

An Iterative Strategy for the Synthesis of Oligothiophenes by Catalytic Cross-Coupling Reactions

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Received 5 September 2003

ABSTRACT: *An iterative strategy for the synthesis of new sulfur-functionalized oligothiophenes by Suzuki or Stille cross-coupling reactions was applied to the reaction of 4-bromo-tert-butylphenylthioether with thiophene derivatives. The planarity of the oligothiophenes obtained was confirmed by the single-crystal X-ray structure analysis of 2-(4'-tert-butylthiophenyl)thiophene, which shows a potentially large electronic conjugation length.* © 2004 Wiley Periodicals, Inc. *Heteroatom Chem* 15:121–126, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10224

INTRODUCTION

During the last two decades, well-defined, monodisperse oligothiophenes have been extensively studied as model compounds in order to understand and to optimize the electronic, optical, and charge transport properties of conjugated polymers such as polythiophenes and their derivatives [1–4]. In addition, oligothiophenes themselves exhibit intrinsic physical properties due to their well-defined structure and their large conjugation length. These effects led to the development of thiophene-based electronic devices such as electroluminescent diodes [5] or field-effect transistors [6]. On the other hand, the

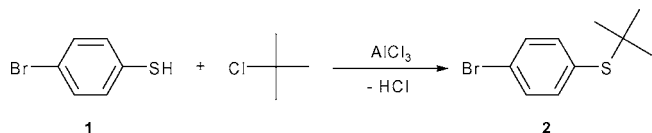
molecular-scale electronic devices have been investigated in particular, in the case of Self Assembled Monolayers built around a gold-surface and thiol-ended organic compounds or for the development of surface-bound molecular motor [7]. However, the insertion of a sulfur atom in oligomers as an anchor leads to a modification of the electronic structure of the starting oligomers [8,9]. In this paper, we propose an iterative strategy for the synthesis of monodisperse oligothiophenes ending with a 4-*tert*-butylphenylthioether group.

RESULTS AND DISCUSSION

The common method to synthesize monodisperse and well-defined oligomers is based on a step-by-step strategy in which a catalytic cross-coupling reaction such as Suzuki, Stille, or Kumada coupling leads to the elongation of the oligomer by one constitutive subunit. However, in the case of the presence of a thiophenol derivative, the free thiol function can be considered as a poison for the palladium catalyst used for the cross-coupling reaction. Therefore, the first step of our synthetic strategy consists in the protection of the free-thiol function by *tert*-butyl moiety, catalyzed by aluminum trichloride (Scheme 1).

(4-Bromo)phenyl-*tert*-butylthioether **2** is obtained in quantitative yield, and the spectroscopic data (^1H or $^{13}\text{C}\{^1\text{H}\}$ NMR) are in accordance with the literature data [10]. This compound can be used as starting material for the generation of oligothiophenes, thanks to the presence of a bromo atom.

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SCHEME 1 Synthesis of (4-bromo)phenyl-*tert*-butylthioether **2**.

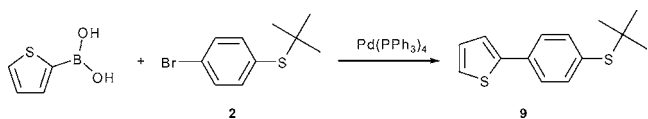
Two different cross-coupling reactions were tested: Suzuki cross-coupling with commercially available 2-thiophene boronic acid (Scheme 2) and Stille cross-coupling with tri-*n*-butyltinthiophene derivatives **6–8** (Scheme 3).

The tin-functionalized compounds **6–8** were synthesized from the reaction of the lithium salt of the thiophene **3**, 2,2'-bithiophene **4**, and 3,4-ethylenedioxythiophene **5**, respectively, with tri-*n*-butyltin chloride [see experimental]. These compounds were used without further purification as starting material for the Stille cross-coupling reaction.

All products were obtained in good yield (75–90%), and they were characterized by their MS and NMR spectroscopic data (^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR). Suitable crystals of **9** were obtained from the resulting oil at 4°C after chromatography on silica gel.

