Synthesis and Electronic Properties of Aldehyde End-Capped Thiophene Oligomers and Other α,ω-Substituted Sexithiophenes

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Received March 12, 1996. Revised Manuscript Received July 15, 1996[⊗]

A series of α,ω-aldehyde end-capped oligomers of thiophene with three, four, five, six, and eight thiophene units have been synthesized using the palladium-catalyzed Stille's coupling reactions. The UV−vis spectral data indicate that these aldehyde end-capped oligomers have longer conjugation lengths as evidenced by the higher λ_{max} values than the corresponding unsubstituted oligothiophenes. The λ_{max} value increases as the number of thiophene units is increased. The intrinsic conductivity of the solution-cast films of the aldehyde end-capped oligothiophenes is generally higher than that of their corresponding unsubstituted counterparts. Other α,ω-substituted sexithiophenes, such as *n*-dodecanoyl, *tert*-butyldimethylsilyl, hydroxymethyl, and [(*n*-butoxyethoxy)ethoxy]methyl sexithiophenes, have also been synthesized. α,ω-Bis([(*n*-butoxyethoxy)ethoxy]methyl)sexithiophene has a remarkably high solubility in chloroform (1.8 g/L) and a conductivity (1×10^{-6} S/cm) comparable to the unsubstituted sexithiophene.

Introduction

Polythiophenes have received considerable attention because of their fascinating electronic and optical properties.[1] Recently, however, the center of attention has been focused more and more on well-defined thiophene oligomers. Given enough conjugation length, the oligomers such as the hexamer of thiophene inherently possess the basic or much improved electronic and optical properties of polythiophenes.[2] With defect-free chemical structures, oligothiophenes serve as model compounds for the intractable polythiophenes and enable a better study of structure−property relationship to achieve fine-tuning of electronic or optical properties by simple modification of their chemical structures. In addition, processibility of the oligomers is generally better than the polymers with the same repeating unit structures, which is particularly important in terms of practical applications. In fact, oligothiophenes have been used as active materials in electronic devices such as field-effect transistors (FET)[3] and light-emitting diodes.[4] For example, α-sexithiophene was found to have a significantly better performance than polythiophene in the FET applications.[2a,3a,b] α-Octithiophene was reported to be a good photoactive component in a photovaltaic cell.[5]

Synthesis and study of unsubstituted thiophene oligomers as well as α- or β-substituted thiophene oligomers have been carried out by many research groups. For the unsubstituted oligothiophenes,[6] the virtual insolubility above hexamer made the search for soluble thiophene oligomers necessary. Much work has been done in β-alkyl substitution since it gave more soluble oligomers that can be thoroughly characterized and readily processed. β-Alkyl-substituted oligomers up to dodecimer have been synthesized.[7] However, because the steric hindrance caused by β-substitution in the internal rings prevents the backbone of thiophene units from full conjugation,[7i] the β-alkyl substituted oligomers often have diminished electronic properties.[7d,g]

In comparison with the β-substitutions, α,ω-substitution should have the advantage of preserving the conjugation and, therefore, the electronic properties of

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

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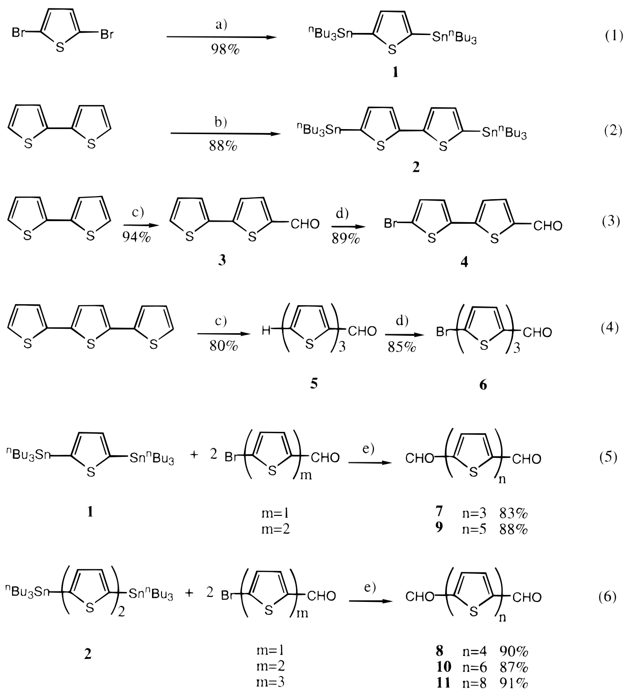
S0897-4756(96)00182-2 CCC: $12.00

oligomers.[8] Indeed, while field-effect mobility of β,β'-dihexylsexithiophene is below detection limit, α,ω-dihexylsexithiophene has comparable or better conductivity and charge-carrier mobility than sexithiophene.[8c] But α,ω-substituted oligothiophenes are still hampered by their poor solubility which makes them difficult to be purified or processed.[8] Perhaps that is why reports on the syntheses of α,ω-end-capped sexithiophenes or higher oligomers (without pendant β-substitution) are few and easily enumerated. Garnier et al. synthesized both α,ω-bis(triisopropylsilyl)sexithiophene[8b] and α,ω-dihexylsexithiophene[8c] by $CuCl_2$-mediated oxidative coupling of α-substituted terthiophene anions. α,ω-Bis(triisopropylsilyl)sexithiophene has by far the best solubility ever reported for the α,ω-sexithiophenes, and it can be chromatographed and gives a good ^1H NMR spectrum. However, it suffers from its very low conductivity (10^{-11} S/cm). Havinga et al.[7g] synthesized, among other β-alkyl oligothiophenes, α,ω-di-*tert*-butylheptathiophene via Stetter's coupling to form 1,4-diketone followed by ring closure to form thiophene rings, albeit without experimental details or spectroscopic data. Its poor solubility (<0.05 g/L in $CHCl_3$) is in sharp contrast to those of β-alkyl-substituted oligomers (1.6−120 g/L). Cycloalkane end-capped sexithiophene and heptathiophene were prepared by Bäuerle et al. via the Grignard cross coupling.[8e] α,ω-Dimethyl sexithiophene was obtained through zinc- and Ni(II)-catalyzed coupling of α-bromo-ω-methylterthiophene by Hotta et al.[8f] and via electrochemical coupling of α-methylterthiophene by Zotti et al.[8g] The synthesis of α,ω-dihexylsexithiophene and α,ω-dihexylthiosexithiophene were also reported recently by Katz and co-workers.[8a,h]

