.71 (d, 4H, phenylene protons, J = 8.4 Hz), 7.76 (s, 4H, phenylene protons), 7.87 ppm (d, 4H, phenylene protons, J = 8.4 Hz). Anal. Calcd. for $C_{28}H_{16}F_6S_2$: C, 63.39; H, 3.04; F, 21.48. Found: C, 63.33; H, 3.24; F, 21.53.

5,5'-Bis(4'-hexylbiphenyl-4-yl)-2,2'-bithiophene (BP2T-He). Thiophene (**9**) (8.40 g, 100 mmoles) was dissolved in anhydrous tetrahydrofuran (29 mL). As in the case of the synthesis of **BP1T-CN**, a solution of 2.6 *M n*-butyllithium (39 mL, 101 mmoles) and anhydrous zinc chloride (13.6 g, 100 mmoles) were successively added to the above solution of thiophene. To the resulting reaction mixture 4-bromo-4'-hexylbiphenyl (**1b**) (23.8 g, 75 mmoles) and tetrakis(triphenylphosphine)-palladium(0) (1.93 g, 1.7 mmoles) were added and kept at 50 °C overnight. The reaction mixture was then cooled to 5 °C and subsequently hydrolyzed with 35% hydrochloric acid (5 mL), yielding precipitates. These precipitates collected by filtration and washed with water and methanol successively were recrystallized from acetone (710 mL) to give 20.3 g (84%) of 2-(4'-hexylbiphenyl-4-yl)thiophene (**13**), mp 172 °C.

Compound **13** obtained above was halved for the subsequent coupling reaction. Compound **13** (9.27 g, 28.9 mmoles) was dissolved in chloroform (100 mL) with acetic acid (1 mL) at 25 °C. To this solution was added *N*-bromosuccinimide (abbreviated as NBS in the Schemes; 5.15 g, 28.9 mmoles), and the reaction mixture was kept at that temperature for 1 hour. To this reaction mixture was added methanol (150 mL). The resulting solution was cooled to 5 °C for crystallization, to yield 11.1 g (96%) of 2-bromo-5-(4'-hexylbiphenyl-4-yl)thiophene (**14**), mp 217 °C; ^{1}H nmr (deuteriodichloromethane): δ 0.91 (t, 3H, methyl protons, J = 6.6 Hz), 1.28–1.40 (m, 6H, methylene protons), 1.65 (quintuplet, 2H, methylene protons, J = 7.2 Hz), 2.66 (t, 2H, methylene protons, J = 8.0 Hz), 7.09 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.15 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.29 (d, 2H, phenylene protons, J = 8.0 Hz), 7.56 (d, 2H, phenylene protons, J = 8.0 Hz), 7.61 (d, 2H, phenylene protons, J = 8.8 Hz), 7.64 ppm (d, 2H, phenylene protons, J = 8.8 Hz).

Out of the other halved portion of compound **13**, 9.38 g (29.3 mmoles) was dissolved in anhydrous tetrahydrofuran (200 mL) and the solution was cooled to -10 °C. Equimolar amounts of *n*-butyllithium and anhydrous zinc chloride were successively added to the above solution. To the resulting reaction mixture, compound **14** (7.51 g, 18.8 mmoles) and tetrakis(triphenylphosphine)palladium(0) (1.5 g, 1.3 mmoles) were added and the reaction solution was kept at 65° for 5 hours. The reaction mixture was then filtrated at that temperature and subsequently diluted with water (500 mL) and 35% hydrochloric acid to adjust pH (≈ 2), yielding precipitates. These precipitates were washed with acetone and recrystallized from 1,2,4-trichlorobenzene (two times) to give 11.1g (93%) of **BP2T-He** as yellow crystals, mp 359 °C. Anal. Calcd. for $C_{44}H_{46}S_2$: C, 82.71; H, 7.25; S, 10.04. Found: C, 82.92; H, 7.26; S, 10.26.

5,5'-Bis(4'-methoxybiphenyl-4-yl)-2,2'-bithiophene (BP2T-OMe). Thiophene (**9**) (23.5 g, 280 mmoles) was dissolved in anhydrous tetrahydrofuran (310 mL) and the solution was cooled to 0 °C. Equimolar amounts of *n*-butyllithium and anhydrous zinc chloride were successively added to the above solution. To the resulting reaction mixture 4-bromo-4'-methoxybiphenyl (**5**) (55.3 g, 210 mmoles) and tetrakis-(triphenylphosphine)palladium(0) (3.1 g, 2.7 mmoles) were added and kept at 50 °C for 18 hours. The reaction mixture was then cooled to 5 °C and subsequently hydrolyzed with 35% hydrochloric acid (50 mL), yielding precipitates. The precipitates were washed successively with water, dilute hydrochloric acid, and methanol to give pale yellow crystals of 51.5 g (92%) of 2-(4'-methoxybiphenyl-4-yl)thiophene (**15**), mp 216 °C.