The molecular structure of **9** is presented in Fig. 1. The bond lengths and angles are in accordance with those in related structures [11,12]. The phenyl-thienyl unit is almost planar, with the mean deviation from the least-square plane formed by S(1), S(2), and C(1) to C(10) being 0.0395 Å. The dihedral angle between the phenyl and thienyl rings is only 4.9(1)°, whereas in the bis[4-(5-methoxycarbonyl-2-thienyl)phenyl] sulfide analogue the dihedral angle was 10.9(1)° [11]. Moreover, this weak torsional angle is ideal for an important π - π overlapped structure as requested for optimal charge transport in conjugated oligomers. It is very close to the corresponding angle observed in the case of α -sexithiophene (4.1°) [5] and smaller than in standard unsubstituted thiophene-phenylene (18°–20°) [13]. Intermolecular contact involving the C(3) H atom and S(2) leads to the formation of infinite chains running parallel to the *a* axis of the crystal.

In the view of developing longer oligomers, the insertion of a bromine atom was necessary, in order to allow a second cross-coupling reaction with



SCHEME 2 Synthesis of 2-(4'-*tert*-butylthiophenyl)-thiophene **9** by Suzuki cross-coupling reaction.

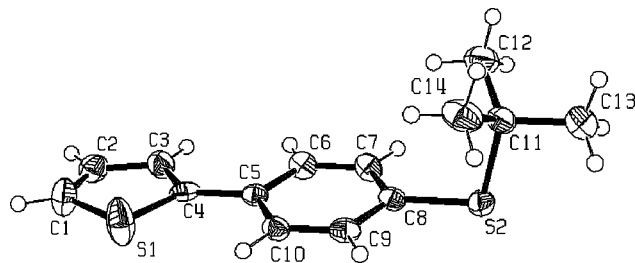


FIGURE 1 ORTEP drawing of compound **9**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–S(1) 1.693(3), C(4)–S(1) 1.697(3), C(4)–C(5) 1.485(4), C(8)–S(2) 1.775(3), C(11)–S(2) 1.857(3), C(1)–S(1)–C(4) 92.39(14), C(8)–S(2)–C(11) 103.48(12), S(1)–C(4)–C(5) 110.6(2), C(3)–C(4)–C(5) 127.6(2).

functionalized (boronic or tri-*n*-butyltin) thiophene derivatives. This was achieved at room temperature by the reaction of compounds **9** and **10** with *N*-bromosuccinimide in acetic acid/chloroform mixture (Scheme 4).

Products **12** and **13** were obtained in good yield (>90%) and characterized by their MS and NMR spectroscopic data (^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR). Compound **12** was used as starting material for Suzuki or Stille cross-coupling reaction with 2-thiophene boronic acid and 2-tri-*n*-butyltinthiophene **6**, respectively (Scheme 5).

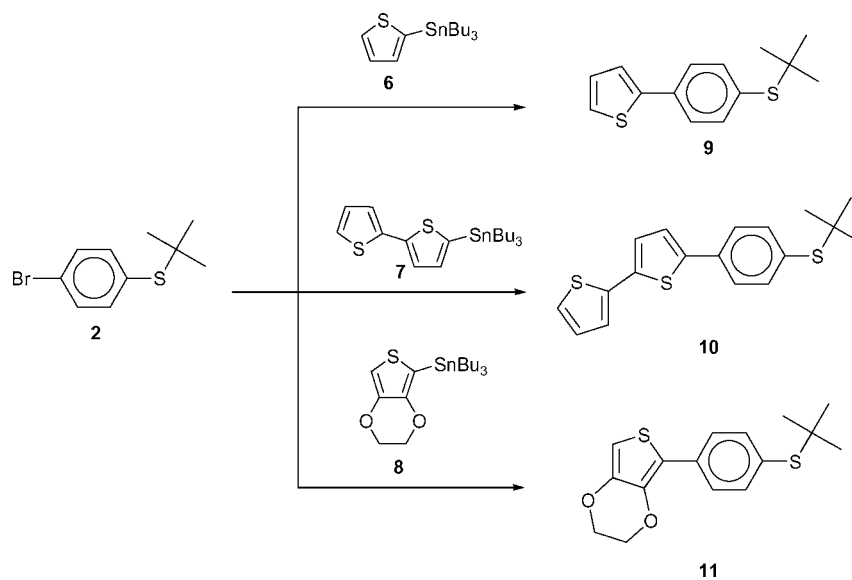
The two types of cross-coupling reactions gave the same product which can be obtained alternatively by direct Stille cross-coupling reaction between **2** and **7**. This could be explored as a fast synthetic way for *tert*-butylthiophenyl-terminated oligothiophenes in which the length of the π -conjugated system is controlled step-by-step.

