OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 400x056yip01&02

Technical Report No. 9

Synthesis of Soluble α-Thiophene Oligomers. Monomer to Octamer.

by

James M. Tour and Ruilian Wu
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

Accepted for Publication in

Macromolecules

April 25, 1992

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 25, 1992	Technical Report #9

4. TITLE AND SUBTITLE
Synthesis of Soluble a-Thiophene Oligomers. Monomer to Octamer

5. FUNDING NUMBERS
G- N00014-89-J3062
R&T 400x056yip01&01

6. AUTHOR(S)
James M. Tour and Ruilian Wu

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

8. PERFORMING ORGANIZATION REPORT NUMBER
N00014-89-J3062

9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Macromolecules

12a DISTRIBUTION AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Described is the detailed synthesis of α-thiophene oligomers ranging from the monomer to the octamer that are silylated at the α' and ω positions. The terminal trimethylsilyl groups allow the monomer, dimer, and trimer to be freely soluble in numerous organic solvents. The higher homologs, trimer through octamer have, in addition to the terminal trimethylsilyl groups, methyl groups symmetrically substituting one or more of the thiophene units in order to enhance the solubility of the systems. Methyl substitution can not be on the 3-position of terminal thiophene units or else rapid protodesilylation occurs in thiophene oligomeric intermediates greater than two units long. The UV-visible spectroscopic characteristics of the synthesized oligomers suggest that, in solution, electrochemically prepared poly(3-alkyl-α-thiophene) effectively has only 6-7 contiguous conjugated α-thiophene units. However, in the solid state, the effective conjugation path in the polymer is much longer. The effect of dπ-pπ-conjugation between the terminal silicon atom and the conjugated system was also investigated by executing the quantitative protodesilylation of the pentameric oligothiophene. The silicon groups do increase the UV absorption maxima

14. SUBJECT TERMS	15. NUMBER OF PAGES
thiophene, polythiophene, oligothiophene, conjugated oligomers optical spectra	29
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

Submitted as an Article

Synthesis of Soluble α-Thiophene Oligomers. Monomer to Octamer

James M. Tour*,[1] and Ruilian Wu
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

Abstract

Described is the detailed synthesis of α-thiophene oligomers ranging from the monomer to the octamer that are silylated at the α' and ω positions. The terminal trimethylsilyl groups allow the monomer, dimer, and trimer to be freely soluble in numerous organic solvents. The higher homologs, trimer through octamer have, in addition to the terminal trimethylsilyl groups, methyl groups symmetrically substituting one or more of the thiophene units in order to enhance the solubility of the systems. Methyl substitution can not be on the 3-position of terminal thiophene units or else rapid protodesilylation occurs in thiophene oligomeric intermediates greater than two units long. The UV properties suggest that there is little effect of the alkylated groups on the extended conjugation of the oligomers unless one of the thiophene units is dialkylated. Additionally, the spectroscopic properties suggest that electrochemically prepared poly(3-methyl-α-thiophene) must be a low defect system with little disruption in the conjugated chains.

Poly- and oligo-α-thiophene derivatives are important compounds for biological studies, electronic semiconducting materials, nonlinear optical materials, and highly ordered molecular assemblies.[2,3] Plants belonging to the family *Compositae* contain mono-, bi- and terthiophene derivatives. These compounds exhibit numerous biologically important properties.[4] For example, α-terthiophene exhibits photoenhanced activities against nematodes,[5] microorganisms,[6] algae,[7] human erythrocytes,[8] and insect eggs[9] and larvae.[10] It has also been shown to act as a skin pigmentation generator[11] and a seed germination inhibitor.[12] Larger unsubstituted thiophene oligomers exhibit poor solubility characteristics and the investigation of structure-activity relationships on higher oligomers would require more soluble derivatives.[4]

From the electronic perspective, poly-α-thiophene is an excellent semiconducting material when doped.[3] While poly-α-thiophene itself is intractable and therefore not processable, the poly(3-alkyl-α-thiophene)s are soluble and still exhibit conductivities comparable to the unsubstituted derivatives.[3,13] Alkylated thiophene oligomers could serve as useful models for understanding the alkylated polymeric systems. Recently, α-sexithiophene has been used for organic semiconductor device fabrications[14] and other unsubstituted oligomers have been studied for their electronic properties while encapsulated in zeolites.[15] Hence the oligomers exhibit many of the desirable electronic characteristics that have been evident in the polymers and soluble oligomers should find electronic applications where effective dissolution of the material is required.

Poly(3-alkyl-α-thiophene) systems show significant third order nonlinear susceptibilities ($\chi^{(3)}$). Though oligothiophenes have been studied for their third order susceptibilities, accurate third order optical nonlinearity data obtained by degenerate four-wave mixing or electric-field-induced second harmonic generation (EFISH) is difficult to reliably attain on samples with poor solubility characteristics.

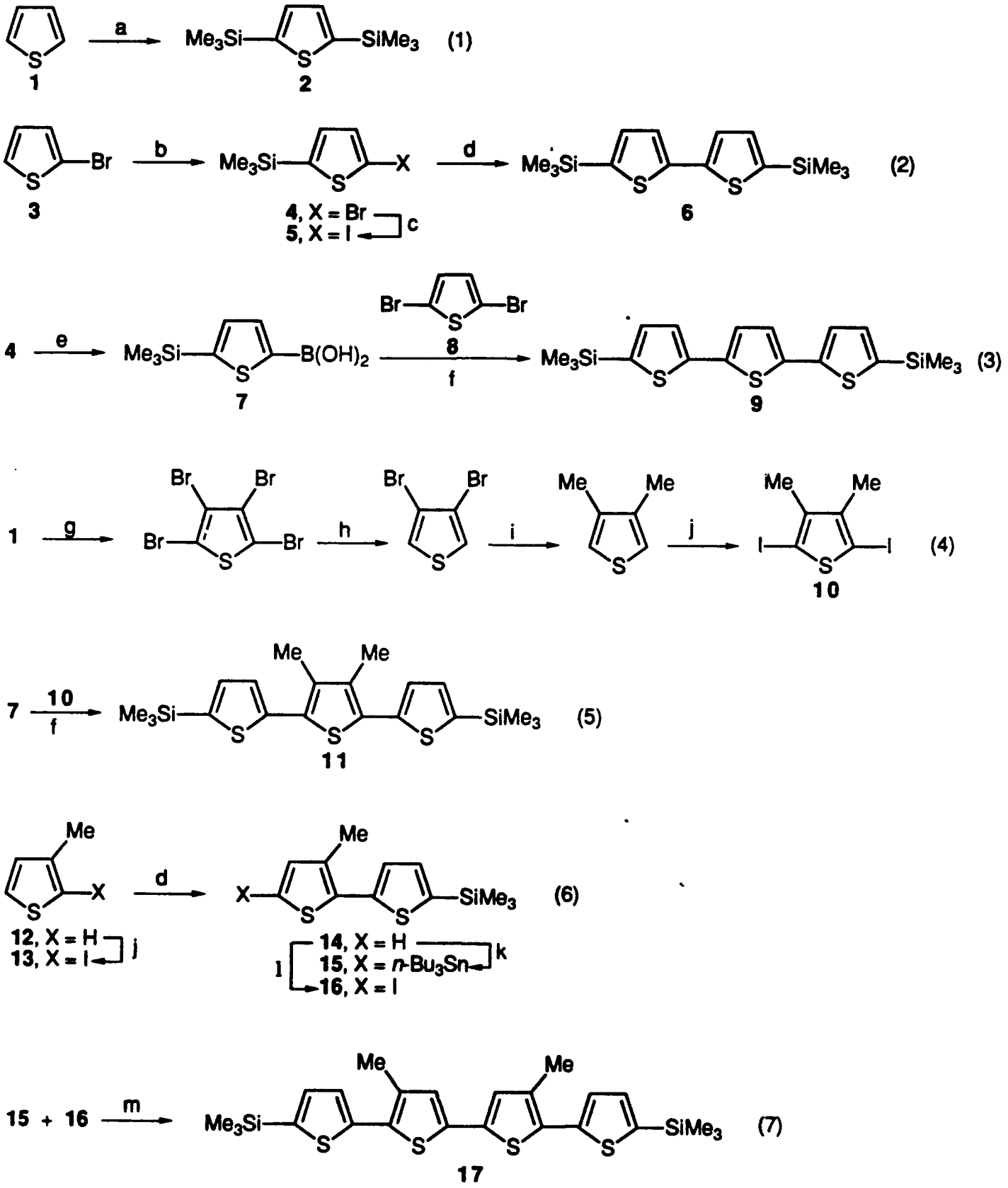
Thus routine studies on unsubstituted oligo-α-thiophenes larger than α-terthiophene can be difficult.[16]

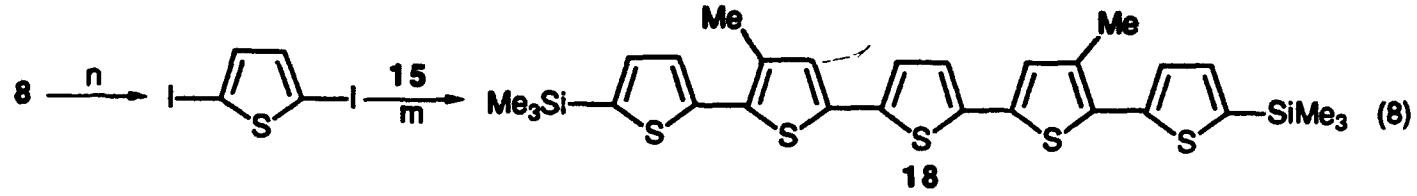
Additionally, formation of highly ordered molecular assemblies can be achieved using Langmuir-Blodgett techniques.[17] The poor solubility characteristics of unsubstituted oligo-α-thiophenes hamper the utilization of oligomers larger than three or four units. Hence, the generation of soluble oligo-α-thiophenes could have widespread applications.

