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Synthesis and Properties of a Series of the Longest Oligothiophenes up to the 48-mer

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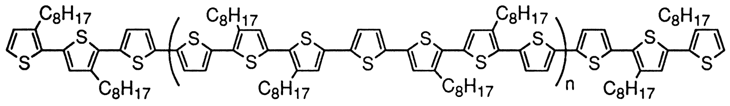
A series of the longest class of oligothiophenes extended at intervals of seven thiophene units from the 6-mer up to the 48-mer has been synthesized by a combination of the random Eglinton coupling reaction of mono- and di-ethynylsexithiophenes and a subsequent sodium sulfide-induced cyclization reaction of the resulting oligo(sexithienylene-diethynylene)s. Their structures were well characterized by MALDI-TOF MS and ^{1}H NMR spectroscopy. The molecular weights of the oligothiophenes and oligo(sexithienylene-diethynylene)s, measured by gel-permeation liquid chromatography using the polystyrene standard, are nearly double the actual ones, indicating that they keep highly rigid rod-type shapes. According to a molecular model, the molecular lengths of the longest oligothiophene 48-mer and the longest oligo(sexithienylene-diethynylene) reach approximately 18.6 nm and 25.0 nm, respectively. In the electronic absorption and emission spectra, the π–π^* transitions of the oligothiophenes demonstrate progressive red shifts with increasing chain length up to the 20-mer. In the cyclic voltammograms, furthermore, the first oxidation potentials tend to continue negative shifts up to the 34-mer. In accordance with these spectral changes, the doped conductivities steadily increase and approach that of a structurally related polymer.

Recently well-defined conjugated oligomeric molecules have attracted much attention in terms of not only useful alternatives to polymer systems, but also advanced nanoscale molecules.[1] As one of the most extensively studied classes,[2] an extended series of non-substituted α-linked oligothiophenes has been intensively prepared,[3] but no higher homologues than octithiophene were accessible because of their insolubility.[4] This inherent disadvantage of oligothiophenes can be overcome by the incorporation of solubilizing long alkyl groups at the β-positions, and thus many extended derivatives have been recently developed: the 9-mer,[5,6] 10-mer,[7] 11-mer,[5] 12-mer,[6,8,9] 15-mer,[6] 16-mer,[9] and 17-mer.[10] In addition, the solubilizing trimethylsilyl-substituted 24-mer[11] and dendron-substituted lengthy oligothiophenes[10,12] were reported very recently. A major topic concerning this research is to understand the correlation between the chain length and properties of polythiophenes; in other words, to establish the concept of an effective conjugation length regulating the characteristics of such conjugated systems. It is well known that oligothiophenes show progressive red shifts of the π–π^* electronic transitions, and an increase in the doped conductivities with increasing chain length. On the basis of an observation that the absorption spectra and doped conductivities of the 11-mer and 12-mer are very similar to those for polythiophenes, Wynberg and co-workers proposed that an effective conjugation length for doped polythiophenes is not much longer than 11 repeat units.[5] Even spectroscopic studies of shorter oligothiophenes also supported such a limited conjugation length.[6b,6d,13] However, it has been observed that for the longer 15-mer[6] and 16-mer,[9] no complete spectroscopic saturation occurs yet, and it was predicted on the basis of the extrapolation of a correlation function for the absorption maxima vs repeat units that the convergence occurs at 17-20 monomer units.[14] Thus, for a more comprehensive understanding, even longer oligothiophenes would be informative. This has prompted us to develop the longest class of oligothiophene systems. Here, we would like to report on the syntheses and properties of a series of oligothiophenes whose molecular lengths increase at intervals of tetraoctyl-substituted septithiophene segment, the 6-mer (abbreviated as **6T**), the 13-mer (**13T**), the 20-mer (**20T**), the 27-mer (**27T**), the 34-mer (**34T**), the 41-mer (**41T**), and the 48-mer (**48T**) (Chart 1).[15] Being long enough to correspond to polymers, these compounds might be very helpful for clarifying the concept of the effective conjugation length of the α-linked polythiophene system. In addition, such long conjugated molecules might acquire current interest as potential molecular wires in growing nanoarchitectures for molecular-scale electronic devices and to stimulate the still undeveloped chemistry