These reactions demonstrate that an oligothiophene can be elongated by several units from successive brominations and cross-coupling reactions (Suzuki- or Stille-type). In principle, each sulfur-functionalized oligothiophene should be accessible by this iterative strategy (Scheme 6).

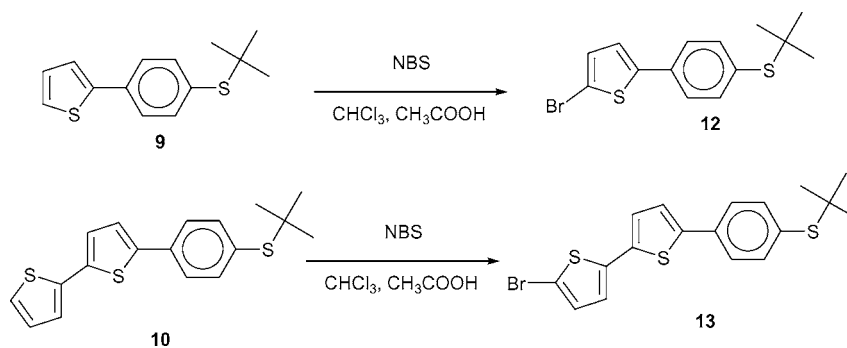
EXPERIMENTAL

General Remarks

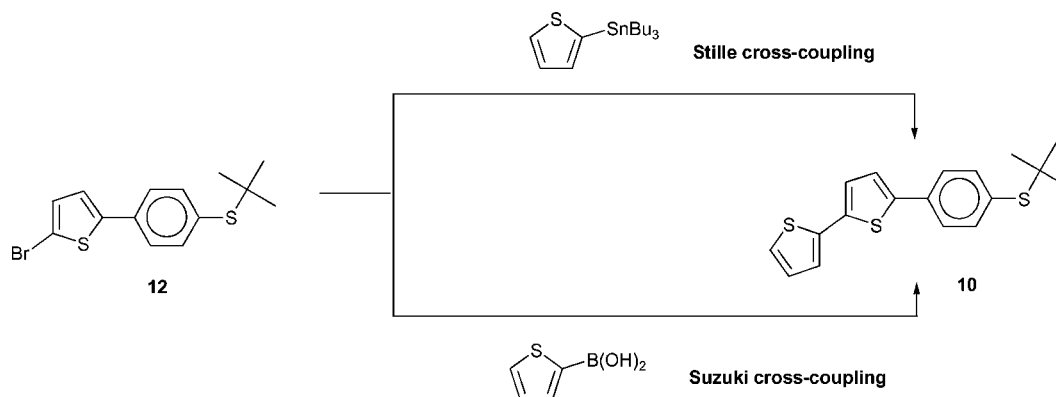
All reactions were carried out under nitrogen by using standard Schlenk techniques. The solvents were degassed prior to use. 2,2'-bithiophene has been synthesized by Stille cross-coupling reaction between 2-bromothiophene and 2-(tri-*n*-butyl)-thiophene [3]. All other reagents were purchased (Acros and Aldrich) and used as received. NMR spectra were recorded with a Varian Gemini 200 BB instrument and referenced to the signals of the