Here we detail routes to soluble oligo-α-thiophenes from the monomer to the octamer. Trimethylsilyl end groups aid in the synthesis and the solubility of the final target systems. While terminal trimethylsilyl groups were affixed to the monomer, dimer, and trimer, the higher homologs, trimer through octamer have, in addition to the terminal trimethylsilyl groups, methyl groups symmetrically substituting one or more of the thiophene units in order to enhance the solubility of the systems. Since the electronic and $\chi^{(3)}$ photonic characteristics are primarily influenced by the conjugated network,[3a-h,18] methyl groups were chosen in order to minimize the electro- or photo-inactive portions of the molecules.[19] If greater solubility is needed, larger alkyl substituents at the three position of thiophenes could be used under analogous coupling conditions.

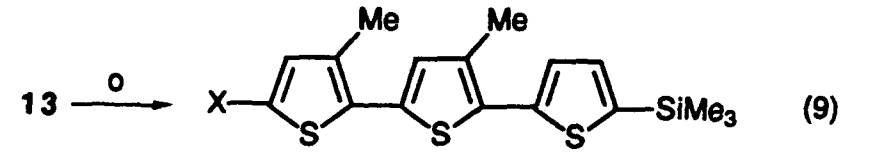
Scheme I outlines the synthetic methods for the synthesis of trimethylsilyl end capped thiophene oligomers from the monomer to the octamer. Thiophene (1) was converted directly into its dianion [*n*-BuLi (2.2 equiv), TMEDA, hexane, 23° C, 2 h] and silylated [TMSCl (2.5 equiv), 0° C to 22° C] to yield 40% of 2 (eq 1).[20] 2-Bromothiophene (3) was deprotonated [LDA (1.2 equiv), THF, -78° C to 0° C] and silylated [TMSCl (1.2 equiv), -78° C to 22° C] to afford 4 in 89% yield which was converted to the iodide 5 in 97% yield by lithium-halogen exchange [*n*-BuLi (1.0 equiv), ether, -78° C, 1 h] and iodination [I_2 (1.0 equiv), THF, -78° C to 22° C]. The dimer 6 was prepared in 56 % yield by forming the Grignard reagent of 5 [Mg (1.5

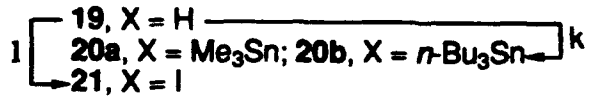
Scheme I

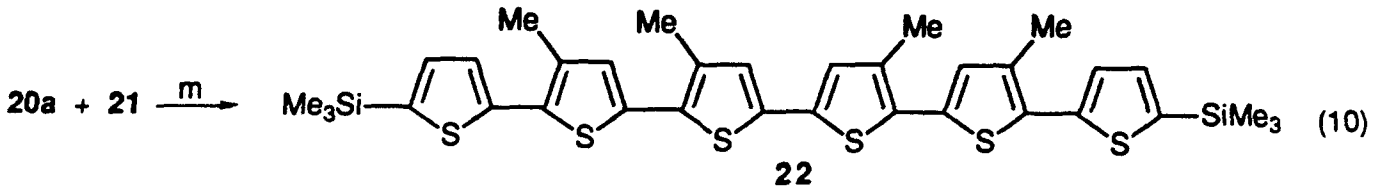

a
Me3Si
SiMe3
1
2
(1)
Br
b
X
d
3
4, X = Br
5, X = I
c
6
(2)
4
e
B(OH)2
7
8
f
9
(3)
1
g
h
i
j
Me
10
(4)
7
10
f
11
(5)
12, X = H
13, X = I
j
14, X = H
15, X = n-Bu3Sn
16, X = I
k
l
(6)
15 + 16
m
17
(7)


8
n
15
m
Me
Me
Me3Si
SiMe3
(8)

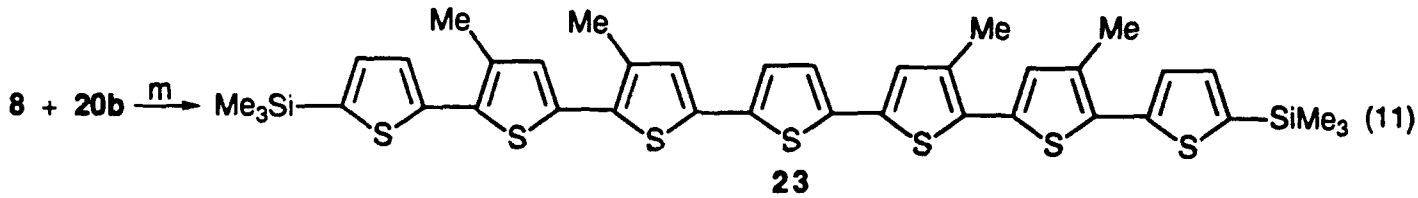
18


13
o
Me
Me
X
SiMe3
(9)

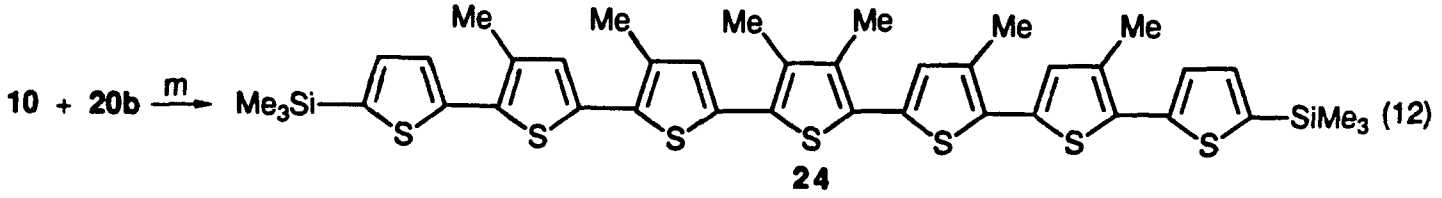

19, X = H
l
20a, X = Me3Sn; 20b, X = n-Bu3Sn
k
21, X = I


20a + 21
m
Me
Me
Me
Me
Me3Si
SiMe3
(10)

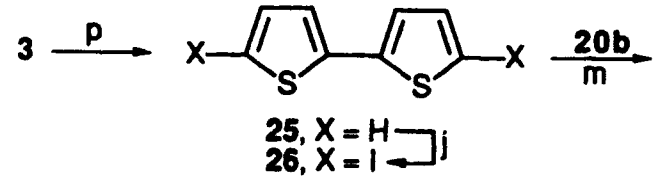
22

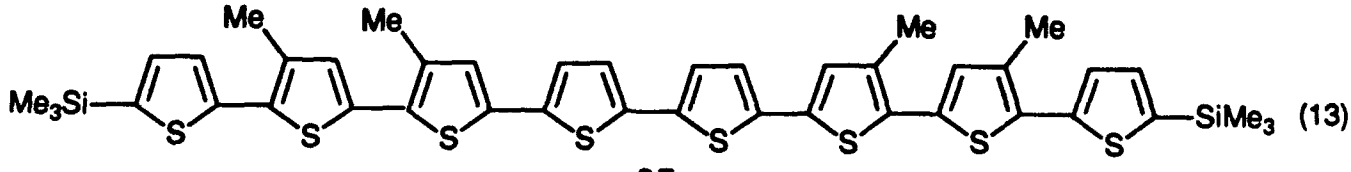

8 + 20b
m
Me
Me
Me
Me
Me3Si
SiMe3
(11)