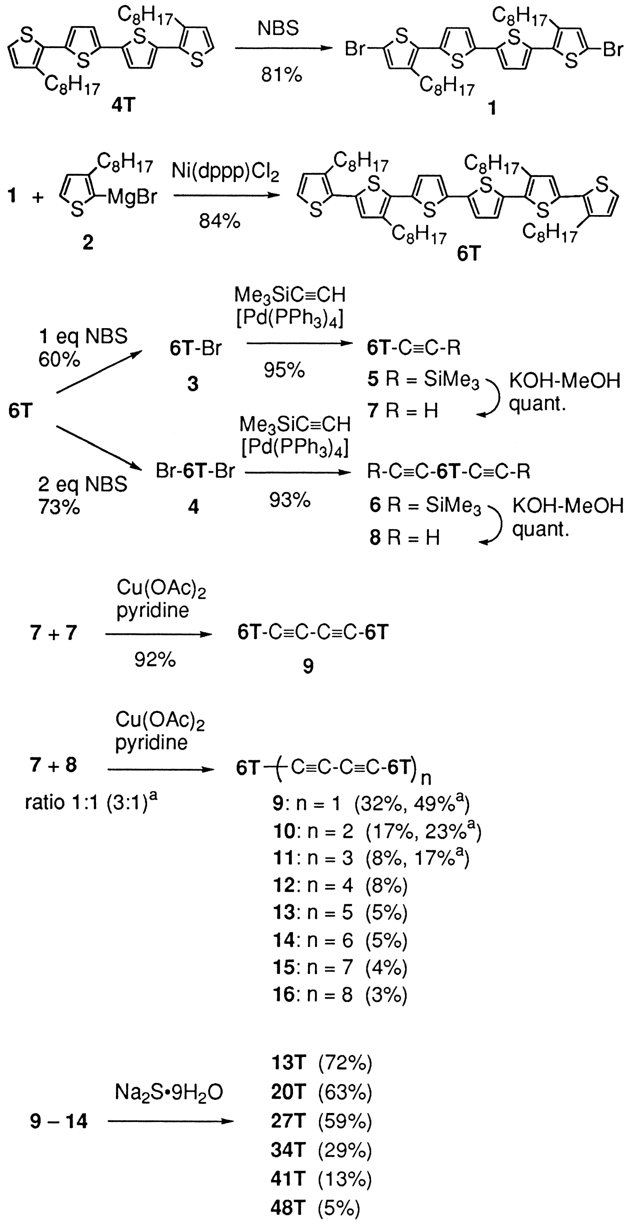
6T: n=0; **13T**: n=1; **20T**: n=2; **27T**: n=3; **34T**: n=4; **41T**: n=5; **48T**: n=6

Chart 1.

of well-defined monodisperse polymers.

Results and Discussion

Synthesis. The present long oligothiophenes were synthesized according to Scheme 1. First, the key intermediate, tetraoctylsexithiophene (**6T**), was obtained in 84% yield by the Ni(II)-catalyzed cross-coupling (Kumada coupling) of the dibromo derivative (**1**), prepared by the bromination of dioctylquaterthiophene (**4T**),[16] with a Grignard reagent of 2-bromo-3-octylthiophene (**2**).[17] Although a repeat of α-monohalogenation or monolithiation of oligothiophenes, and then the usual organometallic aryl–aryl coupling reactions, may lead to the formation of further higher oligomers, one must be troubled with a number of possible side reactions, such as bis-functionalization or β-functionalization for the former[18] and disproportionation coupling or hydrogenation for the latter.[17b] In order to avoid hard work concerning purification in the synthesis of higher oligomers, uncontaminated reactions are desired. For this purpose, we have adopted a combination reaction sequence of Eglinton coupling of ethynyloligothiophenes followed by sodium sulfide-induced 1,3-butadiyne cyclization. Kagan et al. have already used the same methodology for the synthesis of α-oligothiophene hexamer which, however, involves the Glaser reaction in the initial coupling step.[19] This reaction sequence has the advantage of no formation of analogous oligomeric by-products that are hard to remove. Thus, the treatment of **6T** with one equimolar NBS led to the formation of the monobromo derivative of tetraoctylsexithiophene (**3**) (60% yield), which was subsequently reacted with trimethylsilylacetylene in the presence of the [Pd(PPh$_3$)$_4$] catalyst to give the trimethylsilylethynyl derivative (**5**) (95% yield), and was then desilylated with potassium hydroxide to the ethynyl one (**7**) (quantitative yield). An Eglinton homo-coupling of **7** with copper(II) acetate in pyridine gave the bis(sexithienyl) diacetylene (**9**) in 92% yield, of which the diacetylene moiety was converted with sodium sulfide to **13T** in 72% yield.