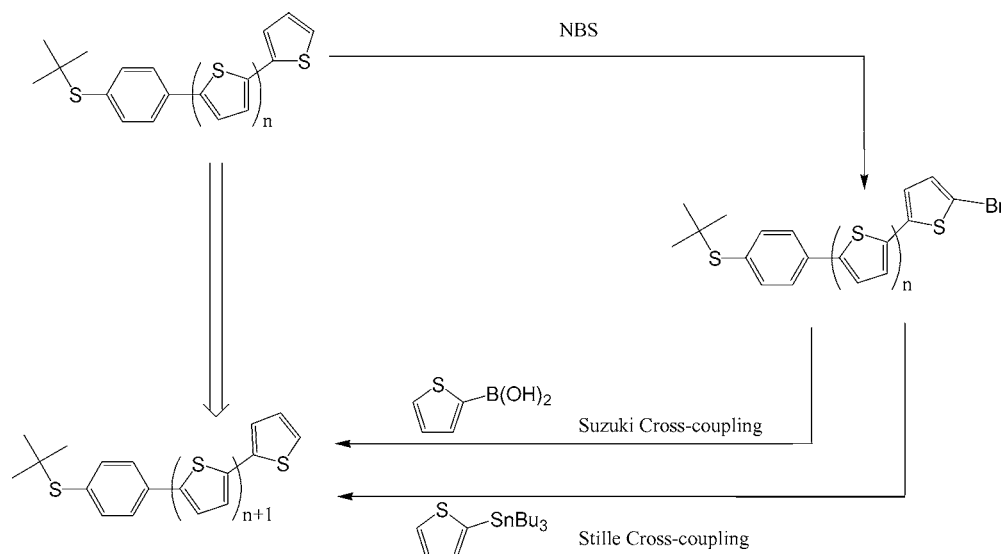
SCHEME 3 Synthesis of thiophene derivatives **9**–**11** by Stille cross-coupling reaction.



SCHEME 4 Bromination of compounds **9** and **10**.



SCHEME 5 Elongation of **12** by Suzuki or Stille cross-coupling reaction.



SCHEME 6 Synthetic route toward one higher generation order.

residual protons in the deuterated solvents. The mass spectra were recorded at the University of Fribourg (Switzerland) by Prof. Titus Jenny. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

(4-Bromo)phenyl-*tert*-butylthioether (**2**)

To a slurry of 4-bromothiophenol **1** (5 g, 26.5 mmol) in 2-chloro-2-methylpropane (20 ml) was added aluminum chloride (175 mg, 1.3 mmol) in small portions at room temperature. The reaction became vigorously foaming and HCl was exhausted. The mixture was stirred for one additional hour, and the solution became orange. The reaction mixture was poured into water and extracted with *n*-pentane (3×25 ml). The combined organic layers were washed with water (3×30 ml), dried over anhydrous MgSO_4 , and the solvent was removed under reduced pressure. The purification of the residual light yellow oil was done using column chromatography (silica gel 60Å, *n*-pentane) to afford colorless oil with quantitative yield. ^1H NMR (200 MHz, CDCl_3) δ 1.30 s (9H, $\text{C}(\text{CH}_3)_3$), 7.41 d (2H, $\text{C}(2)\text{H}$ $^3J_{\text{H}(2)-\text{H}(3)}$ 8.8 Hz), 7.49 d (2H, $\text{C}(3)\text{H}$ $^3J_{\text{H}(3)-\text{H}(2)}$ 8.8 Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 31.23, 46.24, 123.76, 131.92, 132.18, 139.22.

General Procedure for the 2-Stannylation of Thiophene Derivatives

Thiophene derivatives (10 mmol) **3–5** were dissolved into Et_2O (20 ml) at -20°C . *n*-BuLi (1.6 M in hexane,

10 mmol) was slowly added and the reaction was left under strong stirring at -20°C for 1 h, and then 10 mmol of $\text{Sn-}n\text{-Bu}_3\text{Cl}$ were added. The mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 (3×20 ml). The combined organic layers were then washed with water (3×20 ml), dried over anhydrous MgSO_4 , and the solvent was removed under reduced pressure to give pure colorless **6**, green **7**, and brown **8** oils which were used without further purification.