23


10 + 20b
m
Me
Me
Me
Me
Me
Me
Me3Si
SiMe3
(12)

24


3
p
X
X
20b
m
25, X = H
26, X = I
j

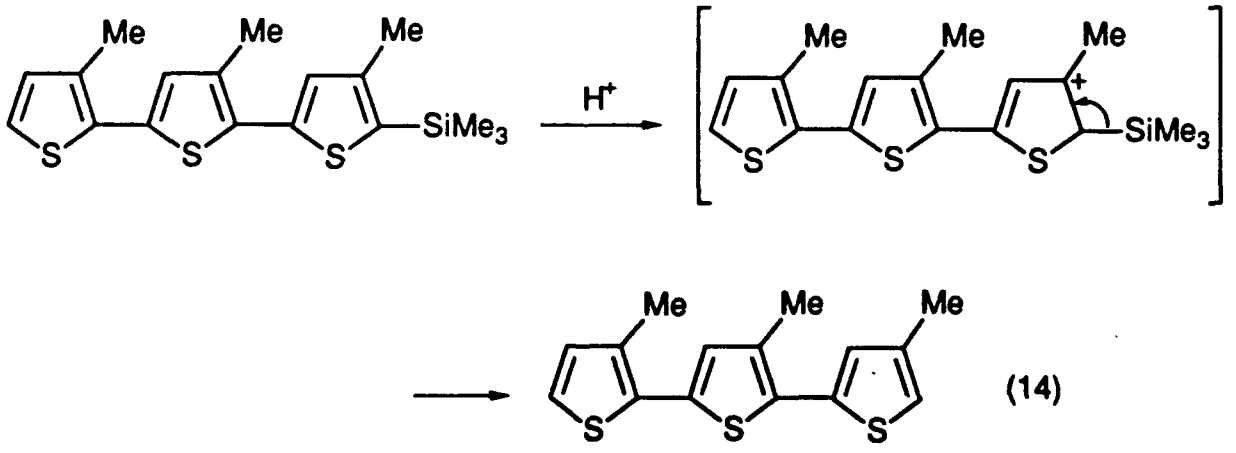

Me
Me
Me
Me
Me3Si
SiMe3
(13)

27

Scheme I con't. Reagents: (a) *n*-BuLi, TMEDA; TMSCl (b) LDA; TMSCl (c) *n*-BuLi; I_2 (d) Mg; **5**, $Cl_2Ni(dppp)$ (e) *t*-BuLi; $B(O\text{-}i\text{-}Pr)_3$; H_3O^+ (f) $Pd(PPh_3)_4$, Na_2CO_3, H_2O (g) Br_2 (h) *n*-BuLi; H_2O (i) MeMgBr, $Cl_2Ni(dppp)$ (j) HgO, I_2 (k) LDA; R_3SnCl (l) LDA; I_2 (m) $Pd(PPh_3)_4$, toluene (n) *t*-BuLi; I_2 (o) Mg; **16**, $Cl_2Ni(dppp)$ (p) Mg; **3**, $Cl_2Ni(dppp)$.

equiv), ether, 23°C to 35° C] and coupling it with a second equivalent of **5** under Ni-catalyzed conditions [$Cl_2Ni(dppp)$ (0.18 mol %), ether, 0° C to 23 °C, 18 h] (eq 2).[21] Bromide **4** was converted to the boronic acid **7** in 77 % yield by lithium halogen-exchange [*t*-BuLi (2.0 equiv), ether, -78° C, 1 h] followed by addition of triisopropylborate [$B(i\text{-}OPr)_3$ (2.0 equiv), THF, -78 °C to 22 °C] and hydrolysis of the isopropoxy groups with aqueous acid. Cross coupling of excess **7** with the dibromide **8** was accomplished under Suzuki conditions [$Pd(PPh_3)_4$ (2 mol %), 2 M Na_2CO_3 in H_2O, DME, reflux, 16 h] to afford the trimer **9** in 60 % (eq 3).[22] A dimethylated trimer could also be prepared starting from thiophene (**1**) and tetrabrominating [Br_2 (4.5 equiv), $CHCl_3$, 22° C, 12 h, 84 %] followed by selective dilithiation [n-BuLi (2 equiv), THF, -78° C] and protonation with water.[23] The 3,4-dibromothiophene thus formed was methylated[21] [MeMgBr (3 equiv), $Cl_2Ni(dppp)$ (0.6 mol %), ether, reflux, 16 h] and iodinated[24] [HgO (1.85 equiv), I_2 (2.05 equiv), C_6H_6, 0° C to 23° C, 16 h] to form **10** in 43 % yield from the tetrabromide (eq 4). The diiodide **10** was treated with excess boronic acid **7** and Pd-catalysis [$Pd(PPh_3)_4$ (2 mol %), 2 M Na_2CO_3 in H_2O, DME, reflux, 16 h] to afford the dimethyl trimer **11** in 73 % yield (eq 5).[22] 3-Methylthiophene (**12**) was converted to the iodide[24] **13** [HgO (0.93 equiv), I_2 (1.03 equiv), C_6H_6, 0° C to 23° C, 0.5 h, 94 %] and then to the corresponding Grignard reagent [Mg (1.5 equiv), ether, 23°C to 35° C] which was coupled with excess **5** [$Cl_2Ni(dppp)$ (2.27 mol %), ether, 0° C to 23 °C, 18 h] to give the dimer **14** in 70 % yield (eq 6).[21] The dimer **14** was converted to the tin reagent **15** in 96 % yield by lithiation [LDA (1 equiv), THF, -78° C, 1 h] and quenching the anion with tributyltin chloride [n-Bu_3SnCl (1 equiv), -78° C to 22° C]. The iodide **16** was similarly prepared in nearly quantitative yield by quenching the LDA-generated anion of **14** with iodine [I_2 (1 equiv), -78° C to 22° C]. Coupling the

iodide **16** with the tin reagent **15** [$Pd(PPh_3)_4$ (5 mol %), toluene, reflux, 14 h] afforded the tetramer **17** in 42 % yield (eq 7).[25] The dibromide **8** was converted to the more reactive 2,5-diiodothiophene in 61 % yield via lithium-halogen exchange [*t*-BuLi (4.0 equiv), ether, -78° C, 1 h] and iodination [I_2, (2.0 equiv), THF, -78° C to 22° C] (eq 8). Cross coupling of 2,5-diiodothiophene with excess tin reagent **15** [$Pd(PPh_3)_4$ (5 mol %), toluene, reflux, 14 h] afforded the pentamer **18** in 47 % yield (eq 8).[25] The Grignard reagent of **13** was coupled with the iodide **16** [$Cl_2Ni(dppp)$ (2.25 mol %), ether, 0° C to 23 °C, 18 h] to afford **19** in 67 % yield.[21] Interestingly, when we initially prepared an analog of **20** that had a methyl substituent α to the trimethylsilyl group, desilylation was rapid upon silica gel chromatography (even with amine-washed silica gel). Carbocationic character in the 3-position was sufficiently stabilized in the trimer (but not the monomer or dimer) by both the β-silicon and α-methyl to allow for this rapid protodesilylation (eq 14). This also occurred with the often more



(14)

resilient triethylsilyl group in place of the trimethylsilyl group. Thus one must keep the terminal thiophene unit free of an alkyl substituent if silyl retention is desired. Analogous to eq 6, **19** was lithiated [LDA (1 equiv), THF, -78° C, 1 h] and then quenched with either the chlorotrimethylstannane or chlorotri-*n*-butylstannane [R_3SnCl (1 equiv), -78° C to 22° C] to afford **20a** and **20b**, respectively, in nearly

quantitative yields. Similarly, the lithiated **19** was iodinated [I_2 (1 equiv), -78° C to 22° C] to give **21** in 66 % yield (eq 9). The tin reagent **20a** was then coupled with the iodide **21** [$Pd(PPh_3)_4$ (5 mol %), toluene, reflux, 22 h] to provide the hexamer **22** in 52 % yield (eq 10).[25] The heptamer **23** was formed in 64 % yield by coupling excess **20b** with dibromide **8** [$Pd(PPh_3)_4$ (5 mol %), toluene, reflux, 20 h] (eq 11). A second more highly substituted heptamer (**24**) was formed in 58 % yield by the reaction of excess **20b** with the previously prepared diiodide **10** [$Pd(PPh_3)_4$ (5 mol %), toluene, reflux, 20 h] (eq 12).[25] Dithiophene (**25**) was prepared by converting 2-bromothiophene (**3**) to the Grignard reagent [Mg (1.5 equiv), ether, 23°C to 35° C] and coupling it with **3** [$Cl_2Ni(dppp)$ (0.14 mol %), ether, 0° C to 23 °C, 14 h] in 99 % yield.[21] Dithiophene (**25**) was then iodinated[24] [HgO (2.0 equiv), I_2 (2.23 equiv), C_6H_6, 0° C to 23° C, 2 h] to form **26** in 78 % yield. Coupling **26** with excess **20b** [$Pd(PPh_3)_4$ (5 mol %), toluene, reflux, 20 h] afforded the octamer **27** in 52 % yield (eq 13).[25] Thus several common intermediates were used throughout the synthetic procedures. For example, the dimeric intermediate **14** was used in the synthesis of tetramer **17**, the pentamer **18**, and the trimeric intermediate **19**. In turn, **19** was used in the synthesis of the hexamer **22**, heptamers **23** and **24**, and the octamer **27**.