Compound **15** obtained above was halved for the subsequent coupling reaction. Compound **15** (20.6 g, 77 mmoles) was brominated as in the case of the bromination of compound **13** using an equimolar amount of *N*-bromosuccinimide. This process produced 25.3 g (95%) of 2-bromo-5-(4'-methoxybiphenyl-4-yl)thiophene (**16**), mp 255 °C; ^{1}H nmr (deuteriodichloromethane): δ 3.86 (s, 3H, methyl protons), 7.00 (d, 2H, phenylene protons, J = 8.8 Hz), 7.08 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.14 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.58 (d, 2H, phenylene protons, J = 8.8 Hz), 7.60 ppm (s, 4H, phenylene protons). It is worthy of note that the 7.60-ppm line due to the central phenylene ring protons is coalesced. This is because the local chemical environments in the vicinity of those protons are closely related to one another [5].

The other halved portion of compound **15** (30.9 g, 116 mmoles) was dissolved in anhydrous tetrahydrofuran (1.9 L) and the solution was cooled to -10 °C. Equimolar amounts of *n*-butyllithium and anhydrous zinc chloride were successively added to the above solution. To the resulting reaction mixture, compound **16** (25.3 g, 73 mmoles) and tetrakis(triphenylphosphine)palladium(0) (7.4 g, 6.4 mmoles) were added and the reaction solution was refluxed for 6 hours to produce precipitates. These precipitates were collected by filtration and successively washed with tetrahydrofuran, 0.5 *N* hydrochloric acid (1.5 L), water, and acetone. The precipitates were recrystallized from 1,2,4-trichlorobenzene (two times) to give 28.4 g (73%) of **BP2T-OMe** as yellow crystals, mp 385 °C. Anal. Calcd. for $C_{34}H_{26}O_2S_2$: C, 76.95; H, 4.94; S, 12.08. Found: C, 76.79; H, 4.99; S, 12.28.

5,5'"-Bis[4-(trifluoromethyl)phenyl]-2,2':5',2":5",2'"-quaterthiophene (P4T-CF_3). 5-Bromo-2,2'-bithiophene (**17**) was synthesized *via* monobromination of bithiophene (**10**) following the methods described in lit [1] bp 131 °C/3 mm Hg, lit [20] mp 33–34 °C. Compound **17** (36.2 g, 148 mmoles) dissolved at room temperature in anhydrous tetrahydrofuran (370 mL) was added dropwise to a suspension of magnesium (3.66 g, 151 mmoles) in anhydrous tetrahydrofuran (20 mL) under a dry nitrogen environment. Following a procedure similar to that in the synthesis of **BP1T-Bu**, the reaction solution was mixed with trimethyl borate (31.7 g, 305 mmoles) to yield greenish crystals of 2,2'-bithiophene-5-boronic acid (**18**) [6], 30.0 g (97%), mp 76 °C, lit [1] mp 89 °C.

Compound **18** (26.3 g, 125 mmoles) and 1-bromo-4-(trifluoromethyl)benzene (**12**) (33.3 g, 148 mmoles) as well as tetrakis(triphenylphosphine)palladium(0) (6.1 g, 5.3 mmoles) were dispersed and dissolved in a mixture of benzene (182 mL) and aqueous sodium carbonate (18.1 g, 171 mmoles in 182 mL of water). After being refluxed for 6 hours, the reaction solution was cooled to 10 °C and filtrated. The resulting precipitates were washed successively with water and methanol and dried to give pale yellow crystals of 26.6 g (69%) of 5-[4-(trifluoromethyl)-phenyl]-2,2'-bithiophene (**19**), mp 181 °C.

Compound **19** obtained above was halved for the subsequent coupling reaction. Compound **19** (13.3 g, 43 mmoles) was brominated as in the case of the bromination of compound **13** using an equimolar amount of *N*-bromosuccinimide. This process produced pale yellow crystals of 14.9 g (89%) of 5-bromo-5'-[4-(trifluoromethyl)phenyl]-2,2'-bithiophene (**20**), mp 156 °C; ^{1}H nmr (deuteriodichloromethane): δ 7.02 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.05 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.17 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.37 (d, 1H, a thienylene proton, J = 4.0 Hz), 7.66 (d, 2H, phenylene protons, J = 8.4 Hz), 7.74 ppm (d, 2H, phenylene protons, J = 8.4 Hz).

