Synthesis of Thiophene/phenylene Co-oligomers. **IV** [1]. 6- to 8-Ring Molecules

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We report the synthesis of various thiophene/phenylene co-oligomers with a total number of thiophene and benzene (phenylene) rings of 6 to 8. These compounds include a phenyl-capped sexithiophene, a thienyl-capped quaterphenylene, as well as block and alternating co-oligomers. The synthesis is based on either the Suzuki coupling reaction or the direct dimerization coupling. The latter method produces symmetric molecules with an even total ring number. These reaction schemes enabled us to obtain the target compounds in high quality. Although the resulting materials are difficult to dissolve in organic solvents and therefore difficult to identify by usual ^{1}H nmr spectroscopy, they have successfully been identified through Fourier-transform ir spectroscopy. The specific group frequencies of ring-stretching and out-of-plane deformation modes are characteristic of the substitution pattern of the individual thiophene and benzene rings.

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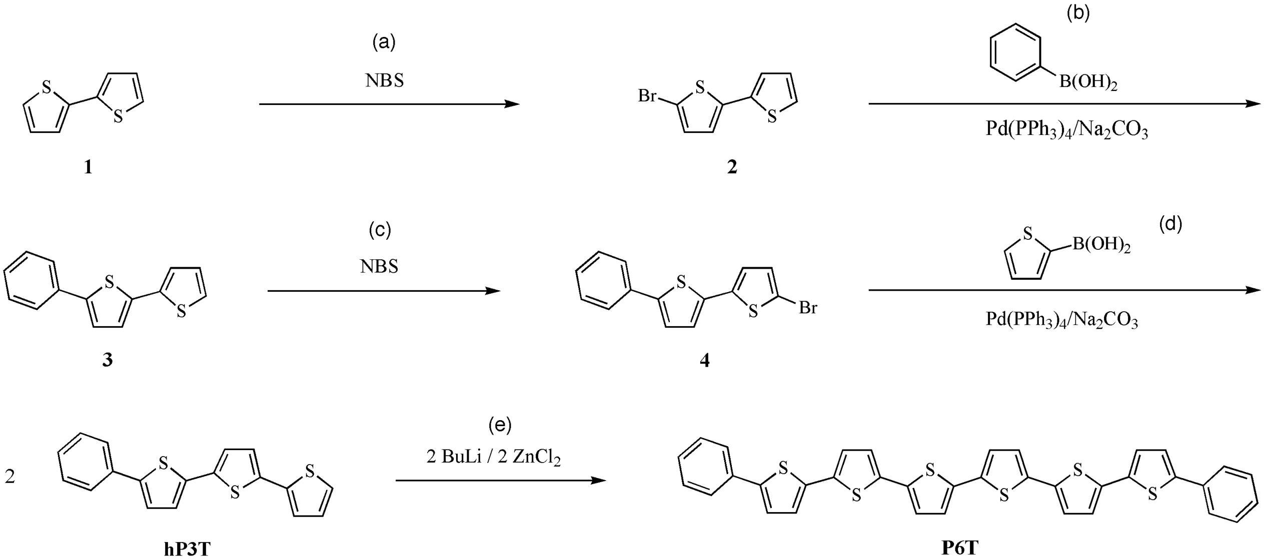
Introduction.