Scheme 1.

In order to avoid any tedious iterative procedure for the synthesis of further higher oligomers, a random approach, including one-pot polymerization, has been used. Thus, a similar treatment of **6T** with two equimolar NBS gave the dibromo derivative (**4**) in 73% yield, which was similarly converted to the diethynyl one (**8**) in an excellent yield. An Eglinton cross-coupling reaction using a mixture of **7** and **8** in a 1:1 molar ratio gave a mixture of a series of the oligo(sexithienylene-diethynylene)s: **9** (32%), **10** (17%), **11** (8%), **12** (8%), **13** (5%), **14** (5%), **15** (4%), and **16** (3%). Thanks to a large difference in the molecular size, due to an interval of tetraoctyl-substituted sexithiophene segment, these oligo(sexithienylene-diethynylene)s could be readily separated by preparative gel-permeation (size exclusion) liquid chromatography (GPLC). An alternative cross-coupling of a mixture of **7** and **8** in a 3:1 molar ratio yielded **9** (49%), **10** (23%), and **11** (17%). Analogously to **9**, the treatments of **10–14** with sodium sulfide afforded the desired long oligothiophenes: **20T** (63%), **27T** (59%), **34T** (29%), **41T** (13%), and **48T** (5%), respectively. However, the yields markedly decreased in the elongated order because of an increasing number of reaction sites. Because of a drastic decrease not only in the yield, but also in the solubility, attempted reactions of **15** and **16** to obtain further longer oligothiophenes failed.

Structures. The obtained oligo(sexithienylene-diethynylene)s (**9–16**) and oligothiophenes (***n*T**) are dark-red or deep-purple amorphous solids; all of the oligo(sexithienylene-diethynylene)s and the lower oligothiophenes up to the 27-mer are relatively soluble in common solvents, but the solubilities of the higher oligothiophenes decrease with further extension of the chain; the longest 48-mer is sparingly soluble. Their structures were unambiguously characterized by MS and NMR measurements as well as elemental analyses. FAB MS was very effective for detecting the molecular ions of oligothiophenes up to the 27-mer. However, MALDI-TOF MS was needed to obtain the molecular ions of the higher oligomers, whose data are summarized in Table 1. In addition, the ^{1}H NMR spectra were very helpful for their structural characterization. For example, all of the complex signals due to the

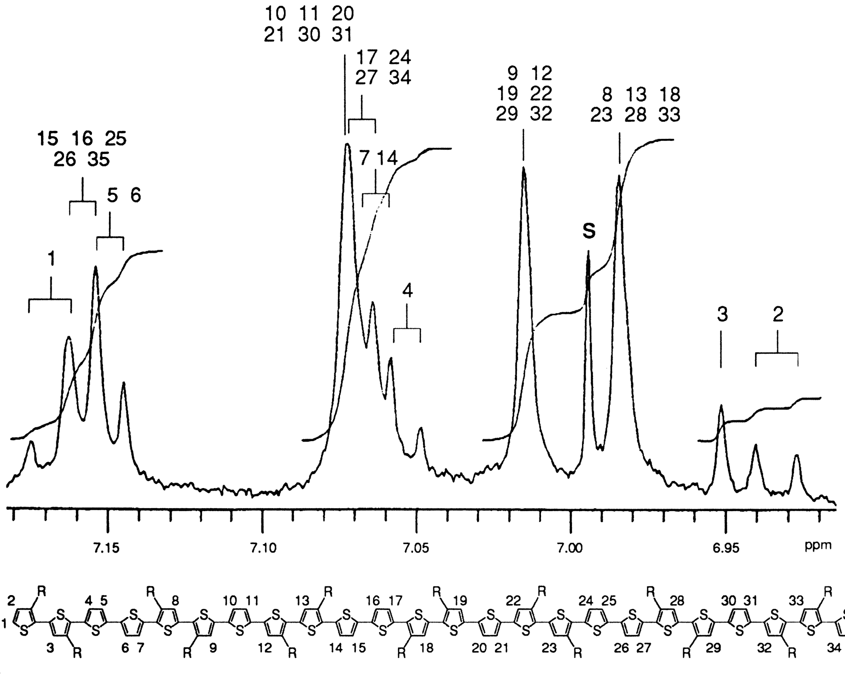


Fig. 1. Assignment of the thienyl proton signals in the ^{1}H NMR spectrum of **48T**; S denotes the ^{13}C satellite of $CHCl_3$.