2-(Tri-*n*-butyltin)thiophene (**6**)

^1H NMR (200 MHz, CDCl_3): δ 0.91 t (9H, $\text{CH}_3\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.12 t (6H, $\text{Sn-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.31 h (6H, $\text{CH}_3\text{-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.57 quint. (6H, $\text{Sn-CH}_2\text{-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 7.22 dd (1H, $\text{C}(4)\text{H}$ $^3J_{\text{H}(4)-\text{H}(3)}$ 3.66 Hz $^3J_{\text{H}(4)-\text{H}(5)}$ 4.82 Hz), 7.26 d (1H, $\text{C}(3)\text{H}$ $^3J_{\text{H}(3)-\text{H}(4)}$ 3.66 Hz), 7.58 d (1H, $\text{C}(5)\text{H}$ $^3J_{\text{H}(5)-\text{H}(4)}$ 4.82 Hz).

5-(Tri-*n*-butyltin)-2,2'-bithiophene (**7**)

δ 0.91 t (9H, $\text{CH}_3\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.12 t (6H, $\text{Sn-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.31 h (6H, $\text{CH}_3\text{-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.57 quint. (6H, $\text{Sn-CH}_2\text{-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 7.02 dd (1H, $\text{C}(4')\text{H}$ $^3J_{\text{H}(4')-\text{H}(3')}$ 3.66 Hz $^3J_{\text{H}(4')-\text{H}(5')}$ 4.86 Hz), 7.09 d (1H, $\text{C}(3')\text{H}$ $^3J_{\text{H}(3')-\text{H}(4')}$ 3.66 Hz), 7.20 d (1H, $\text{C}(5')\text{H}$ $^3J_{\text{H}(5')-\text{H}(4')}$ 4.82 Hz), 7.22 d (1H, $\text{C}(3)\text{H}$ $^3J_{\text{H}(3)-\text{H}(4)}$ 3.69), 7.32 d (1H, $\text{C}(4)\text{H}$ $^3J_{\text{H}(4)-\text{H}(3)}$ 3.69).

3,4-Ethylenedioxy-2-(tri-*n*-butyltin)thiophene (8)

0.91 t (9H, $\text{CH}_3\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.12 t (6H, $\text{Sn-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.31 h (6H, $\text{CH}_3\text{-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 1.57 quint. (6H, $\text{Sn-CH}_2\text{-CH}_2\text{-CH}_2$ $^3J_{\text{H-H}}$ 8.06 Hz), 4.10 m (2H, $\text{O-CH}_2\text{-CH}_2\text{-O}$), 4.17 m (2H, $\text{O-CH}_2\text{-CH}_2\text{-O}$), 6.60 s (1H, C(5)H).

2-(4'-tert-butylthiophenyl)thiophene (9) by Stille Cross-Coupling

(4-Bromo)phenyl-*tert*-butylthioether **2** (1 g, 4.0 mmol) in dry toluene (20 ml), 2-(tri-*n*-butyltin)-thiophene **6** (0.995 ml, 4.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (100 mg, 0.4 mmol) were refluxed overnight. After cooling to room temperature, the solution was washed with an aqueous saturated solution of NH_4Cl (100 ml), and then extracted three times with 100 ml of Et_2O . The organic layers were dried over MgSO_4 and removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel 60 Å, petroleum ether bp. 60–90°C) and yielded a colorless oil that crystallized after one night at 4°C. ^1H NMR (200 MHz, CDCl_3) δ = 1.34 s (9H, $\text{C}(\text{CH}_3)_3$), 7.12 dd (1H, C(4)H $^3J_{\text{H(4)-H(3)}}$ 3.66 Hz $^3J_{\text{H(4)-H(5)}}$ 5.13 Hz), 7.32 d (1H, C(3)H $^3J_{\text{H(3)-H(4)}}$ 3.66 Hz), 7.34 d (1H, C(5)H $^3J_{\text{H(5)-H(4)}}$ 5.13 Hz), 7.56 d (2H, C(2')H $^3J_{\text{H(2')-H(3')}}$ 11.91 Hz), 7.56 d (2H, C(3')H $^3J_{\text{H(3')-H(2')}}$ 11.91 Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 31.25, 46.50, 123.85, 125.62, 126.05, 128.45, 128.63, 132.07, 135.02, 138.22. MS (ESI): m/z = 248.