We have been interested in the synthesis of polythiophenes[9] and the processible oligomers of thiophene having functional groups, such as aldehyde, hydroxy, carboxylic acid, etc., as the end groups that could be incorporated into the backbones of conventional polymers, such as polyesters, polyurethanes, polyamides, etc., through the step-growth polymerization to afford a new family of electroactive polymers. In our previous communication,[10] we reported the preparation of α,ω-aldehyde-capped thiophene oligomers with two, four, and six thiophene units via a Ni-catalyzed coupling reaction. Nearly at the same time, the synthesis of aldehyde end-capped sexithiophene was also reported independently by Deatri et al.[8d] In this article, we present the detailed synthesis and characterization of a series of the α,ω-aldehyde-capped oligothiophenes up to eight thiophene units. In search for better solubility and electronic properties, a number of other α,ω-disubstituted sexithiophenes have also been prepared and characterized. The Stille's coupling reaction[11] was chosen as an alternative method of the Ni-catalyzed reaction[12] for the syntheses because of its proven generality and versatility in preparing aromatic polymers with a variety of functional groups.[13]

Scheme 1[a]



[a] Reagents and conditions: (a) 2^nBuLi, THF, −78 °C; 2^nBu_3SnCl. (b) 2^nBuLi, THF, −78 to 0 °C; 2^nBu_3SnCl. (c) DMF, $POCl_3$, CH_2ClCh_2Cl, reflux. (d) Br_2, $NaHCO_3$, $CHCl_3$. (e) 1% $Pd(PPh_3)_4$, DMF, heat.

Results and Discussion

Scheme 1 outlines the synthesis of the α,ω-aldehyde end-capped oligothiophenes with three to eight thiophene units. Thus, 2,5-dibromothiophene was treated with *n*-BuLi to form its dianion[14] followed by quenching with tri-*n*-butyltin chloride to afford the stannylated thiophene (**1**) in a good yield (98%, eq 1). 2,2′-Bithiophene was directly converted into its dianion[15] and stannylated to give 88% of **2** (eq 2). 2,2′-Bithiophene was formylated to give 94% of **3**, which was then brominated to give 5-bromo-5′-formyl-2,2′-bithiophene (**4**) in 89% yield (equation 3).[10] Compound **6** was obtained via a similar route

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[10] Wei, Y.; Wang, B.; Wang, W.; Tian, J. *Tetrahedron Lett.* **1995**, *36*, 665. In this previous communication, we inadvertently made a wrong assignment to the λ_{max} of the UV−vis spectra of α,ω-diformylsexithiophene. The correct λ_{max} value is given in the present article (Table 1, compound **10**).

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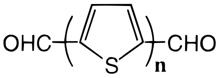
[14] A small amount of the dianion solution was withdrawn from the reaction and hydrolyzed in D_2O; ^1H NMR ($CDCl_3$) showed 2,5-dideuteriothiophene, δ 6.99 (s), to be the only product.

[15] A small amount of the dianion solution was withdrawn from the reaction and hydrolyzed in D_2O; ^1H NMR ($CDCl_3$) showed 5,5′-dideuterium-2,2′-bithiophene, δ 7.01 (d, J = 3.5 Hz, 2H), 7.17 (d, J = 3.5 Hz, 2H), to be the only product.

Table 1. Solubility and Electronic Properties of α,ω-Aldehyde End-Capped Thiophene Oligomers[a]



compd	n	λ_{max} (nm) in THF	λ_{max} (nm) in CH_2Cl_2	visual color	conductivity σ (S/cm)	solubility (g/L)[d]
7	3	410	414 (360)	orange (light yellow)	3×10^{-6} (10^{-11})	1.85
8	4	437	440 (391)	bright red (chrome yellow)	5×10^{-6} (10^{-10})	0.06 (3.5[e])
9	5	453	456 (416)	red (orange)	3×10^{-5} (10^{-8})	0.03 (0.2[e])
10	6	457	461 (438)	red (red)	5×10^{-5} (10^{-6})	$<4 \times 10^{-3}$
11	8	461	464 (−)	dark red (red)	2×10^{-4} (10^{-6})	$<4 \times 10^{-3}$
polythiophene[b]			485[c]	red	10^{-7}	

[a] Data in parentheses are those of corresponding unsubstituted oligothiophenes. Their UV data and colors are from ref 6, conductivity data from ref 3d, and solubilities from ref 7f. [b] PT = polythiophene. Its UV data and color are from ref 16a and conductivity from ref 16b. [c] Thin film. [d] In THF. [e] In $CHCl_3$.

from 2,2′:5′,2″-terthiophene (equation 4). These stannyl and bromo compounds are the major building blocks for the subsequent syntheses.

The stannyl compound **1** couples with different bromothiophenes to give the oligomers with odd numbers of thiophene units, while compound **2** couples to give the oligomers with even numbers of thiophene units. Thus, compound **1** reacted with 2 equiv of 2-bromo-5-formylthiophene or 5-bromo-5′-formyl-2,2′-bithiophene (**4**) to afford the trimer **7** and pentamer **9** in 83% and 88% yields, respectively (eq 5). Similarly, compound **2** reacted with 2 equiv of 2-bromo-5-formylthiophene (**4** and **6**) to afford the tetramer **8**, hexamer **10**, and octamer **11** in 90%, 87%, and 91% yields, respectively (eq 6). 2-Bromo-5-formylthiophene is air and light sensitive, and therefore a few drops of triethylamine were added in the reaction mixture to prevent the possible impurity in the aldehyde (e.g., carboxylic acid) from destannylating compound **1** or **2**. The Stille's coupling reactions are so facile that usually within 15 min of heating, a colored suspension will appear, indicating formation of the coupling product. As a general procedure, a solution of 1 equiv of the stannyl compound (**1** or **2**) and 2 equiv of the bromo compound (i.e., 2-bromo-5-formylthiophene, **4** or **6**) in DMF was deaerated twice with argon at room temperature. Upon addition of the catalyst tetrakis(triphenylphosphine)-palladium, the reaction was heated at 65−85 °C under argon to form a suspension with a yellow to deep red color. The mixture was then cooled to room temperature. The solid was collected by filtration and was washed with hexane, ether, dichloromethane, and/or THF at room temperature. Further purification of the α,ω-aldehyde end-capped oligothiophene product was performed by recrystallization from or washing with hot THF solutions. All the compounds were characterized by elemental analysis, melting point measurement, IR, UV−vis, NMR, and/or mass spectroscopy.