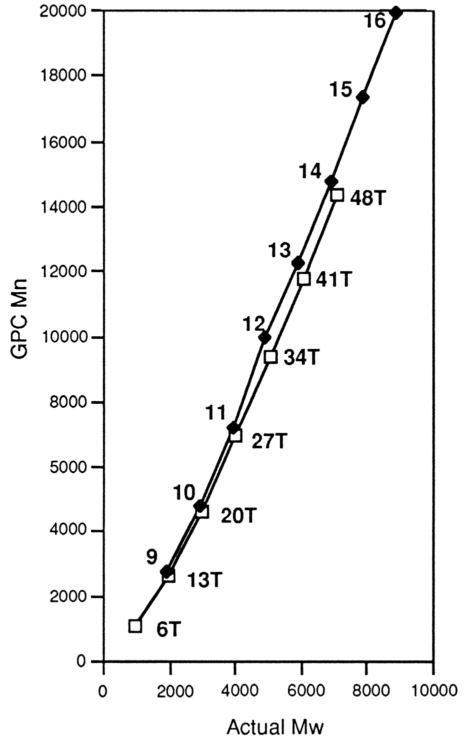


Fig. 2. Relationship of molecular weights determined by GPLC in tetrahydrofuran using polystyrene standards versus the actual molecular weights of oligothiophenes and oligo(sexithienylene-diethynylene)s.

thiophene protons of **48T** were successfully assignable, as depicted in Fig. 1. The complete assignments of all the thiophene protons of the oligothiophenes as well as the oligo(sexithienylene-diethynylene)s are also given in Table 1.

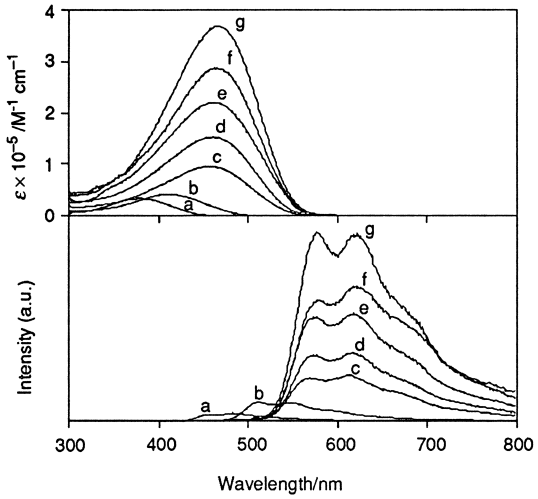


Fig. 3. Electronic absorption (upper) and emission spectra (lower) of oligothiophenes in tetrahydrofuran: (a) **4T**, (b) **6T**, (c) **13T**, (d) **20T**, (e) **27T**, (f) **34T**, and (g) **41T**.

Figure 2 demonstrates a good linear relationship of the actual molecular weights vs analytical GPLC molecular weights of the oligothiophene series. It has already been stated that the molecular weights of rod-type molecules, such as oligo(2,5-thienylene-ethynylene)s[20] and oligo(paraphenylene-ethynylene)s,[21] when measured by GPLC using randomly shaped polystyrene standards, are much inflated relative to the actual, while those of coil-type molecules, such as oligo(3,4-thienylene-ethynylene)s[22] are much deflated. Evidently the present oligothiophene series is the former case: the measured molecular weights are nearly double the actual ones. This strongly suggests that these oligothiophenes keep rigid rod-type shapes, even if the molecular chain is elongated. It is thus

Table 1. MS and ^{1}H NMR Data of Oligo(sexithienylene-diethynylene)s (**9–16**) and Oligothiophenes (***n*T**)