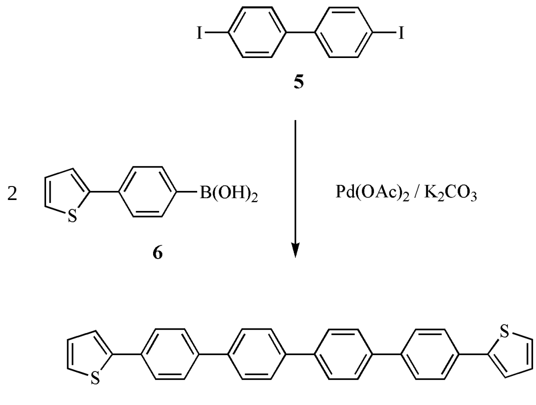
Thiophene/phenylene co-oligomers [*i.e.* hybridized oligomers comprising thiophene and benzene (phenylene) rings] are currently attracting much attention as a novel class of organic semiconductors [2,3]. These co-oligomers exhibit interesting light-emitting and charge transport characteristics [2,3]. 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. In particular, a large number of compounds are possible with increasing total number (n) of rings, because different combinations (*i.e.* compounds) of $2^{(n-1)/2} + 2^{n-1} - 2$ and $2^{n/2-1} + 2^{n-1} - 2$ can be obtained when n is an odd or an even number, respectively [2a]. The physicochemical features of these compounds are expected to vary widely. Note that in the present case we limited the substitution pattern of the thiophene and benzene rings to the 2- (or 2,5-) and 1,4-positions, respectively.

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 [1,4,5]. In the present article we show the syntheses of co-

Scheme 1



Scheme 2



oligomers with a total number of thiophene and benzene rings of 6 to 8. Applying the above rule to these cases, we should in principle be able to synthesize 34, 70, and 134 different compounds for *n* = 6, 7, and 8, respectively. Of these, the compounds synthesized include a phenyl-capped sexithiophene, a thienyl-capped quaterphenylene, and block and alternating co-oligomers in specific cases. These compounds add a realistic diversity to the family of known thiophene/phenylene co-oligomers.

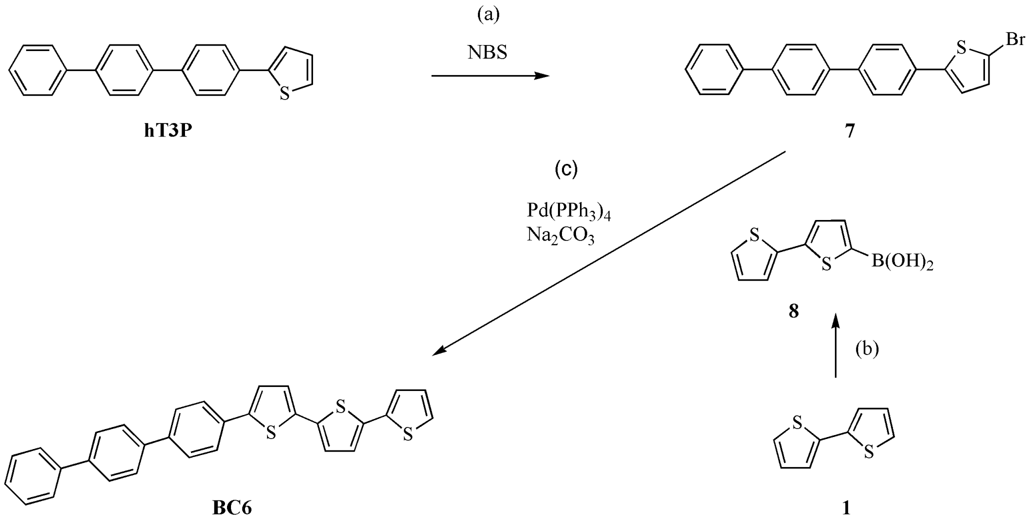
Preparation of the Materials.

Various building blocks for synthesizing thiophene/phenylene co-oligomers are available. In the present study we made use of these compounds. These include the co-oligomers previously obtained in our laboratories [1,4,5] (*e.g.* **hP3T**, **hT3P**, **BC4**, and **T1P**; see the relevant Schemes), as well as halides and boronic acid derivatives as intermediates [6–12]. The synthesis is generally based on the Suzuki coupling reaction involving these intermediates [13]. Some thiophene/phenylene co-oligomers are dimerized through direct coupling [14] which produces symmetric molecules with an even total number of thiophene and benzene rings.

Schemes 1 to 6 summarize the synthetic routes for the co-oligomers prepared. Compounds **P6T** (see Scheme 1) and **AC'7** (Scheme 6) were obtained by five-step and four-step syntheses at overall yields of 3.3% and 3.5%, respectively. Although these yields were low because of the multi-step syntheses, the resulting materials showed a metallic luster and bright luminescence.