5-(4'-tert-Butylthiophenyl)-2,2'-bithiophene (10) by Suzuki Cross-Coupling

5-Bromo-2-(4'-tert-butylthiophenyl)thiophene **12** (400 mg, 1.2 mmol), 2-thiopheneboronic acid (230 mg, 1.8 mmol), and sodium carbonate (191 mg, 1.8 mmol) were dissolved in EtOH (20 ml), and then tetrakis(triphenylphosphine)palladium(0) (69 mg, 0.06 mmol) was added. The reaction mixture was refluxed, then poured in water (70 ml), extracted with CH_2Cl_2 (3 $\times$ 25 ml), and the recombined organic layers were washed with water, dried over MgSO_4 , and the solvent was removed under reduced pressure. The purification was done using column chromatography (silica gel 60 Å, petroleum ether (bp. 60–90°C)/ CH_2Cl_2 3:1) and yielded to a yellowish solid. ^1H NMR (200 MHz, CDCl_3) δ = 1.25 s (9H, $\text{C}(\text{CH}_3)_3$), 7.06 dd (1H, C(4)H $^3J_{\text{H(4)-H(3)}}$ 3.66 Hz $^3J_{\text{H(4)-H(5)}}$ 5.12 Hz), 7.18 d (1H, C(3)H $^3J_{\text{H(3)-H(4)}}$ 3.66 Hz), 7.23 d (1H, C(5)H $^3J_{\text{H(5)-H(4)}}$ 5.13 Hz), 7.22 d (1H, C(3')H $^3J_{\text{H(3')-H(4')}}$ 4.02), 7.32 d (1H, C(4')H $^3J_{\text{H(4')-H(3')}}$

4.02), 7.57 s (4H, C(2')H and C(3')H); ^{13}C NMR (50 MHz, CDCl_3) δ 31.25, 46.56, 124.06, 124.52, 124.83, 124.96, 125.65, 128.19, 132.22, 134.62, 137.53, 138.22, 142.43. MS (ESI): m/z = 330.

5-(4'-tert-Butylthiophenyl)-2,2'-bithiophene (10) by Stille Cross-Coupling

(4-Bromo)phenyl-*tert*-butylthioether **2** (1 g, 4.0 mmol), **7** (1.82 g, 4.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (100 mg, 0.4 mmol) were dissolved in dry toluene (20 ml). The mixture was refluxed overnight. After cooling to room temperature, the solution was washed with an aqueous saturated solution of NH_4Cl (100 ml), then extracted three times with 100 ml of Et_2O , and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel 60 Å, petroleum ether bp. 60–90°C) and yielded to a colorless oil. The spectroscopic data are identical with those obtained by Suzuki cross-coupling reaction.

2-(4'-tert-Butylthiophenyl)-3,4-ethylenedioxythiophene (11)

(4-Bromo)phenyl-*tert*-butylthioether **2** (1 g, 4.0 mmol), **8** (1.12 ml, 4.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (100 mg, 0.4 mmol) were dissolved in dry toluene (20 ml). The mixture was refluxed overnight. After cooling to room temperature, the solution was washed with an aqueous saturated solution of NH_4Cl (100 ml), and then extracted three times with 100 ml of Et_2O and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel 60 Å, petroleum ether bp. 60–90°C) and yielded to a colorless powder. ^1H NMR (CDCl_3 , 200 MHz) δ 1.19 s (9H, $\text{C}(\text{CH}_3)_3$), 4.10 m (2H, $\text{O-CH}_2\text{-CH}_2\text{-O}$), 4.17 m (2H, $\text{O-CH}_2\text{-CH}_2\text{-O}$), 6.60 s (1H, C(5)H) 7.28 d (2H, C(2')H $^3J_{\text{H(2')-H(3')}}$ 8.79 Hz), 7.41 d (2H, C(3')H $^3J_{\text{H(3')-H(2')}}$ 8.79 Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 31.22, 46.32, 64.63, 65.05, 98.48, 117.02, 125.94, 130.84, 133.94, 137.93, 138.93, 142.56. MS (ESI): m/z = 366.