Compd	M$^+$ m/z (Calcd)[a]	Thiophene proton chemical shift δ[b]
9	1932.3, 1933[c] (1932.9)	H_1 7.16, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.07, H_8 6.99, H_9 7.17
10	2922.5, 2922[c] (2922.3)	H_1 7.17, H_2 6.92, H_3 6.95, H_4 7.04, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16
11	3911.8, 3913[c] (3911.9)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.04, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16, H_{14} 7.16, H_{15} 7.07, H_{16} 6.99, H_{17} 7.17
12	4902.0 (4901.6)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16, H_{14} 7.16, H_{15} 7.07, H_{16} 6.99, H_{17} 7.17, H_{18} 7.17, H_{19} 6.99, H_{20} 7.07, H_{21} 7.16
13	5891.1 (5891.3)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16, H_{14} 7.16, H_{15} 7.07, H_{16} 6.99, H_{17} 7.17, H_{18} 7.17, H_{19} 6.99, H_{20} 7.07, H_{21} 7.16, H_{22} 7.16, H_{23} 7.07 H_{24} 6.99, H_{25} 7.17
14	6883.1 (6881.0)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16, H_{14} 7.16, H_{15} 7.07, H_{16} 6.99, H_{17} 7.17, H_{18} 7.17, H_{19} 6.99, H_{20} 7.07, H_{21} 7.16, H_{22} 7.16, H_{23} 7.07 H_{24} 6.99, H_{25} 7.17, H_{26} 7.17, H_{27} 6.99, H_{28} 7.07, H_{29} 7.16
15	7868.5 (7870.6)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16, H_{14} 7.16, H_{15} 7.07, H_{16} 6.99, H_{17} 7.17, H_{18} 7.17, H_{19} 6.99, H_{20} 7.07, H_{21} 7.16, H_{22} 7.16, H_{23} 7.07, H_{24} 6.99, H_{25} 7.17, H_{26} 7.17, H_{27} 6.99, H_{28} 7.07, H_{29} 7.16, H_{30} 7.16, H_{31} 7.07, H_{32} 6.99, H_{33} 7.17
16	8860.4 (8860.3)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.99, H_9 7.17, H_{10} 7.17, H_{11} 6.99, H_{12} 7.07, H_{13} 7.16, H_{14} 7.16, H_{15} 7.07, H_{16} 6.99, H_{17} 7.17, H_{18} 7.17, H_{19} 6.99, H_{20} 7.07, H_{21} 7.16, H_{22} 7.16, H_{23} 7.07, H_{24} 6.99, H_{25} 7.17, H_{26} 7.17, H_{27} 6.99, H_{28} 7.07, H_{29} 7.16, H_{30} 7.16, H_{31} 7.07, H_{32} 6.99, H_{33} 7.17, H_{34} 7.17, H_{35} 6.99, H_{36} 7.07, H_{37} 7.16
6T	942.4, 942[c] (942.4)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5, 7.13
13T	1966.3, 1967[c] (1966.9)	H_1 7.17, H_2 6.92, H_3 6.95, H_4 7.05, H_5, 7.15, H_6 7.15, H_7 7.06, H_8 6.98, H_9 7.01, H_{10} 7.07
20T	2990.1, 2991[c] (2990.3)	H_1 7.16, H_2 6.93, H_3 6.95, H_4 7.04, H_5 7.14, H_6 7.14, H_7 7.05, H_8 6.98, H_9 7.00, H_{10} 7.06, H_{11} 7.06, H_{12} 7.00, H_{13} 6.98, H_{14} 7.05, H_{15} 7.15
27T	4014.7, 4015[c] (4014.2)	H_1 7.16, H_2 6.93, H_3 6.95, H_4 7.04, H_5, 7.14, H_6 7.14, H_7 7.06, H_8 6.98, H_9 7.01, H_{10} 7.07, H_{11} 7.07, H_{12} 7.01, H_{13} 6.98, H_{14} 7.06, H_{15} 7.15, H_{16} 7.15, H_{17} 7.07, H_{18} 6.98, H_{19} 7.01, H_{20} 7.07
34T	5039.3 (5037.9)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.98, H_9 7.01, H_{10} 7.07, H_{11} 7.07, H_{12} 7.01, H_{13} 6.98, H_{14} 7.06, H_{15} 7.16, H_{16} 7.16, H_{17} 7.07, H_{18} 6.98, H_{19} 7.01, H_{20} 7.07, H_{21} 7.07, H_{22} 7.01, H_{23} 6.98, H_{24} 7.07, H_{25} 7.16
41T	6061.2 (6061.7)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15 H_7 7.06, H_8 6.98, H_9 7.02, H_{10} 7.07, H_{11} 7.07, H_{12} 7.02, H_{13} 6.98, H_{14} 7.06, H_{15} 7.16, H_{16} 7.16, H_{17} 7.07, H_{18} 6.98, H_{19} 7.02, H_{20} 7.07, H_{21} 7.07, H_{22} 7.02, H_{23} 6.98, H_{24} 7.07, H_{25} 7.16, H_{26} 7.16, H_{27} 7.07, H_{28} 6.98, H_{29} 7.02, H_{30} 7.07
48T	7085.1 (7085.4)	H_1 7.17, H_2 6.93, H_3 6.95, H_4 7.05, H_5 7.15, H_6 7.15, H_7 7.06, H_8 6.98, H_9 7.02, H_{10} 7.07, H_{11} 7.07, H_{12} 7.02, H_{13} 6.98, H_{14} 7.06, H_{15} 7.16, H_{16} 7.16, H_{17} 7.07, H_{18} 6.98, H_{19} 7.02, H_{20} 7.07, H_{21} 7.07, H_{22} 7.02, H_{23} 6.98, H_{24} 7.07, H_{25} 7.16, H_{26} 7.16, H_{27} 7.07, H_{28} 6.98, H_{29} 7.02, H_{30} 7.07, H_{31} 7.07, H_{32} 7.12, H_{33} 6.98, H_{34} 7.07, H_{35} 7.16