In the final-step Suzuki coupling reaction for the synthesis of **AC7** (Scheme 5) and **AC'7** (Scheme 6), we used 1,2,4-trichlorobenzene as solvent so that monohalide intermediates generated by an equimolar reaction between the dihalide and the boronic acid reagents can retain good solubility in the reaction medium. This ensures the formation of the target compounds in good yield. The same reaction solvent was used for the synthesis of **BC6** (Scheme 3).

Scheme 3

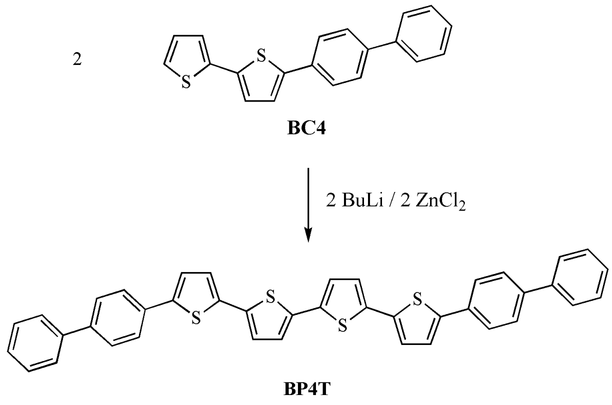


To the best of our knowledge, there has been no report in the literature regarding the syntheses of the target compounds, *i.e.* **P6T**, **T4P**, **BC6**, **BP4T**, **AC7**, and **AC'7**. The melting points of all these compounds exceed 300° (see EXPERIMENTAL), indicating that these materials are thermally stable and potentially useful for industrial applications.

Fourier-Transform ir Spectroscopic Characterization of Materials.

All the target compounds were very sparingly soluble at room temperature in *any* common organic solvent, which made it difficult to identify them by usual ^{1}H nmr spectroscopy. However, Fourier-transform (FT) ir spectroscopy

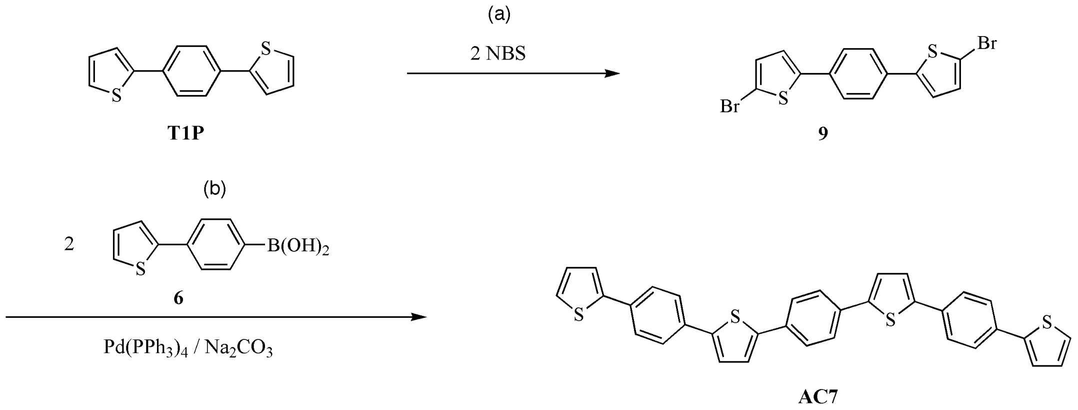
Scheme 4



in the solid state provides a firm basis for the structure identification. In particular, the most reliable clue is provided by close inspection of the ir regions around 1400–1500 cm^{-1} and 700–800 cm^{-1} [15]. Since the materials in the present study comprise solely thiophene and benzene aromatic rings, they display intense ring C–C stretching vibration and C–H out-of-plane deformation vibration bands in the 1400–1500 cm^{-1} and 700–800 cm^{-1} regions, respectively. Furthermore, the exact location of these bands helps determine the substitution modes of the thiophene and benzene rings [15,16].