Oligomers **22**, **23**, **24** and **27** are acid sensitive and it is advantageous to base-washing the glassware prior to use. Though no problems were observed in the short intervals necessary for obtaining ^1H NMR and UV spectra in $CDCl_3$, ^{13}C NMR data acquisition on the octamer **27** in $CDCl_3$ over a period of 10 hours resulted in ~50 % decomposition of the material, presumable due to the reaction with traces of DCl in the solvent. Removal of the DCl from the solvent by passage through an alumina plug may be satisfactory, but we chose to obtained the ^{13}C NMR spectrum in THF with 10% acetone-d_6 for the deuterium lock signal. Generally, THF appears to be optimal for dissolution of these oligomers.

The UV data for the oligo-α-thiophenes are summarized in Table I. The values for λ_{max} increase throughout the series without an apparent saturation. By comparison to the unsubstituted derivatives, there is little, if any, disruption in the conjugation of the contiguous π-systems as a result of the methyl or trimethylsilyl substitution.[26,27] Conversely, there is a noticeable disruption in the conjugation when one of the thiophene units possesses dimethyl substituents (entries 4 and 9). This same lowering in λ_{max} has been observed in poly(3,4-dialkylthiophenes).[27] Another realization is that while the octamer (entry 10) has λ_{max} = 454 nm, electrochemically generated poly(3-methylthiophene) has a considerably larger λ_{max} value of 480 nm.[3b,28] While there has been some speculation that the effective undisturbed conjugation length in conjugated polymers may only be 5-7 monomer units long,[29] the data obtained here suggest that the electrochemically prepared polymers are indeed low defect materials with very long contiguous π-conjugated systems.

Table I

Entry	Compound	No. of thiophenes	λ_{max}(nm)[a]	ε_{max} (x 10^4)
1	**2**	1	252	0.71
2	**6**	2	320 (305)	1.30
3	**9**	3	362 (360)	2.83
4	**11**	3	346	2.97
5	**17**	4	398 (391)	3.19
6	**18**	5	416 (416)	3.79
7	**22**	6	432 (438)	3.95
8	**23**	7	446 (440)[b]	4.57
9	**24**	7	422	5.90
10	**27**	8	454	6.30

a. Obtained in chloroform solution. Numbers in parentheses are the values reported for the unsubstituted oligo-α-thiophenes in chloroform (see ref 2). b. This value for the unsubstituted derivative could not be accurately determined due to the insolubility (ref 2).

In summary, the preparation of soluble thiophene oligomers has been described. These compounds can serve as useful models for understanding the electronic properties of the polymeric systems and soluble thiophene oligomers may find useful applications for electronic, photonic and biological applications.

Experimental

General Procedures. All operations were carried out under a dry, oxygen-free, nitrogen atmosphere. Proton NMR spectra were recorded at 300 or 500 MHz on Brüker AM-300 or Brüker AM-500 spectrometers, respectively. The ^{13}C NMR spectra at 20, 75, or 125 MHz were recorded on a IBM NR-80, Brüker AM-300, or Brüker AM-500 spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm down field from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0-ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm down field from TMS. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical, Ltd., 70SQ high resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. Fast atom bombardment (FAB) mass spectra were recorded on the same instrument noted above and the isotopic ion distributions were compared with those calculated by the ISO program of VG Analytical, Ltd. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Capillary GC analyses were obtained using a Hewlett Packard Model 5890 gas chromatograph using a Hewlett Packard 3396A integrator. 2-Bromothiophene and 2,5-dibromothiophene were purchased from Aldrich Chemical Company Inc. and used without purification. 3-Bromothiophene and 3-methylthiophene were purchased from Lancaster Synthesis Ltd. and used without purification. Alkyllithiums were purchased from Aldrich Chemical Company Inc. or Lithium Corporation of America. Reagent grade diethyl ether, tetrahydrofuran (THF), and 1,4-dioxane were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane and toluene were distilled under nitrogen from CaH_2. Bulk grade hexane was distilled prior to use. Gravity column chromatography and flash chromatography was carried out on silica gel (230-400

mesh from EM Science). In all experimental procedures, unless otherwise noted, flash chromatography refers to chromatography with a nitrogen head pressure.[30]

2,5-Bis(trimethylsilyl)thiophene (2).[20] To a solution of thiophene (1) (1.68 g, 20.0 mmol) in tetramethylethanediamine (5.11 g, 44.0 mmol) was added *n*-butyllithium (15.2 mL, 44.0 mmol, 2.89 M in hexanes) at room temperature. The mixture was heated to reflux for 1 h and trimethylsilylchloride (5.43 g, 50.0 mmol) was added at room temperature and the mixture stirred for 15 min before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by distillation and the residue was distilled at 98-100°C/14 mm Hg to provide 1.82 g (40%) of the title product as colorless liquid. UV ($CHCl_3$) λ_{max} 252 nm, ε_{max} 7.1 x 10^3. IR (neat) 2957, 1490, 1406, 1249, 1202, 1010, 840, 756, 696, 631 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 0.31 (s, 18 H).

2-Bromo-5-trimethylsilylthiophene (4). To a solution of diisopropylamine (2.83 g, 3.92 mL, 28 mmol) in THF (20.0 mL) at -78°C was added dropwise *n*-butyllithium (19.8 mL, 24.0 mmol, 1.21 M in hexanes). The mixture was warmed to 0°C for 5 min and then recooled to -78°C. 2-Bromothiophene (3) (3.26 g, 1.94 mL, 20 mmol) was added dropwise and the solution was warmed to 0°C for 5 min. After recooling to -78°C, trimethylsilyl chloride (2.61 g, 3.95 mL, 24.0 mmol) was added in one portion and the solution was allowed to warm to room temperature for 30 min. The mixture was poured into water with a few drops of 3 N hydrochloric acid to remove the emulsion and the aqueous layer was extracted with ether. The organic extracts were washed with sodium bicarbonate, and brine. After drying over sodium sulfate, the solvent was removed by rotary evaporation. Flash chromatography (silica gel, hexane) afforded 4.20 g (89%) of the title product as colorless liquid. IR (neat) 2957, 1406, 1288, 1251, 1204, 1068, 1001, 956, 841, 796, 756, 697, 648 cm^{-1}. ^1H NMR

(300 MHz, $CDCl_3$) δ 7.06 (d, J = 3.49 Hz, 1 H), 6.97 (d, J = 3.49 Hz, 1 H), 0.28 (s, 9 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 143.05, 134.31, 131.11, 116.72, -0.20.

2-Iodo-5-trimethylsilylthiophene (5). To a solution of 2-bromo-5-trimethylsilylthiophene (4) (17.96 g, 76.4 mmol) in ether (100 mL) at -78°C was added dropwise *n*-butyllithium (30.81 mL, 76.4 mmol, 2.48 M in hexanes). The mixture stirred at -78°C for 1 h and iodine (19.39 g, 76.4 mmol) in ether (100 mL) was added dropwise and the mixture was allowed to warm to room temperature. The solution was poured into water and extracted with ether. The organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide 20.91 g (97%) of the title product as a pale-red liquid which was virtually pure by spectroscopic analysis and used without purification. IR (neat) 2956, 1397, 1250, 1202, 1067, 991, 841, 796, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 3.40 Hz, 1 H), 6.90 (d, J = 3.44 Hz, 1 H) 0.28 (s, 9 H).