a) Measured by MALDI TOF MS, unless otherwise stated. b) Numbered from the terminal ring protons to the central. c) Measured by FAB MS.

estimated on a molecular model with the energetically favorable *all-trans* orientation of the thiophene rings that the molecular size of the 13-mer has a length of 4.9 nm, the 20-mer 7.7 nm, the 27-mer 10.4 nm, the 34-mer 13.1 nm, the 41-mer 15.9 nm, and the 48-mer 18.6 nm. The oligo(sexithienylene-diethynylene)s also demonstrate GPLC retention volumes close to those of the respective oligothiophenes, meaning similar rod-type shapes; the molecular sizes are estimated to be as follows: **9** 5.0 nm; **10** 7.9 nm; **11** 10.7 nm; **12** 13.6 nm; **13** 16.4 nm; **14** 19.3 nm; **15** 22.1 nm; **16** 25.0 nm. These are thus of the longest class in fully conjugated molecular wires.[23]

Electronic Spectra. Figure 3 exhibits the electronic absorption and emission spectra of the oligothiophene series; as expected, the π–π^* transitions are progressively shifted to longer wavelengths with increasing chain length. The absorption and emission maxima are summarized in Table 2, providing definite information on the effective conjugation length. It is noticeable that there are convergent shifts of the absorption maxima up to the 20-mer, but no additional shift in going from the 20-mer to the 27-mer, though the absorption intensity per thiophene unit still increases. This result means that a certain limitation on the extensive conjugation occurs around the 20-mer. A similar chain-length dependence is also observed for the red shifts of their emission wavelengths. In addition, Table 2 gives that the fluorescence quantum yields increase with an extension of the thiophene conjugation from the 4-mer to the 6-mer, but remain constant for longer oligothiophenes.

Table 3 summarizes the spectral data of the oligo(sexithienylene-diethynylene) series. Both the absorption and emission maxima of **9** are considerably red-shifted compared to those of **6T**, meaning that the two sexithienylene segments are extensively conjugated over the diethynylene bridge. However, the

Table 2. Electronic Absorption Spectra,a) Emission Spectra,b) and Oxidation Potentialsc) of Oligothiophenes (**nT**)

Compd	$\lambda_{\max}^{\text{abs}}$/nm	$\varepsilon^{d)}$/M^{-1} cm^{-1}	$\lambda_{\max}^{\text{emis}}$/nm	ϕ_f	Epae)/V	Epcf)/V
4T	378	33500 (8380)	457, 482	0.16	0.93	—g)
6T	413	41900 (6980)	515, 549	0.37	0.78, 0.88h)	0.73, 0.83i)
13T	453	94000 (7230)	567, 616	0.32	0.65	0.51
20T	461	153000 (7650)	577, 622	0.37	0.55	0.46
27T	461	220000 (8150)	577, 622	0.32	0.53	0.44
34T	461	288000 (8470)	577, 622	0.39	0.49	0.40
41T	461	376000 (9170)	577, 622	0.35	0.48	0.39
48T	461	—j)	577, 622	—j)	—j)	—j)

a) Absorption spectra were measured in tetrahydrofuran. b) Emission spectra were measured in tetrahydrofuran on excitation at 440 nm (420 nm for **4T**). Quantum yields were deterimined relative to fluorescenein as standard (ϕ_f = 0.90 in 0.1 M NaOH). c) Cyclic voltammetry was measured at 25 °C for **4T** and **6T** and at 75 °C for the others in benzonitrile containing 0.1 M Bu_4NClO_4 using an Ag/AgCl standard electrode and Pt working electrode (scan rate 100 mV s^{-1}). d) Values in parenthesis indicate absorption intensity per thiophene unit. e) The first anodic peak. f) The first cathodic peak. g) Unmeasurable due to irreversibility. h) The second anodic peak i) The second cathodic peak. j) Unmeasurable due to low solubility.