The UV−vis spectral data of the α,ω-aldehyde end-capped oligothiophenes are summarized in Table 1. For comparison, the literature data are also listed for polythiophene[16] and the corresponding unsubstituted oligothiophenes (in parentheses).[3c,6,7f] Similar to unsubstituted thiophene oligomers,[6,17] the λ_{max} value for the $\pi-\pi^*$ transition becomes higher with increasing number of thiophene units. The increment of the red shift of the λ_{max} value decreases within the series. For example, from the pentamer **9** to hexamer **10**, the increment of wavelength in methylene chloride is 5 nm (i.e., the transition energy decreases by 0.030 eV), while from the hexamer **10** to octamer **11** the increment is only 3 nm (i.e., the energy decreases by 0.017 eV). This suggests that the increase in conjugation length starts to slow down at six to eight thiophene units, which is in agreement with the same trend in the unsubstituted oligothiophenes at six to seven thiophene units.[6] It is evident from the UV−vis spectral data that the aldehyde end-capped oligomers have much higher degrees of conjugation than the corresponding unsubstituted oligothiophenes because of the presence of the aldehyde chromophores. The α,ω-aldehyde end-capped pentathiophene **9** exhibits already a greater λ_{max} value (456 nm) or a lower transition energy (2.72 eV) than the unsubstituted sexithiophene (438 nm, 2.83 eV). The λ_{max} values of hexamer **10** (461 nm, 2.69 eV) and octamer **11** (464 nm, 2.67 eV) are all much closer to that of polythiophene (485 nm, 2.56 eV) than the unsubstituted sexithiophene is (438 nm, 2.83 eV). The same trend is also reflected in the visual colors of the oligomers. The end-capped trimer shows the same orange color as the unsubstituted pentamer. The colors of the end-capped tetramer and higher oligomers are various deepening shades of red. The intrinsic conductivities of the α,ω-aldehyde end-capped oligothiophenes in solution-cast film form (Table 1) were measured using the standard four-probe method at room temperature. The conductivity of these end-capped oligomers is generally higher than that of their unsubstituted counterparts. Even the end-capped trimer **7** showed conductivity (10^{-6} S/cm) similar to that of the unsubstituted sexithiophene, which is significantly greater than the unsubstituted terthiophene (10^{-11} S/cm). To a certain extent, the observed high conductivities might be attributed to the fact that the two aldehyde end groups appreciably increase the conjugation lengths of the oligomers to effect an improved carrier mobility in comparison with the unsubstituted oligothiophenes. There also appears to be a trend of the conductivity increase with the increase in the number of thiophene units in the aldehyde end-capped oligomers. It should be cautioned that conductivity of organic films highly depends on the presence of even a minute of impurities, the underlying order of the compounds in the solid state, and many other factors besides the conjugation length.

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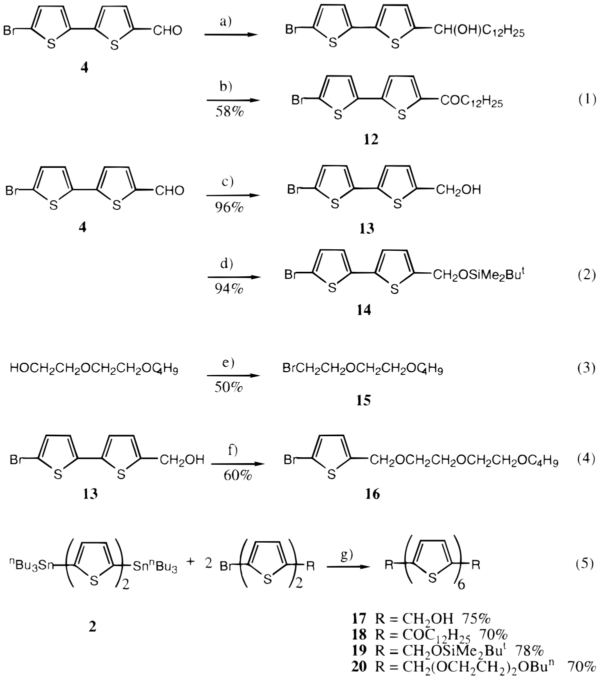
Scheme 2[a]



[a] Reagents and conditions: (a) $C_{12}H_{25}MgBr$, THF, −78 °C to room temperature, 4 h; NH_4Cl. (b) PDC, CH_2Cl_2, room temperature, 5 h. (c) $NaBH_4$, 85% EtOH, room temperature, 1 h. (d) $ClSiMe_2Bu^t$, Et_3N, DMAP, CH_2Cl_2, room temperature, overnight. (e) $ClSiMe_3$, LiBr, CH_3CN, reflux, overnight. (f) NaH, **15**, THF, reflux, 5 h. (g) 1% $Pd(PPh_3)_4$, DMF, heat.

Solubility and processibility are among the most important considerations in terms of practical applications of the conjugated polymers and oligomers. Starting from the tetramer, the solubility of the aldehyde end-capped oligomers in common organic solvents is poor and increasingly so with higher oligomers (Table 1). In fact, ^1H NMR spectra of the tetramer **8** and pentamer **9** required many hours of data acquisition, and the spectra of the hexamer **10** and octamer **11** could not be obtained because of their poor solubility in various deuterated solvents such as $CDCl_3$, DMSO-d_6, benzene-d_6, etc. Since the hexamer of thiophene has been proven applicable in fabricating electronic and electrooptical devices, we have prepared a variety of new α,ω-end-capped sexithiophenes as illustrated in Scheme 2 in the belief that a better solubility can be achieved without compromising electronic properties by designing various substituent groups.

By X-ray analysis, Garnier and co-workers[8c] discovered a good long-range order in a thin film of α,ω-dihexylsexithiophene, which was attributed to the hydrophobic interactions between alkyl side chains. Such an order was believed to contribute favorably to the electronic characteristics of the films.[8c] Along this line of thinking, we sought to introduce α,ω-substitution with longer chains, hoping that it would enhance the solubility while maintaining the electronic properties of the sexithiophene. The synthesis of *n*-dodecanoyl end-capped sexithiophene was depicted in eqs 1 and 5 in Scheme 2. Thus, *n*-dodecylmagnium bromide reacted with 1 equivalent of 5-bromo-5′-formyl-2,2′-bithiophene (**4**) to form an alcohol intermediate which was oxidized with pyridinium dichromate (PDC) to afford 5-bromo-5′-(*n*-dodecanoyl)-2,2′-bithiophene (**12**) in 58% overall yield. α,ω-Didodecanoylsexithiophene (**18**) was then successfully obtained as a red solid in 70% yield by coupling **12** with bistannylbithiophene (**2**). The conductivity of **18** (Table 2), however, was found to be lower than that of the unsubstituted or α,ω-aldehyde-substituted sexithiophene. What is more disappointing is that the solubility of **18** was much worse than that of dihexylsexithiophene (Table 2). The poor solubility might result from the strong intermolecular interactions between the dodecyl groups in the solid state. In fact, a solubility as low as 0.02 g/L was reported for α,ω-didodecyltetrathiophene.[18] In addition, the low solubility of the diacyl compound **18** might also be attributed to the intermolecular quadrupole−quadrupole interactions. The λ_{max} value of **18** (440 nm in THF) was found much smaller than that of the aldehyde end-capped sexithiophene **9** (457 nm in THF). This seems to coincide with the observed difference in conductivity between the two compounds.