The other half of compound **19** (13.3 g, 43 mmoles) was mixed with equimolar amounts of *n*-butyllithium and then with anhydrous zinc chloride in anhydrous tetrahydrofuran (240 mL). To this reaction mixture were added compound **20** (14.9 g, 38 mmoles) and tetrakis(triphenylphosphine)-palladium(0) (2.6 g, 2.2 mmoles) to yield precipitates. These precipitates were washed with acetone and recrystallized from 1,2,4-trichlorobenzene (three times) to give 13.6 g (57%) of **P4T-CF_3** as orange crystals, mp 338 °C, lit [21] mp 332–333 °C; ^{1}H nmr (deuteriotetrahydrofuran): δ 7.24 (d, 2H, thienylene protons, J = 3.6 Hz), 7.27 (d, 2H, thienylene protons, J = 3.6 Hz), 7.31 (d, 2H, thienylene protons, J = 3.6 Hz), 7.53 (d, 2H, thienylene protons, J = 3.6 Hz), 7.70 (d, 4H, phenylene protons, J = 8.8 Hz), 7.84 ppm (d, 4H, phenylene protons, J = 8.8 Hz). Anal. Calcd. for $C_{30}H_{16}F_6S_4$: C, 58.24; H, 2.61; F, 18.42. Found: C, 58.31; H, 2.56; F, 18.32.

General Procedure for the Synthesis of 4-bromo-4'-butylbiphenyl (1a) and 4-bromo-4'-hexylbiphenyl (1b). Butyryl chloride or hexanoyl chloride was added to a dichloromethane suspension of aluminum chloride at room temperature. To this suspension was added a dichloromethane solution of biphenyl (**21**) over an ice/water bath. The reaction solution was kept at 25 °C for 2 hours and then poured into ice water. The resulting mixture was extracted with chloroform, dried with anhydrous magnesium sulfate, and subsequently recrystallized from methanol. This yielded 4-butyrylbiphenyl (**22a**), mp 95 °C, lit [22] mp 94 °C, or 4-hexanoylbiphenyl (**22b**), mp 95 °C, lit [22] mp 96.5 °C.

Compound **22a** or compound **22b** was dissolved in di(ethylene glycol) with potassium hydroxide. To this solution was added hydrazine monohydrate, and the reaction mixture was heated to 200 °C for 3 hours. The resulting solution was then poured into ice water and filtrated to give crystals. These crystals were dissolved with ethyl acetate and washed with 5% hydrochloric acid, saturated aqueous solution of sodium bicarbonate, and water. The resulting solution was dried with anhydrous magnesium sulfate and then purified by column chromatography on silica gel with hexane as eluent to give 4-butylbiphenyl (**23a**) as liquid, bp 140 °C/3 mmHg, lit [23] ,or 4-hexylbiphenyl (**23b**), mp 29 °C, lit [23] mp 31 °C.

Compound **23a** or compound **23b** was dissolved in carbon tetrachloride with iron(III) chloride at -10 °C. To this solution was added bromine, and the reaction mixture was kept at that temperature for 1 hour. The reaction solution was poured into ice water. The resulting mixture was extracted with chloroform, dried with anhydrous magnesium sulfate, and subsequently recrystallized from ethanol. This yielded 4-bromo-4'-butylbiphenyl (**1a**), mp 101 °C, lit [24] mp 155 °C; ^{1}H nmr (deuteriochloroform): δ 0.94 (t, 3H, methyl protons, J = 7.2 Hz), 1.39 (sextuplet, 2H, methylene protons, J = 7.2 Hz), 1.63 (quintuplet, 2H, methylene protons, J = 7.6 Hz), 2.65 (t, 2H, methylene protons, J = 8.0 Hz), 7.25 (d, 2H, phenylene protons, J = 8.4 Hz), 7.44 (d, 2H, phenylene protons), 7.46 (d, 2H, phenylene protons), 7.54 ppm (d, 2H, phenylene protons, J = 8.4 Hz) and 4-bromo-4'-hexylbiphenyl (**1b**), mp 91 °C, lit [25] mp 94–95 °C; ^{1}H nmr (deuteriochloroform): δ 0.89 (t, 3H, methyl protons, J = 6.8 Hz), 1.28–1.40 (m, 6H, methylene protons), 1.64 (quintuplet, 2H, methylene protons, J = 7.6 Hz), 2.64 (t, 2H, methylene protons, J = 7.6 Hz), 7.25 (d, 2H, phenylene protons, J = 8.4 Hz), 7.44 (d, 2H, phenylene protons), 7.46 (d, 2H, phenylene protons), 7.54 ppm (d, 2H, phenylene protons, J = 8.4 Hz), respectively.