The relevant characteristic frequencies as well as those associated with the C–H stretching modes are collected in Table 1. Their assignments have been carried out as

Scheme 5



Scheme 6

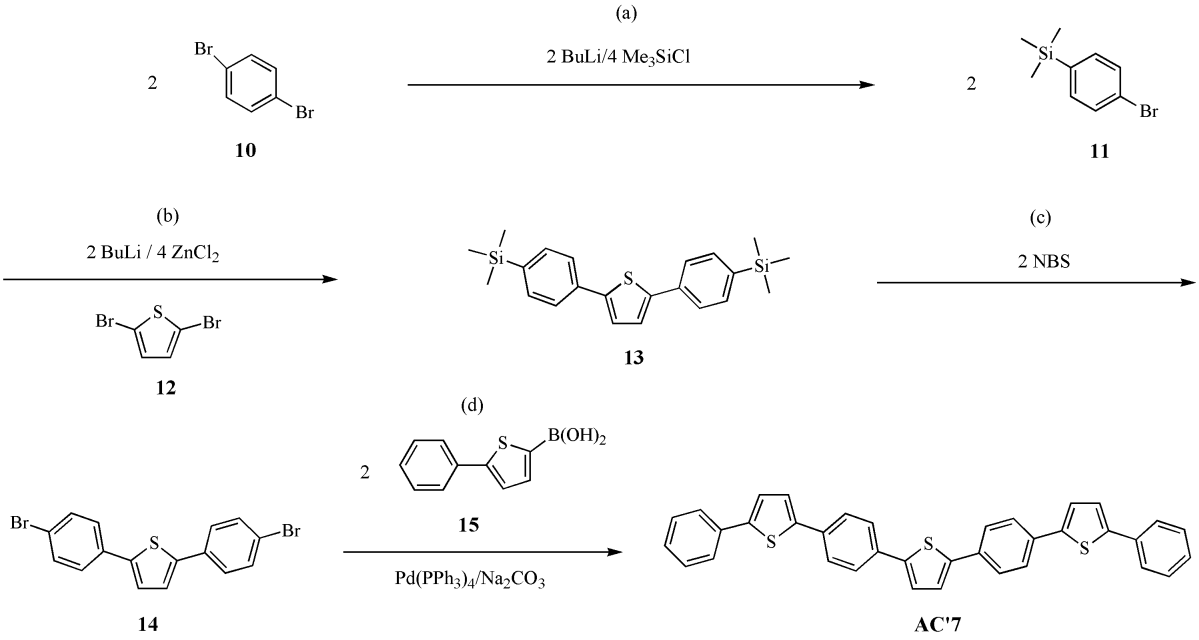


Table 1

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

Compound	C–H stretching	Ring C–C stretching		C–H out-of-plane deformation	
		Thiophene	Benzene	Thiophene	Benzene
P6T	3059	1442	1489	793	749, 685
T4P	3069	1425	1485	694	808
BC6	3064	1448, 1423	1483, 1402	796	835, 764, 687 [a]
BP4T	3057	1441	1483, 1408	790	833, 758, 687
AC7	3068	1448, 1427	1491	800, 696	816
AC'7	3058	1450	1489	798	833, 750, 687

[a] A thiophene-associated mode is involved as a shoulder.

described in our previously published work [1,4,5] dealing with the synthesis of other co-oligomers and in relevant literature [17,18]. In practice, **P6T** and **T4P** exhibit ir spectra closely related to those of the phenyl-capped oligothiophenes and thienyl-capped oligophenylenes, respectively, in both spectral profile and the positions of characteristic bands [1,5]. This is similarly the case with **BP4T** in that its ir spectrum is related to those of the biphenylyl-capped oligothiophenes [4]. The situation is again the same with **AC7**, **AC'7**, and **BC6** in that these compounds display spectra that are closely related to those of the alternating or block co-oligomers previously reported [1,4].

Thus, on the basis of these spectroscopic features we conclude that the co-oligomers in the present study possess the molecular structures shown in Schemes 1–6.