Trialkylsilyl groups are known to induce good solubility. The relatively high solubility of α,ω-bis(triisopropylsilyl) sexithiophene is a good example.[8b] Tour and co-workers[7e] also reported the synthesis and good solubility of a series of trimethylsilyl end-capped oligomers of β-methylthiophenes. We decided to make a silyl ether compound using the *tert*-butyldimethylsiloxy group, which is more stable than the trimethylsilyl group toward acids. As shown in eqs 2 and 5 in Scheme 2, compound **4** was reduced with sodium borohydride to the corresponding alcohol (**13**) in a good yield. The silyl ether **14** was obtained by reaction of the alcohol **13** with *tert*-butyldimethylsilyl chloride in dichloromethane in the presence of excess triethylamine and a catalytic amount of 4-(dimethylamino)pyridine (DMAP). Coupling of **14** with bistannylbithiophene (**2**) afforded *tert*-butyldimethylsiloxy end-capped sexithiophene (**19**) in 78% yield. The compound **19** indeed has a higher solubility but does not offer significant improvements in conductivity over the unsubstituted or aldehyde end-capped sexithiophene. We also synthesized α,ω-hydroxymethyl end-capped sexithiophene (**17**) by coupling the alcohol **13** with **2** (Scheme 2). It was found, again, that both the solubility and conductivity of **17** were low (Table 2).

The above-described three types (i.e., **17**−**19**) of substitution systems failed to yield the sexithiophene products with significantly improved solubility and conductivity. At last we decided to explore the use of bis(ethylene glycol) butyl ether as the end-capping group, in part for the reason that ethylene glycol ethers are themselves industrial solvents. Thus, bis(ethylene glycol) butyl ether reacted with chlorotrimethylsilane and lithium bromide in acetonitrile to afford (*n*-butoxyethoxy)ethyl bromide (**15**, eq 3, Scheme 2). Ether **16** was obtained in 60% yield by adding the bromide **15** in excess to a suspension of the sodium salt of alcohol **13**, which was generated from the reaction of **13** with sodium hydride (eq 4, Scheme 2). One possible side product which could not be readily separated from the main product **16** by chromatography had the same structure as **16** except that the bromine was replaced by hydrogen from reduction by sodium hydride. To

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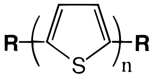
Table 2. Solubility and Electronic Properties of α,ω-Substituted Sexithiophenes



compd	R	λ_{max} (nm) in THF	λ_{max} (nm) in CH_2Cl_2	visual color	conductivity σ (S/cm)	solubility (g/L)[a]
17	$-CH_2OH$	441	*b*	deep red	3×10^{-7}	$<4 \times 10^{-3}$
18	$-COC_{12}H_{25}$	440	444	red	4×10^{-7}	$<4 \times 10^{-3}$
19	$-CH_2OSiMe_2Bu^t$	442	442	orange	8×10^{-6}	0.1
						0.1[c]
20	$-CH_2(OCH_2CH_2)_2OBu^n$	440	445	red	1×10^{-6}	0.08
						1.8[c]
DH6**T**[f]	$-(CH_2)_5CH_3$		444	red	6×10^{-5} [d]	
					5×10^{-7} [e]	1[c]

[a] Measured in THF. [b] Not measured because of insolubility. [c] In $CHCl_3$. [d] Conductivity perpendicular to substrate plane. [e] Conductivity parallel to substrate plane. [f] DH6T = α,ω-dihexylsexithiophene. The data are taken from ref 8b.

minimize such a reduction, the amount of sodium hydride was limited to no more than 1 equiv. Compound **16** was then coupled with **2** to give the (*n*-butoxyethoxy)ethoxymethyl end-capped sexithiophene (**20**) as a red waxy solid in 70% yield. Compound **20** has a limited solubility in THF (0.1 g/L), but it dissolves remarkably well in chloroform (1.8 g/L). As far as we know, this is one of the most soluble α,ω-end-capped sexithiophenes ever reported. The excellent solubility may be explained by the alternate distribution of hydrophobic ethylene group and the hydrophilic ether oxygen atom, which may prevent the strong aggregation of the molecules. Furthermore, the hydrophilic ether oxygen atom may also increase interaction with the solvent. Moreover, as shown in Table 2, both the λ_{max} value (445 nm) and conductivity (1×10^{-6} S/cm) of **20** were found to be greater or comparable to those of the unsubstituted sexithiophene. Further studies of the electronic and optical properties of **20** and its analogues are in progress.

Conclusions

We have described the successful synthesis of a series of α,ω-aldehyde end-capped oligomers including the trimer, tetramer, pentamer, hexamer, and octamer of thiophene using the palladium-catalyzed Stille's coupling reactions. The UV−vis spectral data indicate that these aldehyde end-capped oligomers have longer conjugation lengths as evidenced by the higher λ_{max} values than the corresponding unsubstituted oligothiophenes because of the presence of the aldehyde chromophores. The λ_{max} value increases as the number of thiophene units is increased. The intrinsic conductivity of the solution-cast films of the aldehyde end-capped oligothiophenes is generally higher than that of their corresponding unsubstituted counterparts. In the search for better solubility and electronic properties, other α,ω-substituted sexithiophenes, such as *n*-dodecanoyl, *tert*-butyldimethylsilyl, hydroxymethyl, and (*n*-butoxyethoxy)-ethoxymethyl sexithiophenes, have been synthesized. α,ω-Bis((*n*-butoxyethoxy)ethoxymethyl)sexithiophene was found to be one of the most soluble α,ω-substituted sexithiophenes ever reported and also to have a good conductivity that is comparable to the unsubstituted sexithiophene.

Experimental Section

Materials and Instrumentation. 2-Bromo-5-formylthiophene (Aldrich) was freshly distilled under reduced pressure prior to use. 2,5-Dibromothiophene, 2,2′-bithiophene, 2,2′:5′,2″-terthiophene, *n*-BuLi, tri-*n*-butyltin chloride, phosphorous oxychloride, 4-(dimethylamino)pyridine, *tert*-butyldimethylsilyl chloride, bis(ethylene glycol) butyl ether, chlorotrimethylsilane, (*n*-butoxyethoxy)ethoxymethyl bromide, *n*-dodecylmagnesium bromide, and tetrakis(triphenylphosphine)palladium were used as received from Aldrich. Tetrahydrofuran (THF, HPLC grade from Aldrich) was distilled over sodium benzophenone ketyl under argon. Dichloromethane (EM Science), dimethyl diformimide (DMF, Fisher) and chloroform (Fisher) distilled from CaH_2. Acetonitrile (Fisher) was first distilled from P_2O_5 and then from K_2CO_3. Melting points were determined with a Mel Temp apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrophotometer. The NMR spectra were measured on a Bruker WM 250 FT NMR spectrometer. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard or to the resonance of residual protons in the deuterated solvents, e.g., 7.26 ppm in $CDCl_3$ and 5.23 ppm for the central line of the triplet in CD_2Cl_2. Mass spectra were recorded on a Finnigan-450 mass spectrometer at an ionization energy of 35 eV for the stannyl compounds and of 70 eV for others. Mass spectra of compounds **10** and **19** were also measured on a TSQ46 Finnigan MAT with chemical desorption ionization. Exact mass spectra were determined on a VG ZAB-HF high-resolution mass spectrometer. UV−vis spectra were recorded on a Perkin-Elmer HP8451 spectrophotometer. Elemental analyses were performed at the Department of Chemistry, University of Pennsylvania, Philadelphia, and by Microanalysis Inc., Wilmington, DE. For a general procedure of conductivity measurement, the compound (about 10 mg) was added to 0.5 mL of 1-methyl-2-pyrrolidinone (NMP, HPLC grade, Aldrich) followed by ultrasonication for 30 min at room temperature. The solution was cast dropwise onto a clean glass plate and the solvent was allowed to evaporate in an oven at 100 °C for 0.5 h. Conductivity was then measured on the resultant thin film on the glass plate using the standard four-probe technique at ambient temperature in air. The film thickness was about 50 μm. An EG&G PAR Model 173 potentiostat/galvanostat was employed as a constant current source. The solubility tests were performed by adding finely ground powders of the oligomers to 50−500 mL of organic solvents (e.g., chloroform and THF) with agitation and ultrasonication at room temperature until saturation.