Acknowledgement. This work was partly supported by a Grant-in-Aid for Scientific Research B (No. 15350115) from the Ministry of Education, Culture, Sports, Science and Technology. This work was also partly supported by a Grant-in-Aid for Science Research in a Priority Area "Super-Hierarchical Structures" (No. 17067009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES AND NOTES

[*] Author to whom correspondence should be addressed.

[1] Hotta, S.; Katagiri, T. *J. Heterocycl. Chem.* **2003**, *40*, 845.

[2a] Lee, S. A.; Yoshida, Y.; Fukuyama, M.; Hotta, S. *Synth. Met.* **1999**, *106*, 39. [b] Hotta, S.; Lee, S. A. *Synth. Met.* **1999**. *101*, 551.

[3a] Ichikawa, M.; Yanagi, H.; Shimizu, Y.; Hotta, S.; Suganuma, N.; Koyama, T.; Taniguchi, Y. *Adv. Mater.* **2002**, *14*, 1272. [b] Nagawa, M.; Hibino, R.; Hotta, S.; Yanagi, H.; Ichikawa, M.; Koyama, T.; Taniguchi, Y. *Appl. Phys. Lett.* **2002**, *80*, 544.

[4] Hotta, S. *J. Heterocycl. Chem.* **2001**, *38*, 923.

[5] Hotta, S.; Kimura, H.; Lee, S. A.; Tamaki, T. *J. Heterocycl. Chem.* **2000**, *37*, 281.

[6] Hotta, S.; Lee, S. A.; Tamaki, T. *J. Heterocycl. Chem.* **2000**, *37*, 25.

[7] Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

[8] Negishi, E.-I.; Luo, F.-T.; Frisbee, R.; Matsushita, H. *Heterocycles* **1982**, *18*, 117.

[9] Silverstein, R. M.: Webster, F. X. *Spectroscopic Identification of Organic Compounds, 6th edition*, John Wiley & Sons Inc., New York, NY, 1998.

[10] Hotta, S.; Waragai, K. *J. Mater. Chem.* **1991**, *1*, 835.

[11a] Curtis, R. F.; Phillips, G. T. *Tetrahedron* **1967**, 23, 4419. [b] Horak, M.; Hyams, I. J.; Lippincott, E. R. *Spectrochim. Acta* **1966**, *22*, 1355. [c] Schulte, K. E.; Kreutzberger, A.; Bohn, G. *Chem. Ber.* **1964**, *97*, 3263.

[12] Pouchert, C. J. *The Aldrich Library of FT-IR Spectra, Edition I*, Aldrich Chemical Company, Milwaukee, Wisconsin, 1985, Vol. 1, pp 948–949.

[13] Shimizu, K.; Mori, Y.; Hotta, S. *J. Appl. Phys.* **2006**, *99*, 063505.

[14] Hotta, S.; Waragai, K. *Adv. Mater.* **1993**, *5*, 896.

[15] Yamao, T.; Kawasaki, Y.; Ota, S.; Hotta, S.; Azumi, R. *Macromol. Symp.* **2006**, *242*, 315.

[16] Hotta, S.; Ichino, Y.; Yoshida, Y.; Yoshida, M. *J. Phys. Chem. B* **2000**, *104*, 10316.

[17] Schubert, H.; Sagitdinov, I.; Svetkin, J. V. *Z. Chem.* **1975**, *15*, 222.

[18] Le Barny, P. ; Ravaux, G.; Dubois, J. C. ; Parneix, J. P. *Mol. Cryst. Liq. Cryst.* **1985**, *127*, 413.

[19] Pummerer, R.; Seligsberger, L. *Chem. Ber.* **1931**, *64*, 2477.

[20] Bäuerle, P.; Würthner, F.; Göetz, G.; Effenberger, F. *Synthesis* **1993**, *11*, 1099.

[21] Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996.

[22] Long, L. M.; Henze, H. R. *J. Am. Chem. Soc.* **1941**, *63*, 1939.

[23] Plaut, D. J.; Martin, S. M.; Kjaer, K.; Weygand, M. J.; Lahav, M.; Leiserowitz, L.; Weissbuch, I.; Ward, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 15922.

[24] Liu, X.-M.; Xu, J.; He, C. *Tetrahedron Lett.* **2004**, *45*, 1507.

[25] Jawdosiuk, M.; Kmiotek-Skarzynska, I. *Rocz. Chem.* **1977**, *51*, 2023.