EXPERIMENTAL

Melting points were determined on a Seiko Instruments SSC5200 thermal analysis system. 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 sulfur) were carried out on a CEInstruments EA 1110 CHNS-O apparatus.

Tetrahydrofuran and diethyl ether 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.

5,5'''''-Diphenyl-2,2':5',2'':5'',2''':5'''2'''':5'''',2'''''-sexithiophene (**P6T**).

(a) 2,2'-Bithiophene (**1**) (145.1 g, 873 mmoles) was dissolved at -35° in a mixture of chloroform (1.3 L) and acetic acid (13 mL) [19]. To this solution was added *N*-bromosuccinimide (abbreviated as NBS in the Schemes; 155.6 g, 874 mmoles). The reaction mixture was allowed to stand for 1 hour and the precipitated succinimide was removed by filtration. The filtrate was washed successively with 1% aqueous sodium hydroxide and dried with anhydrous magnesium sulfate. After removal of the drying agent, *n*-hexane was added to the filtrate so that the 5,5'-dibromo-2,2'-bithiophene formed as by-product was precipitated and removed. Evaporation of the solvent and subsequent distillation under reduced pressure gave 126.6 g (59%) of 5-bromo-2,2'-bithiophene (**2**), bp 131°/3 mm Hg, lit [11] mp 33–34°.

(b) Compound **2** (10.5 g, 43 mmoles) and phenylboronic acid (7.7 g, 63 mmoles) as well as tetrakis(triphenylphosphine)palladium(0) [abbreviated as $Pd(PPh_3)_4$ in the Schemes; 3.1 g, 2.7 mmoles] were dispersed and dissolved in a mixture of benzene (92 ml) and aqueous sodium carbonate (9.2 g, 87 mmoles in 92 mL of water). After being refluxed for 7 hours, the reaction solution was cooled to room temperature and extracted with a mixture of ethyl acetate (140 mL) and tetrahydrofuran (50 mL). The organic phase was washed with saturated aqueous sodium chloride and dried with anhydrous magnesium sulfate. After removing the drying reagent by filtration, the solvent was evaporated *in vacuo* to give an oily residue. This was purified by column chromatography on silica gel with benzene as eluent to give crude 5-phenyl-2,2'-bithiophene (**3**) [9]. This was recrystallized from benzene/*n*-hexane (2:1, v/v) to yield 8.3 g (80%) of a purified compound **3**, mp 123°, lit [20] mp 117–118°.

(c) Compound **3** (8.3 g, 34 mmoles) was brominated following the procedure for bromination of compound **1**, generating 5-bromo-5'-phenyl-2,2'-bithiophene (**4**) [7], 8.1 g (74%), lit [20] mp 135–140°.

(d) Compound **4** (8.1 g, 25 mmoles) was used in the Suzuki coupling reaction as for step (b) using 2-thiopheneboronic acid in place of phenylboronic acid to yield 5-phenyl-2,2':5',2''-terthiophene (**hP3T**), 5.5 g (67%), mp 216°. Another synthetic method for **hP3T** is described in Ref. [21].

(e) Compound **hP3T** (17.4 g, 54 mmoles) was dissolved in dry tetrahydrofuran (350 mL) and cooled to -10°. To this solution was added dropwise 21 mL (54 mmoles) of 2.6 *M* *n*-butyllithium. Subsequent addition of anhydrous zinc chloride (7.3 g, 54 mmoles) into the solution spontaneously elevated its temperature to ~25° and the reaction mixture was stirred at that temperature for 1 hour. Following addition of tetrakis(triphenylphosphine)-palladium(0) (1.8 g, 1.6 mmoles), the resulting mixture was refluxed for 8 hours. The reaction mixture was then cooled to room temperature, yielding a precipitate of the target compound **P6T**. The precipitate was collected by filtration, washed with tetrahydrofuran, and recrystallized from 1,2,4-trichlorobenzene to give 2.3 g (14%) of **P6T** as a bright red solid with metallic luster, mp 388°. The overall yield of the above five-step synthesis (a)-(e) was 3.3%.