2,5-Bis(tri-*n*-butylstannyl)thiophene (1): 2.5 M *n*-BuLi (8.2 mL, 20.5 mmol) was added dropwise to a solution of 2,5-dibromothiophene (1.1 mL, 10 mmol) in THF (40 mL) at −78 °C with stirring. A thick white precipitation was formed. After stirring for 0.5 h at −78 °C, tri-*n*-butyltin chloride (5.7 mL, 21 mmol) was added. The reaction mixture was stirred at −78 °C for additional 3 h and was then gradually warmed to room temperature and stirred overnight. The clear solution was diluted with *n*-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5%, 20 mL), and water (20 mL). The organic layer was dried over $MgSO_4$, and the solvents were concentrated on a rotavap. Column chromatography of the residue over grade II neutral alumina with hexane as eluant gave **1** as a colorless liquid (6.5 g, 98%) which was directly used in the subsequent reactions: MS *m*/*z* 662 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2, 7.2 Hz, 18H), 1.09 (t, *J* = 8.1, 8.1 Hz, 12H), 1.33 (m, 12H), 1.57 (m, 12H), 7.34 (s, 2H).

5,5′-Bis(tri-*n*-butylstannyl)-2,2′-bithiophene (2): 2.5 M *n*-BuLi (5.0 mL, 12.5 mmol) was added dropwise to a solution of 2,2′-bithiophene (1.0 g, 6.0 mmol) in THF (40 mL) at −78 °C with stirring. Upon formation of white precipitation, the mixture was warmed to room temperature and stirred for 1 h followed by addition of tri-*n*-butyltin chloride (3.3 mL, 12.2 mmol). The clear solution was heated to gentle reflux for 1 h, and it turned cloudy. *n*-Hexane (200 mL) was added to the mixture. The organic layer was washed with aqueous sodium bicarbonate solution (5%, 20 mL) and water (20 mL), dried over $MgSO_4$, and concentrated in vacuo. Chromatography of the residue over grade II neutral alumina with *n*-hexane as eluant gave the pure product **2** as a colorless oil (3.9 g, 88%): MS *m*/*z* 744 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.2, 7.2 Hz, 18H), 1.11 (t, *J* = 8.1, 8.1 Hz, 12H), 1.34 (m, 12H), 1.58 (m, 12H), 7.04 (d, *J* = 3.3 Hz, 2H), 7.28 (d, *J* = 3.3 Hz, 2H).

5-Formyl-2,2′-bithiophene (3): Phosphorous oxychloride (12.5 mL, 134 mmol) was added to a solution of 2,2′-bithiophene (20 g, 120 mmol) and DMF (10.5 mL, 135 mmol) in 1,2-dichloroethane (200 mL) cooled in an ice bath. The solution was then warmed up to room temperature and heated to reflux. Upon refluxing overnight, the yellow suspension was cooled to room temperature and poured into a saturated aqueous sodium acetate solution (500 mL) and stirred for several hours to complete the hydrolysis. The yellow suspension formed was extracted with dichloromethane (3 × 300 mL). The organic layer was combined and washed with water (1 × 100 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography of the residue over silica gel (hexane: ethyl acetate 15:1) yielded **3** as yellow crystals (22 g, 94%): mp 57−59 °C (lit. 58−59 °C);[19] ^{1}H NMR ($CDCl_3$) δ 7.08 (t, *J* = 4.3, 4.3 Hz, 1H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.36 (d, *J* = 4.3 Hz, 2H), 7.67 (d, *J* = 3.8 Hz, 1H), 9.86 (s, 1H).

5-Bromo-5′-formyl-2,2′-bithiophene (4): To a solution of 5-formyl-2,2′-bithiophene (9 g, 46 mmol) in chloroform (100 mL) was added sodium bicarbonate (4.28 g, 51 mmol), followed by the dropwise addition of a solution of bromine (8.16 g, 51 mmol) in chloroform (100 mL) over a period of 1 h. The reaction mixture was refluxed for 4 h and then cooled and filtered. The filtrate was washed with water (2 × 100 mL) and dried over $MgSO_4$. Upon evaporation of solvents, the solid residue was chromatographed (silica, hexane:ethyl acetate 15: 1) to give product **4** as yellow solids (11.2 g, 89%): mp 141−145 °C, decompose (lit. decomposed without melting);[20] ^{1}H NMR ($CDCl_3$) δ 7.04 (d, *J* = 4.0 Hz, 1H), 7.11 (d, *J* = 3.9 Hz, 1H), 7.18 (d, *J* = 4.0 Hz, 1H), 7.66 (d, *J* = 3.9 Hz, 1H), 9.87 (s, 1H).

5-Formyl-2,2′:5′,2″-terthiophene (5): Phosphorous oxychloride (1.9 mL, 20.4 mmol) was added to a solution of 2,2′:5′,2″-terthiophene (4.4 g, 17.7 mmol) and DMF (1.5 mL, 19.3 mmol) in 1,2-dichloroethane (50 mL) cooled in an ice bath. The solution was allowed to reflux overnight. The resultant orange suspension was poured into a cold saturated aqueous sodium acetate solution (150 mL) and stirred for several hours followed by extraction with dichloromethane (3 × 100 mL). The organic layer was washed with water (1 × 100 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography of the residue (silica, hexane:ethyl acetate 15:1) yielded **5** as a yellow solid (3.5 g, 80%): mp 136−138 °C; MS *m*/*z* 276 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.12 (dd, *J* = 3.6, 5.1 Hz, 1H), 7.31 (d, *J* = 3.87 Hz, 1H), 7.38 (dd, *J* = 1.0, 3.6 Hz, 1H), 7.48 (d, *J* = 3.7 Hz, 1H), 7.50 (dd, *J* = 1.0, 3.6 Hz, 1H), 7.93 (d, *J* = 3.98 Hz, 1H), 9.92 (s, 1H). Exact mass calcd. for $C_{13}H_8OS_3$ 275.9737, found 275.9737.