2,5'-Bis(trimethylsilyl)-5,2'-bithiophene (6).[27] To magnesium (0.23 g, 9.46 mmol) in ether (4.0 mL) was added 2-iodo-5-trimethylsilylthiophene (5) (1.76 g, 6.25 mmol) dropwise at room temperature while an ice bath was used occasionally to maintain a mild reflux. The mixture was stirred at room temperature for 1 h and transferred to a solution of 2-iodo-5-trimethylsilylthiophene (5) (1.41 g, 5.0 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (5.0 mg, 0.009 mmol) in ether (2.5 mL) at 0°C. The mixture was allowed to warm to room temperature and stirred overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography to give 0.81 g (56%) of the title product as white crystals. UV ($CHCl_3$) λ_{max} 320 nm, ε_{max} 1.30 x 10^4. IR (KBr) 2953, 1424, 1249, 1198, 1075, 989, 873, 840, 799, 755, 639, 488 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 3.42 Hz, 2 H), 7.11 (d, J = 3.44 Hz, 2 H), 0.31 (s, 18 H).

2-Trimethylsilyl-5-thienylboronic acid (7). To a solution of *t*-butyllithium (3.53 mL, 6.0 mmol, 1.7 M in pentane) in ether (3.0 mL) was added 2-bromo-5-trimethylsilylthiophene (4) (0.706 g, 3.0 mmol) in ether (3.0 mL) at -78°C. The mixture was stirred at -78° for 1 h and transferred via cannula to a solution of triisopropylborate (1.128 g, 1.38 mL, 6.0 mmol) in THF (2.0 mL) at -78°C. The mixture was allowed to warm to room temperature and stirred for 10 min. Hydrochloric acid (5%, 2.0 mL) was added and the aqueous layer was extracted with ether. The organic extracts were washed with 1 N sodium hydroxide (4 x 10 mL). The sodium hydroxide solution was washed with ether and the aqueous solution was then acidified with 3 N hydrochloric acid and then extracted with ether. The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure to provide 0.422 g (70%) of the title product as thick liquid which was used directly for the next reaction. IR (neat) 3354, 2957, 1506, 1344, 1250, 1119, 1072, 987, 841, 756, 715, 636 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.04 (d, J = 3.3 Hz, 2 H), 7.40 (d, J = 3.3 Hz, 2 H), 0.37 (s, 9 H).

5,5"-Bis(trimethylsilyl)-2,2':5',2"-terthiophene (9). A 25 mL round bottom flask was charged with 2-trimethylsilyl-5-thienylboronic acid (7) (0.627 g, 3.13 mmol), 2,5-dibromothiophene (8) (0.303 g, 1.25 mmol), tetrakis(triphenylphosphine)palladium(0) (0.086 g, 0.075 mmol), 2 M sodium carbonate (2.0 mL) and dimethoxylethane (4.0 mL). The mixture was heated to 85-90°C (oil temp) overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography to provide 0.294 g (60%) of the title product as light-green crystals. UV ($CHCl_3$) λ_{max} 362 nm, ε_{max} 2.83 x 10^4. IR (KBr) 2953, 1431, 1247, 1200, 1070, 987, 912, 839, 795, 757, 625, 480 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 3.45 Hz, 2 H), 7.12 (d, J = 3.44 Hz, 2 H), 7.07 (s, 2 H), 0.32 (s, 18 H). ^{13}C NMR (20

MHz, $CDCl_3$) δ 142.17, 139.96, 136.28, 134.77, 124.88, 124.40, -0.12. HRMS calc'd for $C_{18}H_{24}S_3Si_2$: 392.0579. Found: 392.0571.

2,3,4,5-Tetrabromothiophene.[31] To a solution of thiophene (1) (8.42 g, 100 mmol) in chloroform (4.0 mL) was added bromine (72.0 g, 23.0 mL, 450.0 mmol) dropwise at room temperature. The reaction mixture was stirred overnight and then was heated to reflux for 2 h. A solution of potassium hydroxide (11.0 g) in 95% ethanol (60.0 mL) was then added slowly. The reaction mixture was heated to reflux for 4 h and then poured into ice water. The suspension was filtered and the filtrate was extracted with ether. The organic extracts were washed with brine, dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was dissolved in hot 95% ethanol and upon cooling, 33.66 g (84%) of the title product was obtained as colorless crystals. (MP 116-118°C)

2,5-Diiodo-3,4-dimethylthiophene (10).[24] To a solution of 2,3,4,5-tetrabromothiophene (4.00 g, 10.0 mmol) in THF (20.0 mL) was added dropwise *n*-butyllithium (9.02 mL, 22.0 mmol, 2.44 M in hexanes) at -78°C. Water was poured into the reaction mixture immediately after complete addition of the *n*-butyllithium and the aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by careful rotary evaporation. To the crude product was added [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.033 g, 0.06 mmol), THF (5.0 mL) and then methylmagnesium bromide (5.0 mL, 15.0 mmol, 3.0 M in ether). The reaction mixture was heated to 50°C (oil temp) overnight and then poured into water with a few drops of 3 N hydrochloric acid to destroy the emulsion. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by careful rotary evaporation. To the above crude product in benzene (20.0 mL) was alternately added in small portions at 0°C mercuric oxide (4.01 g, 18.5 mmol) and iodine (5.20 g, 20.5 mmol). The mixture

was allowed to warm to room temperature and stirred overnight. The reaction mixture was filtered and washed with ether. The filtrate was poured into water and the aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography (silica gel, hexane) to provide 1.55 g (43%) of the title product as a pale-red liquid which was ca. 90% pure. IR (neat) 2914, 1430, 1132, 1020, 918 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 6 H).

5,5"-Bis(trimethylsilyl)-3',4'-dimethyl-2,2':5'2"-terthiophene (11). A 25 mL round bottom flask was charged with 2-trimethylsilyl-5-thienylboronic acid (7) (0.63 g, 3.15 mmol), 2,5-diiodo-3,4-dimethylthiophene (10) (0.364 g, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (0.046 g, 0.04 mmol), 2 M sodium carbonate (2.0 mL) and dimethoxylethane (4.0 mL). The mixture was heated to 85-90°C (oil temp) overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography to provide 0.309 g (73%) of the title product as light-green crystals. UV ($CHCl_3$) λ_{max} 346 nm, ε_{max} 2.97 x 10^4. IR (KBr) 2954, 1432, 1251, 1074, 983, 841, 800, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 4 H), 2.31 (s, 6 H), 0.32 (s, 18 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 141.71, 140.42, 134.94, 134.36, 129.71, 126.98, 14.43, -0.07. HRMS calc'd for $C_{20}H_{28}S_3Si_2$: 420.0892. Found: 420.0893. Anal. calc'd for $C_{20}H_{28}S_3Si_2$: C, 57.09; H, 6.71. Found: C, 56.68; H, 6.57.

3-Iodo-2-methylthiophene (13).[24] To a solution of 3-methylthiophene (12) (9.8 g, 100 mmol) in benzene (20.0 mL) at 0°C was added (in small portions) mercuric oxide (20 g, 92.5 mmol, yellow) and iodine (26 g, 102.5 mmol). The mixture was stirred at room temperature for 0.5 h and the precipitate was filtered and washed with ether. The filtrate and washings were washed with aqueous sodium thiosulfate

and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide 21.2 g (94%) of the title product as a pale-red liquid which was virtually pure by spectroscopic analysis and used without purification. IR(neat) 2918, 1396, 1227, 967, 916, 825, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 5.4 Hz, 1 H), 6.74 (d, J = 5.4 Hz, 1 H), 2.21 (s, 3 H).

3-Methyl-2-(5'-trimethylsilylthienyl)thiophene (14). To magnesium turnings (0.82 g, 33.75 mmol) in ether (20.0 mL) was added dropwise 2-iodo-3-methylthiophene (13) (5.04 g, 22.5 mmol) at 0°C. The mixture stirred for 2 h at room temperature and was transferred to a solution of 2-iodo-5-trimethylsilylthiophene (5) (4.26 g, 15.0 mmol), and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.183 g, 0.34 mmol) in ether (10.0 mL) at 0°C and the mixture stirred at room temperature overnight. The mixture was poured into water and filtered through Celite. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by gravity chromatography on silica gel (hexane) to provide 2.67 g (70%) of the title produci as a yellow liquid. IR (neat) 2955, 1443, 1250, 1071, 990, 840, 756, 707 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (ABq, J = 3.46 Hz, Δv = 4.24 Hz, 2 H), 7.11 (d, J = 5.1 Hz, 1 H), 6.86 (d, J = 5.1 Hz, 1 H), 2.39 (s, 3 H), 0.33 (s, 9 H).