Anal. Calcd. for $C_{36}H_{22}S_6$: C, 66.83; H, 3.43; S, 29.74. Found: C, 66.51; H, 2.96; S, 29.80.

4,4'''-Di(2-thienyl)-1,1':4',1'':4'',1'''-quaterphenyl (**T4P**).

4-(2-Thienyl)phenylboronic acid (**6**) was synthesized using a procedure similar to that described in Ref. [1]. Compound **6** (16.7 g, 82 mmoles) and 4,4'-diiodobiphenyl (**5**) (13.2 g, 33 mmoles) as well as palladium(II) acetate (0.27 g, 1.2 mmoles) were dispersed and dissolved in a mixture of tetrahydrofuran (500 mL) and aqueous potassium carbonate (26.9 g, 195 mmoles in 196 mL of water). This solution was stirred at 65° overnight and then cooled to room temperature, generating a precipitate. This precipitate was collected by filtration, washed with acetone, and recrystallized from 1,2,4-trichlorobenzene to give 3.9 g (26%) of **T4P** as a pale yellow solid, mp 442°.

Anal. Calcd. for $C_{32}H_{22}S_2$: C, 81.66; H, 4.71; S, 13.63. Found: C, 81.37; H, 4.54; S, 13.54.

5-(1,1':4',1''-Terphenyl-4-yl)-2,2':5',2''-terthiophene (**BC6**).

2-(1,1':4',1''-Terphenyl-4-yl)thiophene (**hT3P**) was synthesized by a reaction route different from that described in Ref. [1]. In the present study this compound was synthesized *via* a coupling reaction between 4-bromo-1,1':4',1''-terphenyl and thiophene under the presence of butyllithium and zinc chloride. Comparing the FT ir spectra of the products of the two syntheses, however, we have established that they are identical. Below, we describe the synthetic route for **BC6** starting from **hT3P**.

(a) Compound **hT3P** (16.3 g, 52 mmoles) was dispersed in a mixture of *N*,*N*-dimethylformamide (1.54 L) and acetic acid (15 mL) and the temperature of the mixture was elevated to 80° for **hT3P** to dissolve. To this solution was added *N*-bromosuccinimide (10.3 g, 58 mmoles), and the reaction mixture was kept at 80° for 1 hour and then cooled to 5° to produce a precipitate. This precipitate was washed with methanol to give 2-bromo-5-(1,1':4',1''-terphenyl-4-yl)thiophene (**7**), 18.5 g (91%).

(b) 2,2'-Bithiophene (**1**) (51.8 g, 312 mmoles) was dissolved in dry tetrahydrofuran (489 mL) and the solution was cooled to -10°. To this solution was added dropwise 120 mL (312 mmoles) of 2.6 *M n*-butyllithium with the temperature kept at -10°. After stirring for 30 minutes at that temperature, the reaction mixture was further cooled to -65°. Then a solution of trimethyl borate (97.3 g, 936 mmoles) in dry tetrahydrofuran (195 mL) was added dropwise followed by stirring for another 1 hour. The reaction mixture was subsequently warmed up to ~25° to ensure completion of the reaction. After the reaction mixture had been cooled to 0°, 10 wt% aqueous sulfuric acid (159 g) was slowly added keeping the temperature at ~25°. The resulting mixture was then washed with saturated aqueous sodium chloride and dried with anhydrous magnesium sulfate. The solution was washed with chloroform and extracted successively with aqueous sodium hydroxide and water. Addition of hydrochloric acid to adjust pH (= 1) yielded 2,2'-bithiophene-5-boronic acid (**8**) [6], 33.9 g (52%), mp 89°.