5-Bromo-5″-formyl-2,2′-terthiophene (6): To a solution of 5-formyl-2,2′:5′,2″-terthiophene (**5**, 1.77 g, 6.42 mmol) in chloroform (100 mL) was added sodium bicarbonate (1.5 g, 17.8 mmol), followed by the dropwise addition of a solution of bromine (1.1 g, 6.88 mmol) in chloroform (10 mL) over a period of 1 h. The reaction mixture was stirred for additional 5 h and then filtered. The filtrate was washed with water (2 × 20 mL) and dried over $MgSO_4$. After evaporation, the solid residue was recrystalized from dichloromethane to give golden brown needle-shaped crystals (1.9 g, 85%): mp 158−160 °C; MS *m*/*z* 355 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.18 (d, *J* = 3.9 Hz, 1H), 7.21 (d, *J* = 3.9 Hz, 1H), 7.31 (d, *J* = 3.9 Hz, 1H), 7.50 (dd, *J* = 1.0, 3.9 Hz, 2H), 7.93 (d, *J* = 3.9 Hz, 1H), 9.93 (s, 1H). Anal. Calcd for $C_{13}H_7BrOS_3$: C 43.95, H 1.99. Found: C 43.67, H 2.23.

5,5″-Diformyl-2,2′:5′,2″-terthiophene (7): A solution of 2,5-bis(tri-*n*-butylstannyl)thiophene (1 g, 1.51 mmol) and 2-bromo-5-formylthiophene (578 mg, 3.02 mmol) in DMF (20 mL) was deaerated twice with argon followed by the addition of tetrakis(triphenylphosphine)palladium (19 mg, 0.016 mmol). The reaction mixture was heated at 65−70 °C for 6 h under argon. The resultant reddish brown suspension was concentrated under a reduced pressure. The solids were collected by filtration and were washed sequentially with *n*-hexane (400 mL), ether (200 mL) and dichloromethane (200 mL) to give product **7** as an orange solid (380 mg, 83%). The product was further purified by recrystallization from THF: mp 222−224 °C; MS *m*/*z* 304 (M^+); IR (KBr) 1650, 1432, 1221, 1041, 793, 665, 462 cm^{-1}; UV λ_{max} 410 nm (THF), 414 nm (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.30 (d, *J* = 4.0 Hz, 2H), 7.32 (s, 2H), 7.70 (d, *J* = 4.0 Hz, 2H), 9.87 (s, 2H). Anal. Calcd for $C_{14}H_8O_2S_3$: C 55.24, H 2.65. Found: C 55.16, H 2.79.

5,5‴-Diformyl-2,2′:5′,2″:5″,2‴-quarterthiophene (8): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (0.98 g, 1.3 mmol) and 2-bromo-5-formylthiophene (503 mg, 2.63 mmol) in DMF (20 mL) was deaerated twice with argon. Upon addition of tetrakis(triphenylphosphine)palladium (15 mg, 0.013 mmol), the reaction mixture was heated at 70−75 °C for 6 h under argon. The bright red suspension formed was concentrated under a reduced pressure and filtered. The solid residue was washed sequentially with *n*-hexane (400 mL) and ether (200 mL) to afford **8** as a bright red solid (450 mg, 90%). Further purification was carried out by boiling the red solid (200 mg) with THF (400 mL) and filtering while hot. The filtrate was concentrated to 100 mL and cooled to room temperature. Bright golden red crystals (100 mg) of **8** were obtained upon filtration: mp 270−275 °C (decompose); MS *m*/*z* 386 (M^+); IR (KBr) 1652, 1448, 1223, 1043, 788, 665, 452 cm^{-1}; UV λ_{max} 437 nm (THF), 440 nm (CH_2Cl_2); ^{1}H NMR (CD_2Cl_2) δ 7.23 (d, *J* = 3.8 Hz, 2H), 7.30 (d, *J* = 4.0 Hz, 2H), 7.34 (d, *J* = 3.8 Hz, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 9.86 (s, 2H). Exact mass calcd for $C_{18}H_{10}O_2S_4$ 385.9564, found 385.9563.

5,5′′′′-Diformyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene (9): A solution of 2,5-bis(tri-*n*-butylstannyl)thiophene (1.04 g, 1.57 mmol) and 5-bromo-5′-formyl-2,2′-bithiophene (920 mg, 3.3 mmol) in DMF (20 mL) was deaerated twice with argon. Upon addition of tetrakis(triphenylphosphine)palladium (19 mg, 0.016 mmol), the reaction was heated at 70−75 °C for 4 h under argon. The resultant bright red suspension was cooled and filtered. The solid residue was washed sequentially with ether (400 mL) and dichloromethane (50 mL) to afford **9** as a red solid (640 mg, 88%). Further purification was carried out by boiling the red solid (100 mg) with THF (500 mL) and filtered while hot. The filtrate was concentrated to 50 mL and cooled to room temperature. Red crystals with a golden hue were obtained upon filtration: mp 254−256 °C (decompose); MS *m*/*z* 468 (M^+); IR (KBr) 1653, 1439, 1209, 1041, 788, 667, 459 cm^{-1}; UV λ_{max} 453 nm (THF), 456 nm (CH_2Cl_2); ^{1}H NMR ($CDCl_2$) δ 7.19 (d, *J* = 4.0 Hz, 2H), 7.21 (s, 2H), 7.30 (d, *J* = 3.9 Hz, 2H), 7.33 (d, *J* = 3.9 Hz, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 9.86 (s, 2H). Exact mass calcd for $C_{22}H_{12}O_2S_5$ 467.9449, found 467.9440.

5,5′′′′′-Diformyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene (10): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (0.73 g, 0.98 mmol) and 5-bromo-5′-formyl-2,2′-bithiophene (535 mg, 1.96 mmol) in DMF (25 mL) was deaerated twice with argon. After addition of tetrakis(triphenylphosphine)palladium (11 mg, 0.01 mmol), the reaction was heated at 80 °C for 6 h under argon. The resultant red

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suspension was cooled and filtered. The solid residue was washed sequentially with ether (200 mL), dichloromethane (200 mL), and THF (200 mL) to afford **10** as a red solid (430 mg, 87%). Further purification was carried out by boiling the red solid (100 mg) with THF (2000 mL) and filtering while hot. The filtrate was concentrated to 100 mL and cooled to room temperature. Filtration afforded red crystals of **10** (18 mg): mp 307−310 °C decompose (lit. mp 310 °C);[8d] IR (KBr) 1653, 1431, 1217, 1043, 789 cm^{-1}; UV λ_{max} 457 nm (THF), 461 nm (CH_2Cl_2); MS *m/z* 551 ($M^+ + H$); high-resolution MS calcd (relative isotope intensities) for $C_{26}H_{14}O_2S_6$ (M^+): 550 (100%), 551 (34%), 552 (33%), 553 (10%), found: 550 (100%), 551 (35%), 552 (33%), 553 (9%).