3-Methyl-5-tri-*n*-butylstannyl-5'-trimethylsilyl-2,2'-bithiophene (15). To a solution of diisopropylamine (0.369 g, 0.511 mL, 3.65 mmol) in THF (5.0 mL) was added *n*-butyllithium (1.47 mL, 3.65 mmol, 2.48 M in hexanes) at -78°C and the mixture was warmed to 0°C for 5 min and recooled to -78°C. 3-Methyl-2-(5'-trimethylsilylthienyl)thiophene (14) (0.92 g, 3.65 mmol) in THF (5.0 mL) was added dropwise via cannula and the mixture stirred at -78°C for 1 h before adding tributyltin chloride (1.19 g, 0.99 mL, 3.65 mmol) and the mixture was allowed to warm to room temperature for 20 min. The mixture was poured into water and the aqueous

layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed in vacuo to provide 1.90 g (96%) of the title product as a light-yellow thick liquid which was > 95% pure by spectroscopic analysis. IR (neat) 2957, 1464, 1250, 1073, 991, 840, 799, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (AB_q, J = 0.90 Hz, Δν = 1.0 Hz, 2 H), 6.89 (s, 1 H), 2.40 (s, 3 H), 1.70-1.50 (pent, J = 8.0 Hz, 6 H), 11.40-1.25 (sext, J = 7.32 Hz, 6 H), 1.11-1.05 (t, J = 8.10 Hz, 6 H), 0.91-0.86 (t, J = 7.27 Hz, 9 H), 0.31 (s, 9 H).

5-Iodo-3-methyl-2-(5'-trimethylsilylthienyl)thiophene (16). To a solution of diisopropylamine (0.401 g, 0.56 mL, 3.96 mmol) in THF (5.0 mL) was added dropwise *n*-butyllithium (1.60 mL, 3.96 mmol, 2.48 M in hexanes) at -78°C . The mixture was warmed to 0°C for 5 min and then recooled to -78°C. 3-Methyl-2-(5'-trimethylsilylthienyl)thiophene (**14**) (1.00 g, 3.96 mmol) in THF (50 mL) was added dropwise and the solution stirred at -78°C for 1 h. Iodine (1.01 g, 3.96 mmol) in THF (5.0 mL) was added dropwise and the solution was allowed to warm to room temperature for 30 min. The mixture was poured into water and the aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and the residue was virtually pure by spectroscopic analysis and used without purification. ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, J = 3.47 Hz, 1 H), 7.11 (d, J = 3.42 Hz, 1 H), 7.01 (s, 1 H), 2.34 (s, 3 H), 0.32 (s, 9 H).

5,5'''-Bis(trimethylsilyl)-2,2':5',2'':5'',2'''-quaterthiophene (17). A flask was charged with **15** (0.541 g, 1.0 mmol), **16** (0.378 g, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (0.035 g, 0.03 mmol) and toluene (2.0 mL). The mixture was heated to 100-105°C (oil temp) overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography to provide

0.209 g (42%) of the title product as yellow-orange crystals. UV ($CHCl_3$) λ_{max} 398 nm, ε_{max} 3.19 x 10^4. IR (KBr) 1438, 990, 843, 795 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (AB_q, J = 2.0 Hz, Δν = 4.0 Hz, 4 H), 6.92 (s, 2 H), 2.37 (s, 6 H), 0.33 (s, 18 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 141.56, 140.33, 134.51, 134.41, 134.31, 130.29, 127.76, 126.50, 15.64, -0.08. MS calc'd for $C_{24}H_{30}S_4Si_2$: [M^+]: 502, [M^+-CH_3]: 487. Found: [M^+]: 502, [M^+-CH_3]: 487.

2,5-Diiodothiophene.[32] To a solution of *t*-butyllithium (23.5 mL, 40.0 mmol, 1.7 M in pentane) in ether (40.0 mL) was added 2,5-dibromothiophene (8) (2.42 g, 10.0 mmol) dropwise at -78°C. The mixture was stirred at -78°C for 0.5 h and iodine (5.08 g, 20.0 mmol) in THF (15.0 mL) was added via cannula. The mixture was allowed to warm to room temperature for 1 h and poured into water. The aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by recrystallization from 95% ethanol to provided 2.04 g (61%) of the title product as off-white crystals. IR (KBr) 1388, 950, 784, 458 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2 H).

5,5''''-Bis(trimethylsilyl)-3',4'''-dimethyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (18). An oven-dried test tube (washed with ammonium hydroxide) was charged with 15 (0.609 g, 1.125 mmol), 2,5-diiodothiophene (0.084 g, 0.25 mmol), tetrakis(triphenylphosphine)palladium(0) (0.012 g, 0.01 mmol) and toluene (1.0 mL). The mixture was slowly heated to 50°C for 1 h followed by 80°C for 2 h and the 100-105°C (oil temp) overnight before being poured into water. The aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography (silica gel, hexane) to provide 0.069 g (47%) of the title product as an orange solid. UV ($CHCl_3$) λ_{max} 416 nm, ε_{max} 3.79 x 10^4. IR (neat) 1250, 991, 836 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (ABq, J = 3.5 Hz, Δν = 6.6 Hz, 4 H), 7.03 (s, 2 H), 6.95 (s, 2 H), 2.38 (s, 6 H), 0.33 (s, 18

H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 141.49, 140.36, 135.89, 134.51, 134.42, 134.25, 130.45, 127.86, 126.53, 124.15, 15.64, -0.08. Anal. Calc'd for $C_{28}H_{32}S_5Si_2$: C, 57.49; H, 5.51. Found: C, 56.89; H, 5.47.

3',3''-Dimethyl-2-trimethylsilyl-5,2':5',2''-terthiophene (19). To a solution of **16** prepared as described above and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.054 g, 0.1 mmol) in ether (5.0 mL) was added the Grignard reagent made from 2-iodo-3-methylthiophene (**13**) (1.49 g, 6.66 mmol) dropwise at 0°C and the mixture was allowed to warm to room temperature overnight. The mixture was poured into water and filtered through Celite. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by gravity chromatography on silica gel (hexane) to provide 1.04 g (67%) of the title product as a thick light-green liquid. IR (neat) 2954, 1448, 1250, 1075, 991, 840, 756, 707 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (AB_q, J = 3.46 Hz, Δν = 7.30 Hz, 2 H), 7.11 (d, J = 5.13 Hz, 1 H), 6.91 (s, 1 H), 6.86 (d, J = 5.13 Hz, 1 H), 2.40 (s, 3 H), 2.39 (s, 3 H), 0.33 (s, 9 H).

3,4'-Dimethyl-5''-trimethylsilyl-5-trimethylstannyl-2,2':5',2"-terthiophene (20a). To a solution of diisopropylamine (0.653 g, 0.90 mL, 6.65 mmol) in THF (10.0 mL) was added dropwise at -78°C *n*-butyllithium (5.5 mL, 6.65 mmol, 1.21 M in hexanes). The mixture was warmed to 0°C for 10 min and then recooled to -78°C. 3',3"-Dimethyl-2-trimethylsilyl-5,2':5',2"-terthiophene (**19**) (2.25 g, 6.65 mmol) in THF (6.0 mL) was added dropwise via cannula. The mixture was stirred at -78°C for 2 h and trimethyltin chloride (1.33 g, 6.65 mmol) in THF (6.0 mL) was added via cannula. The mixture was warmed to room temperature for 0.5 h and poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by reduced pressure to provide 3.1 g (96%) of the title product as a thick

dark-yellow oil. IR (neat) 2955, 1429, 1250, 1074, 991, 840, 757 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$) δ 7.17 (AB_q, J = 3.6 Hz, Δν = 6.9 Hz, 2 H), 6.93 (s, 1 H), 6.90 (s, 1 H), 2.40 (s, 3 H), 2.39 (s, 3 H), 0.36 (s, 9 H), 0.32 (s, 9 H).

3,4'-Dimethyl-5-tri-*n*-butylstannyl-5''-trimethylsilyl-2,2':5',2''-terthiophene (20b). To a solution of diisopropylamine (0.65 g, 0.90 mL, 6.43 mmol) in THF (10.0 mL) was added dropwise at -78°C *n*-butyllithium (3.92 mL, 6.43 mmol, 1.64 M in hexanes). The mixture was warmed to 0°C for 10 min and then recooled to -78°C. 3',3''-Dimethyl-2-trimethylsilyl-5,2':5',2''-terthiophene **(19)** (2.24 g, 6.43 mmol) in THF (6.0 mL) was added dropwise via cannula. The mixture was stirred at -78°C for 2 h and tributyltin chloride (2.09 g, 1.74 mL, 6.65 mmol) was added dropwise. The mixture was warmed to room temperature for 0.5 h and poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by reduced pressure to provide 3.98 g (97%) of the title product as a thick dark-yellow oil which is >95% pure by spectroscopic analysis. IR (neat) 2956, 1459, 1250, 1073, 992, 840, 756 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$) δ 7.17 (ABq, J = 3.0 Hz, Δν = 6.0 Hz, 2 H), 6.91 (s, 1 H), 6.89 (s, 1 H), 2.41 (s, 3 H), 2.39 (s, 3 H), 1.55 (m, 6 H), 1.34 (sext, J = 7.28 Hz, 6 H), 1.09 (m, 6 H), 0.89 (t, J = 7.28 Hz, 9 H), 0.32 (s, 9 H).