(c) Compounds **7** (16.3 g, 42 mmoles) and **8** (17.8 g, 85 mmoles) as well as tetrakis(triphenylphosphine)palladium(0) (3.2 g, 2.8 mmoles) were dispersed and dissolved in a mixture of 1,2,4-trichlorobenzene (1.0 L) and aqueous sodium carbonate (15.0 g, 141 mmoles in 324 mL of water), and the solution was kept at ~80° for 8 hours. The reaction mixture was then filtered at that temperature and the collected precipitate was washed successively with water and methanol. This precipitate was recrystallized from 1,2,4-trichlorobenzene to give 12.0 g (60%) of **BC6** as a yellow solid, mp 343°. The overall yield of reactions (a) and (c) was 55%.

Anal. Calcd. for $C_{30}H_{20}S_3$: C, 75.59; H, 4.23; S, 20.18. Found: C, 76.26; H, 3.83; S, 19.91.

5,5'''-Bis(4-biphenylyl)-2,2':5',2'':5'',2'''-quaterthiophene (**BP4T**).

In the present studies 5-(4-biphenylyl)-2,2'-bithiophene (**BC4**) was synthesized *via* the Suzuki coupling reaction between 2,2'-bithiophene-5-boronic acid (**8**) and 4-bromobiphenyl. Earlier **BC4** had been synthesized in a different manner [4]. Comparing the FT ir spectra of the products of the two syntheses, however, we have confirmed that they are identical. Below, we describe the synthetic route for **BP4T** starting from **BC4**.

The dimerization reaction was carried out as in the synthesis of **P6T** [see step (e)], except for using compound **BC4** (25.0 g, 79 mmoles) instead of **hP3T**. The resulting precipitate was recrystallized from 1,2,4-trichlorobenzene to give 10.5 g (42%) of **BP4T** as a shiny orange solid with metallic luster, mp 417°.

Anal. Calcd. for $C_{40}H_{26}S_4$: C, 75.67; H, 4.13; S, 20.20. Found: C, 75.02; H, 3.90; S, 20.02.

1,4-Bis{5-[4-(2'-thienyl)phenyl]thiophen-2-yl}benzene (**AC7**).

In the present study 1,4-di(2-thienyl)benzene (**T1P**) was synthesized *via* the Suzuki coupling reaction between 2-thiopheneboronic acid and 1,4-dibromobenzene (**10**). Earlier **T1P** had been synthesized by a Grignard coupling [1]. Since we have confirmed from their FT ir spectra that the products of the two syntheses are identical, we describe the synthetic route starting from **T1P**.

(a) Compound **T1P** (16.2 g, 67 mmoles) was dispersed at room temperature in a mixture of chloroform (486 mL) and acetic acid (486 mL) and the temperature of the mixture was raised to 60° for **T1P** to dissolve. To this solution was added *N*-bromosuccinimide (25.9 g, 146 mmoles), and the reaction mixture was cooled to 5° to yield a precipitate. This precipitate was collected by filtration and repeatedly recrystallized from tetrahydrofuran to give 21.7 g (81%) of 1,4-bis(5-bromothiophen-2-yl)benzene (**9**), lit [10] mp 251–252°.

(b) Compounds **9** (11.0 g, 27 mmoles) and **6** (16.7 g, 82 mmoles), as well as tetrakis(triphenylphosphine)palladium(0) (5.9 g, 5.1 mmoles) were dissolved in a mixture of 1,2,4-trichlorobenzene (890 mL) and aqueous sodium carbonate (17.4 g, 164 mmoles in 410 mL of water) and stirred for 8 hours at ~80°. The resulting solution was then cooled to 10°, generating a precipitate. This precipitate was collected by filtration, washed successively with benzene, water, and acetone, and recrystallized from 1,2,4-trichlorobenzene to give 10.5 g (68%) of **AC7** as a yellow powder, mp 404°. The overall yield was 55%.

Anal. Calcd. for $C_{34}H_{22}S_4$: C, 73.08; H, 3.97; S, 22.95. Found: C, 73.06; H, 3.67; S, 22.44.

2,5-Bis[4-(5'-phenylthiophen-2'-yl)phenyl]thiophene (**AC'7**).