5,5′′′′′′-Diformyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′-octithiophene (11): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (0.50 g, 0.67 mmol) and 5-bromo-5″-formyl-2,2′:5′,2″-terthiophene (487 mg, 1.37 mmol) in DMF (25 mL) was deaerated twice with argon. After addition of tetrakis(triphenylphosphine)palladium (11 mg, 0.01 mmol), the reaction was heated at 80−85 °C for 5.5 h under argon. The resultant red suspension was cooled and filtered. The solid residue was washed sequentially with ether (200 mL), dichloromethane (200 mL), and THF (200 mL) to afford **11** as a dark red solid (436 mg, 91%). Further purification was carried out by boiling the red solid (100 mg) with THF (2000 mL) and filtering while hot. The filtrate was concentrated to 50 mL and cooled to room temperature. Filtration afforded a dark red solid (20 mg): darkened above 400 °C without melting; MS *m/z* 687 ($M^+ - CO$); IR (KBr) 1664, 1456, 1441, 1216, 1051, 784, 454 cm^{-1}; UV λ_{max} 461 nm (THF), 464 nm (CH_2Cl_2).

5-Bromo-5′-(*n*-dodecanoyl)-2,2′-bithiophene (12): To a suspension of **4** (1 g, 3.9 mmol) in THF (30 mL) at −78 °C under nitrogen was added a 1.0 M solution of *n*-dodecylmagnesium bromide in ether (4.0 mL, 4 mmol). The reaction was slowly warmed to room temperature and stirred for 4 h under nitrogen. A saturated NH_4Cl aqueous solution (20 mL) was added and the mixture was extracted with ether (3 × 50 mL). The organic layer was washed with water (2 × 10 mL) and dried (Na_2CO_3) and evaporated to give the crude alcohol product as yellowish solids. Upon drying under vacuum, the solids were dissolved in dry CH_2Cl_2 (50 mL). To this solution, pyridinium dichromate (5.5 g, 14.6 mmol) was added under nitrogen, followed by oven-dried $MgSO_4$ (5 g). The mixture was stirred at room temperature for 5 h. Ether (200 mL) was added and the resultant mixture was filtered through Celite. The filtrate was dried over $MgSO_4$ and concentrated in vacuo. Chromatography of the residue (silica, hexane:ethyl acetate 20:1) gave product **12** (1.0 g, 58%) as an off-white waxy solid: mp 96−99 °C, MS *m/z* 441 (M^+); ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.26 (br s, 18H), 2.86 (t, J = 7.5 Hz, 2H), 7.01 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.9 Hz, 1H), 7.10 (d, J = 4.0 Hz, 1H), 7.58 (d, J = 4.0 Hz, 1H). Exact mass calcd for $C_{21}H_{29}BrOS_2$ 441.0917, found 441.0921.

5-Bromo-5′-hydroxymethyl-2,2′-bithiophene (13): To a suspension of 5-bromo-5′-formyl-2,2′-bithiophene (**4**, 1.54 g, 5.64 mmol) in 85% ethanol (40 mL) was added sodium borohydride (170 mg, 17.9 mmol). The mixture was stirred at room temperature for 1 h. The yellow suspension turned gradually into a light yellow solution which was then concentrated by evaporation. Ether (80 mL) was added and the organic layer was washed with water (3 × 20 mL), dried with $MgSO_4$, and concentrated in vacuo. Chromatography of the residue (silica, *n*-hexane:ethyl acetate 6:1 v/v) yielded compound **13** as off-white crystals (1.5 g, 96%): mp 123−125 °C, MS *m/z* 275 (M^+); ^1H NMR ($CDCl_3$) δ 0.12 (s, 6H), 0.94 (s, (H), 4.84 (s, 2H), 6.80 (d, J = 3.6 Hz, 1H), 6.87 (d, J = 3.6 Hz, 1H), 6.95 (m, 2H). Exact mass calcd for $C_9H_7BrOS_2$ 273.9120, found 273.9122.

5-Bromo-5′-((*tert*-butyldimethylsiloxy)methyl)-2,2′-bithiophene (14): To a solution of **13** (0.6 g, 2.18 mmol) and triethylamine (2 mL, 14.3 mmol) in dry dichloromethane (5 mL) under nitrogen was added 4-(dimethylamino)pyridine (15 mg, 0.12 mmol) and *tert*-butyldimethylsilyl chloride (0.67 mg, 4.4 mmol). After stirring overnight at room temperature, the reaction mixture was diluted with diethyl ether (80 mL), followed by addition of 5% sodium bicarbonate solution (10 mL). The organic layer was washed with water, dried over ($MgSO_4$), and evaporated. Chromatography (silica, *n*-hexane:ethyl acetate 30:1 v/v) gave the product **14** as a yellowish oil (0.8 g, 94%): MS *m/z* 389 (M^+); ^1H NMR ($CDCl_3$) δ 1.85 (t, J = 5.3 Hz, 1H), 4.79 (d, J = 5.3 Hz, 2H), 6.89 (m, 2H), 6.96 (d, J = 3.8 Hz, 2H). Exact mass calcd for $C_{15}H_{21}BrOS_2Si$ 387.9989, found 387.9986.

(*n*-Butoxyethoxy)ethyl Bromide (15): To a solution of bis(ethylene glycol) butyl ether (10.1 mL, 0.06 mol) and lithium bromide (10.4 g, 0.12 mol) in acetonitrile (100 mL) was added chlorotrimethylsilane (19 mL, 0.15 mol). The resultant solution was refluxed overnight under nitrogen. The reaction was then diluted with ether (100 mL). The organic layer was washed successively with water (20 mL), 10% $NaHCO_3$ aqueous solution (20 mL), and brine (20 mL). After drying over $MgSO_4$, evaporating solvents and chromatography (silica, hexane:ethyl acetate 20:1), the product **15** was obtained as a colorless liquid (6.75 g, 50%): MS *m/z* 225 (M^+); ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3H), 1.34 (sextet, J = 7.4 Hz, 2H), 1.56 (quintet, J = 7.4 Hz, 2H), 3.45 (m, 4H), 3.58 (m, 2H), 3.64 (m, 2H), 3.80 (t, J = 6.4 Hz, 2H).