5-Iodo-3,4'-dimethyl-5''-trimethylsilyl-2,2':5',2''-terthiophene (21). To a solution of diisopropylamine (0.203 g, 0.28 mL, 2.01 mmol) in THF (2.0 mL) was added dropwise *n*-butyllithium (0.82 mL, 2.01 mmol, 2.44 M in hexanes) at -78°C. The mixture was warmed to 0°C for 5 min and recooled to -78°C. To the above solution was added **19** (0.70 g, 2.01 mmol) in THF (2.0 mL) dropwise via cannula and the mixture stirred at -78°C for 1 h before iodine (0.635 g, 2.50 mmol) in THF (4.0 mL) was added via cannula. The reaction mixture was allowed to warm to room temperature for 20 min and poured into water. The aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The

solvent was removed by rotary evaporation and the residue was purified by flash chromatography (silica gel, hexane) to provide 0.616 g (66%) of the title product as a light-green liquid which was ca. 90% pure by spectroscopic analysis. IR (neat) 2953, 1446, 1378, 1249, 1074, 991, 839, 799, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (ABq, J = 3.0 Hz, Δν= 6.0 Hz, 2 H), 7.00 (s, 1 H), 6.84 (s, 1 H), 2.38 (s, 3 H), 2.35 (s, 3 H), 0.32 (s, 9 H).

5,5'''''-Bis(trimethylsilyl)-3',3'',4''',4''''-tetramethyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''-sexithiophene (22). A 25 mL round bottom flask was charged with **20a** (0.213 g, 0.44 mmol), **21** (0.103 g, 0.22 mmol), tetrakis(triphenylphosphine)palladium(0) (0.005 g, 0.0044 mmol) and toluene (1.0 mL). The mixture was heated at 100-105°C (oil temp) overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by gravity chromatography to provide 0.079 g (52%) of the title product as orange-red crystals. UV ($CHCl_3$) λ_{max} 432 nm, ε_{max} 3.95 x 10^4. IR(KBr) 1459, 1239, 992, 838 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (AB_q, J = 3.47 Hz, Δν = 8.23 Hz, 4 H), 6.92 (s, 2 H), 6.91 (s, 2 H), 2.40 (s, 6 H), 2.38 (s, 6 H), 0.33 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.88, 140.72, 135.03, 134.85, 134.57, 134.51, 134.15, 131.47, 130.44, 129.80, 128.30, 126.87, 16.15, 16.02, 0.34.

5,5'''''-Bis(trimethylsilyl)-3',3'',4''',4''''-tetramethyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''-septithiophene (23). An oven-dried test tube was charged with 2,5-dibromothiophene (0.142 g, 0.59 mmol), **20b** (1.13 g, 1.75 mmol), tetrakis(triphenylphosphine)palladium(0) (0.068 g, 0.059 mmol) and toluene (4.00 mL). The mixture was heated to 100°C overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was washed with hexane several times before drying under reduced pressure to provide 0.295 g (64%) of the title

compound as dark red crystals. Mp 181-183°C. UV ($CHCl_3$) λ_{max} 446 nm, ε_{max} 4.57 x 10^4. IR (KBr) 1438, 1250, 992, 839 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.20 (AB_q, J = 3.46 Hz, Δν = 8.41 Hz, 4 H), 7.03 (s, 2 H), 6.94 (s, 2 H), 6.93 (s, 2 H), 2.40 (s, 6 H), 2.39 (s, 6 H), 0.33 (s, 18 H). ^{13}C NMR(125 MHz, $CDCl_3$) δ 141.86, 140.74, 136.27, 135.04, 134.85, 134.58, 134.49, 134.07, 131.53, 130.58, 129.85, 128.40, 126.88, 124.63, 16.15, 16.02, 0.34.

5,5''''''-Bis(trimethylsilyl)-3',3'',3''',4''',4'''',4''''''-hexamethyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2''''''-septithiophene (24). In an oven-dried test tube (washed with ammonium hydroxide) was charged with **20b** (0.57 g, 0.9 mmol), 3,4-diiodo-2,5-dimethylthiophene (**10**) (0.072 g, 0.2 mmol), tetrakis(triphenylphosphine)palladium(0) (0.0093 g, 0.008 mmol) and toluene (1.0 mL). The mixture was slowly heated to 80-85°C (oil temp) overnight followed by heating to 100-105°C (oil temp) for 10 h. To the reaction mixture was added 95% ethanol (10 mL) and the liquid was removed by decantation. This process was repeated two more times. The residue was then filtered through filter paper and washed with hexane. The solvent was removed in vacuo to provide 0.094 g (58%) of the title product as a red solid. UV ($CHCl_3$) λ_{max} 422 nm, ε_{max} 5.90 x 10^4. IR (KBr) 1250, 992, 940 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (AB_q, *J* = 3.0 Hz, Δν = 8.5 Hz, 4 H), 6.94 (s, 2 H), 6.91 (s, 2 H), 2.41 (s, 6 H), 2.40 (s, 6 H), 2.30 (s, 6 H), 0.33 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.92, 140.68, 135.67, 134.84, 134.63, 134.56, 134.10, 134.07, 131.45, 131.32, 130.44, 129.80, 129.74, 126.83, 16.10, 16.02, 14.92, 0.32. MS calc'd for $C_{40}H_{44}S_7Si_2$ [M^+]: 804. Found [M^+]: 804.

2,2'-Bithiophene (25).[21] A procedure analogous to that of Kumada and co-workers was used as follows. To magnesium turnings (0.912 g, 37.5 mmol) in ether (15.0 mL) was added about 0.5 mL of 2-bromothiophene (3) (4.076 g, 2.42 mL, 25 mmol). An exothermic reaction occurred in a few minutes and the remaining bromide was added dropwise with an ice bath used occasionally to maintain a mild reflux. After the addition, the resulting mixture was heated to reflux for 30 min and

cooled to room temperature. To a solution of 2-bromothiophene (3) (3.26 g, 1.94 mL, 20 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (15 mg) in ether (10.0 mL) was added dropwise via cannula the above Grignard reagent at 0°C. The resulting mixture was heated to reflux for 4 h and poured into water with a few drops of 3 N hydrochloric acid to remove the emulsion. The aqueous layer was extracted with ether and the organic extracts were washed with sodium bicarbonate, brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography on silica gel (hexane) to afford 3.32 g (99.8%) of the title product as a colorless liquid. IR (neat) 3064, 1794, 1649, 1500, 1416, 1238, 1208, 1078, 1051, 856, 817, 704 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.20 (dd, J = 5.1, 1.2 Hz, 2 H), 7.17 (dd, J = 3.6, 1.2 Hz, 2 H), 7.01 (dd, J = 5.1, 3.6 Hz, 2 H).

2,5'-Diiodo-5,2'-bithiophene (26).[33] To a solution of bithiophene (25) (1.48 g, 8.88 mmol) in benzene (4.0 mL) was added alternately in small portion at 0°C mercuric oxide (3.85 g, 17.77 mmol) and iodine (4.51 g, 17.77 mmol). The reaction mixture was then allowed to warm to room temperature and stirred overnight. An additional portion of iodine (0.51 g, 2.01 mmol) was added at room temperature and the mixture stirred at room temperature overnight. The reaction mixture was dissolved in chloroform and washed with saturated potassium iodide (3x20 mL) followed by sodium thiosulfate (3x20 mL). The organic layer was then washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was recrystallized from a mixture of chloroform and 95% ethanol to provide 2.90 g (78%) of the title product as off-grey flakes. IR (KBr) 1410, 864, 789 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, J = 3.79 Hz, 2 H), 6.76 (d, J = 3.77 Hz, 2 H).