5-Bromo-2-(4'-tert-butylthiophenyl)thiophene (12)

5-(4'-tert-Butylthiophenyl)thiophene **9** (425 mg, 1.7 mmol) and *N*-bromosuccinimide (308 mg, 1.7 mmol) were dissolved in chloroform (10.0 ml) and acetic acid (10.0 ml). The mixture was stirred in the absence of light for 6 h. The aqueous layer was

extracted with ether (30 ml), then the combined organic layers were washed multiple times with water (50 ml), and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residual oil was purified by column chromatography (silica gel, petroleum ether 60–90°C, then petroleum ether 60–90°C/CH₂Cl₂ 10:1). ¹H NMR (CDCl₃, 200 MHz) δ = 1.11 s (9H, C(CH₃)₃), 7.04 d (1H, C(4)H ³J_{H(4)–H(3)} 3.66 Hz), 7.09 d (1H, C(3)H ³J_{H(3)–H(4)} 3.66 Hz), 7.47 d (2H, C(2')H ³J_{H(2')–H(3')} 8.58 Hz), 7.54 d (2H, C(3')H ³J_{H(3')–H(2')} 8.58 Hz); ¹³C NMR 21.11, 31.20, 123.98, 125.65, 128.63, 131.27, 132.66, 134.15, 138.25, 145.27. MS (ESI): *m/z* = 327.

5'-Bromo-5-(4''-tert-butylthiophenyl)-2,2'-bithiophene (**13**)

5-(4'-tert-Butylthiophenyl)-2,2'-bithiophene **10** (82 mg, 0.25 mmol), and *N*-bromosuccinimide (44.5 mg, 0.25 mmol) were dissolved in chloroform (10.0 ml) and acetic acid (10.0 ml). The mixture was stirred in the absence of light for 6 h. The aqueous layer was extracted with ether (30 ml), then the combined organic layers were washed multiple times with water (50 ml), and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residual oil was purified by column chromatography (silica gel, petroleum ether 60–90°C). ¹H NMR (CDCl₃, 200 MHz) δ = 1.34 s (9H, C(CH₃)₃), 6.97 d (1H, C(4)H ³J_{H(4)–H(3)} 4.02 Hz), 7.02 d (1H, C(3)H ³J_{H(3)–H(4)} 3.66 Hz), 7.12 d (1H, C(5)H ³J_{H(5)–H(4)} 5.13 Hz), 7.27 d (1H, C(3')H ³J_{H(3')–H(4')} 4.02), 7.57 s (4H, C(2'')H and C(3'')H); ¹³C NMR (50 MHz, CDCl₃) δ 31.25, 46.56, 124.06, 124.52, 124.83, 124.96, 125.65, 128.19, 128.64, 132.22, 134.62, 137.53, 138.22. MS (ESI): *m/z* = 409.

X-ray Crystallographic Study

X-ray data for **9**: C₁₄H₁₆S₂, *M* = 248.39 g mol^{−1}, orthorhombic, *P*2₁2₁2₁ (no. 19), *a* = 8.204(2), *b* = 10.846(2), *c* = 14.825(3) Å, *U* = 1319.1(5) Å³, *T* = 153 K, *Z* = 4, μ (Mo K α) = 0.374 mm^{−1}, 2554 reflections measured, 1858 unique (*R*_{int} = 0.0585) which were used in all calculations. The final *wR* (*F*²) was 0.0730 (all data). The data were measured using a Stoe Image Plate Diffraction system equipped with a ϕ circle, using Mo K α graphite monochromated

radiation (λ = 0.71073 Å) with ϕ range 0–200°, increment of 1.5°, 2 θ range from 2.0–26°, *D*_{max}–*D*_{min} = 12.45–0.81 Å^{−1}. The structure was solved by direct methods using the program SHELXS-97 [14]. The refinement and all further calculations were carried out using SHELXL-97 [15]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on *F*². Figure 1 was drawn with the ORTEP program [16].

CCDC-218223 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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