(a) Compound **10** (123 g, 521 mmoles) was dissolved in dehydrated diethyl ether (610 mL) and the solution was cooled to -10°. To this was added dropwise 200 mL (520 mmoles) of 2.6 *M n*-butyllithium. The reaction mixture was stirred for 1 hour at that temperature and then treated with trimethylsilyl chloride (113 g, 1.04 moles). The reaction mixture was allowed to warm to ~20° while being stirred for 1 hour. It was then cooled to -10° and quenched with water (280 mL). The organic phase was extracted with diethyl ether and the extract was washed with saturated aqueous sodium chloride and dried with anhydrous magnesium sulfate. Evaporation of diethyl ether and subsequent distillation under reduced pressure gave 107.3 g (90%) of 1-bromo-4-(trimethylsilyl)benzene (**11**), lit [22] bp 99°/ 23 mm Hg.

(b) Compound **11** (40.5 g, 177 mmoles) was dissolved in dehydrated diethyl ether (200 mL) together with *N*,*N*,*N*',*N*'-tetramethylethylenediamine (20.3 g, 175 mmoles) and the solution was cooled to -65°. To this was added dropwise 67 mL (174 mmoles) of 2.6 *M* *n*-butyllithium. After stirring the reaction mixture for 1 hour at that temperature, anhydrous zinc chloride (47.7 g, 350 mmoles) dissolved in dry tetrahydrofuran (400 mL) was added, which caused the temperature to rise to ~25°. The reaction mixture was stirred at that temperature for another 1 hour and then 2,5-dibromothiophene (**12**) (19.3 g, 80 mmoles) and tetrakis(triphenylphosphine)palladium(0) (2.93 g, 2.5 mmoles) were added. The resulting solution was left to stand overnight and further stirred for 7 hours at 50°. The reaction mixture was then quenched with 5 wt % hydrochloric acid (350 g). The organic phase was extracted with ethyl acetate (300 mL) and the extract was washed with saturated aqueous sodium chloride and dried with anhydrous magnesium sulfate. After the solvent was evaporated, the residual material was purified by column chromatography on silica gel with hexane/ethyl acetate (50:1, v/v) as eluent. The resulting material was recrystallized from acetonitrile to give 10.9 g (32%) of 2,5-bis(4-trimethylsilylphenyl)thiophene (**13**), mp 111°, lit [23] mp 126–127°.

(c) Compound **13** (10.0 g, 26 mmoles) was dissolved in a mixture of tetrahydrofuran (200 mL) and acetic acid (2 mL). To this solution was added *N*-bromosuccinimide (10.3 g, 58 mmoles), and the reaction mixture was kept at 60° for 30 minutes. The crude material obtained after evaporating the solvent was recrystallized from chloroform to give 8.5 g (82%) of 2,5-bis(4-bromophenyl)thiophene (**14**), mp 201°, lit [24] mp 198–199°.

Anal. Calcd. for $C_{16}H_{10}SBr_2$: C, 48.76; H, 2.56; S, 8.13; Br, 40.55. Found: C, 48.85; H, 2.33; S, 8.09.

(d) 2-Phenyl-5-thiopheneboronic acid (**15**) was synthesized essentially following the method described in the literature [8]. Compounds **14** (15.4 g, 39 mmoles) and **15** (32.2 g, 158 mmoles) as well as tetrakis(triphenylphosphine)palladium(0) (8.3 g, 7.2 mmoles) were dissolved in a mixture of 1,2,4-trichlorobenzene (1.24 L) and aqueous sodium carbonate (24.4 g, 230 mmoles in 570 mL of water) and the solution was stirred for 8 hours at ~80°. The precipitate generated was collected by filtration, washed successively with water and acetone, and recrystallized from 1,2,4-trichlorobenzene to give 3.2 g (15%) of **AC'7** as a shiny yellow solid, mp 376°. The overall yield for the above four-step synthesis (a)-(d) was 3.5%.

Anal. Calcd. for $C_{36}H_{24}S_3$: C, 78.22; H, 4.38; S, 17.40. Found: C, 77.84; H, 4.16; S, 17.19.

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