5,5'''''''-Bis(trimethylsilyl)-3'3'',4''''',4'''''''-tetramethyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5'''''''-octithiophene (27). In an oven-dried test tube (washed with ammonium hydroxide) was charged with **20b** (0.73 g, 1.35 mmol), 2,5'-Diiodo-5,2'-bithiophene (26) (0.084 g, 0.2 mmol),

tetrakis(triphenylphosphine)palladium(0) (0.0093 g, 0.008 mmol) and toluene (1.0 mL). The mixture was heated slowly to 50°C for 1 h and 80°C for 2 h and then 100-105°C (oil temp) overnight before being poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and the residue was purified by gravity column chromatography on silica gel (hexane) to provide 0.089 g (52%) of the title product as a bright-red solid. UV ($CHCl_3$) λ_{max} 454 nm, ε_{max} 6.30 x 10^4. IR (KBr) 1438, 1292, 992, 839 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (AB_q, J = 3.47 Hz, $\Delta\nu$ = 8.12 Hz, 4 H), 7.04 (m, 4 H), 6.94 (br s, 2 H), 6.93 (br s, 2 H), 2.40 (s, 6 H), 2.39 (s, 6 H), 0.33 (s, 18 H). ^{13}C NMR (75 MHz, 10% acetone-d_6 + 90% THF) δ 142.15, 140.74, 136.76, 136.58, 135.66, 135.55, 135.12, 134.77, 134.40, 131.85, 130.92, 130.33, 129.02, 127.38, 125.38, 125.24, 15.75, 15.60, -.11. (There is a smaller peak at 128.96 that we attributing to an impurity). FAB/MS (NBA) calc'd relative isotopic intensities for $C_{80}H_{84}S_{14}Si_5$ (M+): 858 (100%), 859 (64%), 860 (62%), 861 (31%), 862 (17%), 863 (7%), 864 (3%). Found: 858 (100%), 859 (78%), 860 (71%), 861 (39%), 862 (23%), 863 (10%), 864 (5%).

Acknowledgements

This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), and the National Science Foundation (RII-8922165).

References and Notes

(1) Recipient of an Office of Naval Research, Young Investigator Award (1989-92) and National Science Foundation Presidential Young Investigator Award (1991-96).

(2) For a review on unsubstituted oligothiophene syntheses, see: Nakayama, J.; Konishi, T.; Hoshino, M. *Heterocycles* **1988**, *27*, 1731.

(3) For some recent works covering polythiophene and other related conjugated polymers, see: (a) Chandler, G. K.; Pletcher, D. *Electrochem.* **1985**, *10*, 117. (b) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (c) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76. (d) Adamcova, Z.; Dempirova, L. *Prog. Org. Coat.* **1989**, *16*, 295. (e) Diaz, A. F.; Lacroix, J. C. *New J. Chem.* **1988**, *12*, 171. (f) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183. (g) Heinze, J. *Topics in Current Chemistry*; vol 152, Springer: Berlin 1990. (h) Roncali, J.; Garreau, R.; Delaboglise, D.; Garnier, F.; Lemaire, M. *Makromol. Chem., Macromol. Symp.* **1988**, *20-21*, 601. (i) Maior, R. M. S.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268. (j) Ueda, M.; Miyaji, Y.; Ito, T.; Oba, Y.; Sone, T. *Macromolecules* **1991**, *24*, 2694. (k) Ikenoue, Y.; Saida, Y.; Kira, M.-a.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc. Chem. Commun.* **1990**, 1694.

(4) Kagan, J.; Arora, S. K. *J. Org. Chem.* **1983**, *48*, 4317.

(5) Gommers, F. J. *Nematologica* **1972**, *18*, 458.

(6) (a) Downum, K. R.; Hancock, R. E. W.; Towers, G. H. N. *Photochem. Photobiol.* **1982**, *36*, 517. (b) Kagan, J.; Gabriel, R.; Reed, S. A. *Photochem. Photobiol.* **1980**, *31*, 465. (c) Chan, G. F. Q.; Towers, G. H. N.; Mitchell, J. C. *Phytochemistry* **1975**, *14*, 2295. (d) Kagan, J.; Gabriel, R. *Experientia* **1980**, *36*, 587.

(7) Arnason, T.; Stein, J. R.; Graham, E.; Wat, C.-K.; Towers, G. H. N.; Lam, J. *Can. J. Bot.* **1981**, *59*, 54.

(8) Wat, C.-K.; MacRae, W. D.; Yamamoto, E.; Towers, G. H. N .; Lam, J. *Photochem. Photobiol.* **1980**, *32*, 167.

(9) Kagan, J. Chan, G. *Experientia* **1983**, *39*, 402.

(10) (a) Wat, C.-K.; Prasad, S. K.; Graham, E. A.; Partington, S.; Arnason, T.; Towers, G. H. N. Lam, J. *Biochem. Syst. Ecol.* **1981**, *9*, 59. (b) Arnason, T.; Swain, T.; Wat, C.-K.; Graham, E. A.; Partington, S.; Towers, G. H. N.; Lam, J. *J. Biochem. Syst. Ecol.*

1981, *9*, 63. (c) Kagan, J.; Beny, J. P.; Chan, G.; Dhawan, S. N.; Jaworski, J. A.; Kagan, E. D.; Kassner, P. D.; Murphy, M.; Rogers, J A. *Insect Sci. Its Appl.* **1983**, *4*, 377.

(11) Towers, G. H. N.; Arnason, T.; Wat, C.-K.; Graham, E. A.; Lam, J.; Mitchell, J. C. *Contact Dermatitis* **1979**, *5*, 140.

(12) Campbell, G.; Lambert, J. D. H.; Arnason, T.; Towers, G. H. N. *J. Chem. Ecol.* **1982**, *8*, 961.

(13) The polymerization of α-terthiophene affords polythiophene that is more conductive and more crystalline than polythiophene generated from thiophene itself. This suggests that a more regularly connected polymer (or lower defect systems) can be formed by this method. Though no study has been carried out using pre-formed oligo(3-alkyl-α-thiophenes) to afford tractable poly(3-alkyl-α-thiophene) materials, there is the expectation that the polymerization of the well-defined oligomers would afford tractable materials that are more highly conducting than the polymers generated by the polymerization of the 3-substituted monomers. See, Yumoto, Y.; Yoshimura, S. *Synth. Met.* **1986**, *13*, 185.

(14) (a) Xu, B.; Fichou, D.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1991**, *3*, 150. (b) Garnier, F.; Horowitz, G.; Peng, X.; Fichou, D. *Adv. Mater.* **1990**, *2*, 592.

(15) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

(16) (a) Zhao, M.-T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535. (b) Fichou, D.; Garnier, F.; Charra, F.; Kajzar, F.; Messier, J. *Spec. Publ.-R. Soc. Chem.* **1989**, *69*, 176. (c) A report of third order nonlinear optical data obtained on alkylated oligo-α-thiophenes has recently appeared but no synthetic procedures were described. Thienpont, H.; Rikken, G. L. J. A.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Phys. Rev. Lett.* **1990**, *65*, 2141.

(17) (a) Royappa, A. T.; Rubner, M. F. *Polym. Prepr.* **1991**, *32*, 196. (b) Rikukawa, M.; Rubner, M. F. *Polym. Prepr.* **1991**, *32*, 234.

(18) (a) Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O.; Garito, A. F. *Phys Rev. B.* **1988**, *38*, 1573. (b) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91* 2696. (c) de Melo, C. P.; Silbey, R. *Chem. Phys. Lett.* **1987**, *140*, 537. (d) Papadopoulos, M. G.;Waite, J.; Nicolaides, C. A. *J. Chem. Phys.* **1982**, *77*, 2527.

(19) From the biological perspective, the important structural features of oligothiophenes for are more elusive. The oligomers probably interact with DNA and the heteroatomic arrangement, planarity of the systems, redox and photochemical properties may be significant. (a) *Chemistry and Physics of DNA-Ligand Interactions*, Kallenbach, N. R., Ed.; Adenine: New York, 1990. (b) *Bioorganic Chemistry, A Chemical Approach to Enzyme Action*, Springer: New York, 1989.

(20) Brandsma, L.; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry* ; vol 1, Springer: Berlin, 1987.

(21) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.

(22) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Fu, J.-m., Sharp, M. J.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 5463.

(23) Kobayashi, K. *Chem. Lett.* **1985**, 1423.

(24) Uhlenbroek, J. H.; Bijloo, J. D. *Rec. Trav. Chim.* **1960**, *79*, 1181.

(25) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

(26) Leclerc, M.; Daoust, G. *J. Chem. Soc., Chem. Commun.* **1990**, 273.

(27) Lamaire, M.; Büchner, W.; Garreau, R.; Hoa, H. A.; Guy, A.; Roncali, J. *J. Electroanal. Chem.* **1990**, *281*, 293.

(28) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Solid State Commun.* **1983**, *46*, 389.

(29) (a) Kanatzidis, M. G. *Chem. Enginer. News* December 3 1990, 36. (b) Reynolds, J. R. *Chemtech* **1988**, *18*, 440.

(30) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923

(31) Janda, M.; Srogl, J.; Stibor, I.; Nemec, M.; Vopatra, P. *Synthesis* **1972**, 545.

(32) Minnis, W. *Org. Synth.* Coll. Vol 2, 357.

(33) Curtis, R. F.; Philips, G. T. *J. Chem. Soc.* **1965**, 5134.