5-Bromo-5′-((*n*-butoxyethoxy)ethoxymethyl)-2,2′-bithiophene (16): Sodium hydride (227 mg, 5.68 mmol) was added to a solution of 5-bromo-5′-(hydroxymethyl)-2,2′-bithiophene (**13**, 1.42 g, 5.16 mmol) in THF (60 mL). After the initial gas evolution ceased, (*n*-butoxyethoxy)ethoxymethyl bromide (2.8 g, 12 mmol) was added. The reaction mixture was refluxed for 5 h under nitrogen, cooled to room temperature and diluted with ether (100 mL). The organic layer was washed with water (3 × 30 mL), dried over $MgSO_4$, and concentrated in vacuo. Chromatography of the residue (silica, hexane:ethyl acetate 10:1) gave product **16** as a yellowish oil (1.3 g, 60%): MS *m/z* 419 (M^+); ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3H), 1.35 (sextet, J = 7.4 Hz, 2H), 1.56 (quintet, J = 7.4 Hz, 2H), 3.46 (t, J = 7.4 Hz, 2H), 3.59 (m, 2H), 3.64 (m, 6H), 4.68 (s, 2H), 6.87 (m, 2H), 6.95 (t, J = 3.7 Hz, 2H). Exact mass calcd for $C_{17}H_{21}BrO_3S_2$ 418.0284, found 418.0272.

5,5′′′′′-Bis(hydroxymethyl)-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene (17): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (**2**, 583 mg, 0.78 mmol) and compound **13** (0.43 g, 1.56 mmol) in DMF (15 mL) was deaerated twice with argon followed by addition of tetrakis(triphenylphosphine)palladium (9 mg, 0.08 mmol). The reaction was heated at 75−85 °C for 8 h under argon. The resultant dark red suspension was cooled and filtered. The solid residue was successively washed with hexane (400 mL), CH_2Cl_2 (400 mL), and ethanol (300 mL). The solids were further purified on a Soxhlet extractor with THF for 2 days to yield product **17** (585 mg, 75%): no melting within the limit of thermometer (410 °C) and darkened above 300 °C; MS *m/z* 536 ($M^+ - H_2O$); IR (KBr) 790, 991, 1435, 2857, 2920, 3412 cm^{-1}; UV λ_{max} 441 nm (THF).

5,5′′′′′-Bis(*n*-dodecanoyl)-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene (18): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (**2**, 346 mg, 0.46 mmol) and compound **12** (410 mg, 0.93 mmol) in DMF (20 mL) was deaerated twice with argon. Upon addition of tetrakis(triphenylphosphine)palladium (5.3 mg, 0.046 mmol), the reaction mixture was heated at 70−80 °C overnight under argon. The resultant deep red suspension was cooled and filtered. The solid residue was successively washed with hexane (800 mL) and CH_2Cl_2 (400 mL). The solids were then purified by Soxhlet extraction with THF for 2 days to yield product **18** (285 mg, 70%): mp 280 °C; IR (KBr) 790, 1068, 1204, 1446, 1656, 2850, 2918 cm^{-1}; UV λ_{max} 440 nm (THF), 444 nm (CH_2Cl_2). MS calcd (relative isotope intensities) for $C_{50}H_{62}O_2S_6$ (M^+): 886 (100%), 887 (62%), 888 (46%), 889 (20%), 890 (9%). Found: 886 (100%), 887 (63%), 888 (47%), 889 (19%), 890 (9%).

5,5′′′′′-Bis((*tert*-butyldimethylsiloxy)methyl)-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene (19): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (**2**, 0.48 g, 0.645 mmol) and compound **14** (0.5 g, 1.28 mmol) in DMF (10 mL) was deaerated twice with argon followed by addition of tetrakis(triphenylphosphine)palladium (7.5 mg, 0.006 mmol). The reaction was heated at 80−85 °C overnight under argon. The resultant orange red suspension was cooled and filtered. The solid residue was washed with hexane (800 mL) and recrystalized from THF to give product **15** as orange-red crystals (395 mg, 78%): mp 254−255 °C; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 12H), 0.95 (s, 18H), 4.85 (s, 4H), 6.83 (d, $J = 3.6$ Hz, 2H), 7.02 (d, $J = 3.6$ Hz, 2H), 7.05 (d, $J = 3.7$ Hz, 2H), 7.07 (d, $J = 3.7$ Hz, 2H), 7.08 (s, 4H); IR (KBr) 793, 840, 1073, 1089, 1255, 1386, 1470, 1506, 2854, 2927, 3061 cm^{-1}; UV $\lambda_{\max}$ 442 nm (THF), 442 nm (CH_2Cl_2); MS m/z 783 ($M^+ + H$). High-resolution MS calcd (relative isotope intensities) for $C_{38}H_{46}O_2S_6Si_2$ (M^+): 782 (100%), 783 (58%), 784 (50%), 785 (22%), 786 (11%). Found: 782 (100%), 783 (57%), 784 (48%), 785 (21%), 786 (10%).

5,5′′′′′-Bis((*n*-butoxyethoxy)ethoxymethyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (20): A solution of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene (**2**, 538 mg, 0.72 mmol) and compound **16** (606 mg, 1.45 mmol) in DMF (20 mL) was deaerated twice with argon followed by addition of tetrakis-(triphenylphosphine)palladium (8.3 mg, 0.07 mmol). The reaction mixture was heated at 75−80 °C under argon for 8 h. The bright red suspension formed was cooled and filtered. The solid residue was washed with hexane (800 mL) and CH_2Cl_2 (100 mL) followed by recrystallization from THF/$CHCl_3$ to give product **20** as a red solid (366 mg, 60%). Characterization data: mp 250 °C; MS m/z 844 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.91 (t, $J = 7.4$ Hz, 6H), 1.36 (sextet, $J = 7.4$ Hz, 4H), 1.57 (m, 4H), 3.47 (t, $J = 6.7$ Hz, 4H), 3.61 (m, 4H), 3.67 (m, 12H), 4.71 (s, 4H), 6.91 (d, $J = 3.7$ Hz, 2H), 7.03 (d, $J = 3.7$ Hz, 2H), 7.06 (d, $J = 4.0$ Hz, 2H), 7.07 (d, $J = 4.0$ Hz, 2H), 7.08 (s, 4H); IR (KBr) 785, 1094, 1124, 1439, 2851, 2945 cm^{-1}; UV $\lambda_{\max}$ 440 nm (THF), 445 nm (CH_2Cl_2). Anal. Calcd for $C_{42}H_{50}O_6S_6$: C 59.82, H 5.98. Found: C 59.39, H 5.83.

Acknowledgment. We are most grateful to the Harry Stern Foundation and Akzo-Nobel Corporate Research for partial support of this project. We thank Dr. J. Honovich and M. Lalevic of Drexel University for their assistance in measuring the mass spectra.

Supporting Information Available: Collection of NMR spectra of the compounds prepared in this work (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet. See any current masthead page for ordering information and Internet access instructions.

CM960182P