Table 3. Electronic Absorptiona) and Emission Spectrab) of Oligo(sexithienylene-diethynylene)s

Compd	$\lambda_{\max}^{\text{abs}}$/nm	ε/M^{-1} cm^{-1}	$\lambda_{\max}^{\text{emis}}$/nm	ϕ_f
9	441	96500	568, 598	0.28
10	448	177000	568, 606	0.28
11	450	233000	568, 610	0.33
12	452	321000	568, 610	0.28
13	454	367000	568, 610	0.34
14	454	400000	568, 610	0.33
15	454	478000	568, 610	0.33
16	454	557000	568, 610	0.37

a) Absorption spectra were measured in tetrahydrofuran. b) Emission spectra were measured in tetrahydrofuran on excitation at 440 nm. Quantum yields were determined relative to fluorescein as standard (ϕ_f = 0.90 in 0.1 M NaOH).

somewhat shorter absorption maximum (441 nm) of **9** than that (453 nm) of **13T** indicates less effective conjugation for the former. In addition, the red-shifts with structural extension in this series last up to **13**, being more continual than the conjugation convergence in the oligothiophene series.

Cyclic Voltammetry. As shown in Fig. 4, the cyclic voltammogram of **4T** in a sweep from 0 to 1.2 V shows only one irreversible oxidation wave at 0.93 V. In the repeated sweep, a pair of redox peaks appears at lower potentials (E_{pa} 0.75 V and E_{pc} 0.69 V), suggesting the occurrence of dimerization. Unlike that of **4T**, the voltammogram of **6T** is reversible and shows two oxidation waves at 0.78 and 0.88 V. On the other hand, those of the longer oligothiophenes have a broad redox wave due to the superposition of multi-step oxidation processes over a wide range of 0.5–1.2 V. Although the waves are scarcely structured, the first oxidation peak and the corresponding reduction peak are distinguishable. As summarized in Table 2, the potentials of both peaks also decrease along the oligomeric series. Apparently, there is an appreciable difference in the oxidation potentials between the 27-mer and the 34-mer, in contrast to the above-discussed electronic spectra. This indicates that the long oligothiophenes in the cationic state assume more extensive conjugation for charge delocalization than in the neutral one.

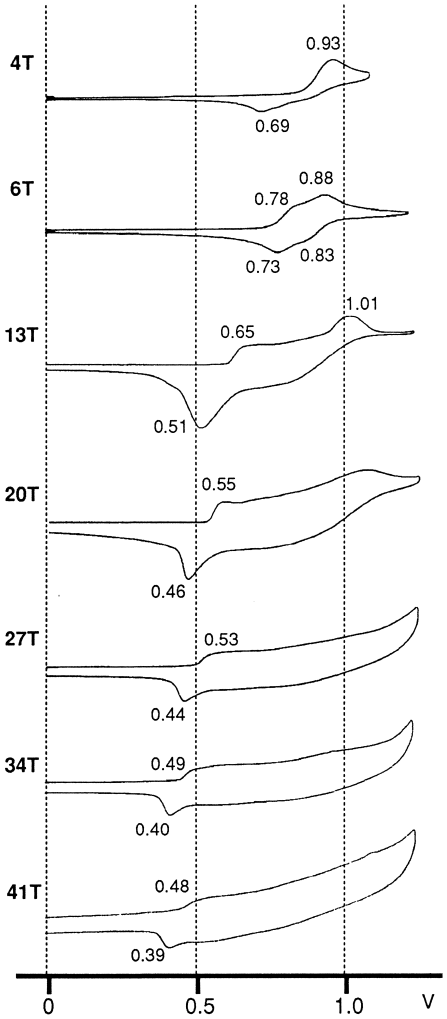


Fig. 4. Cyclic voltammograms of oligothiophenes (vs. Ag/AgCl in benzonitrile).

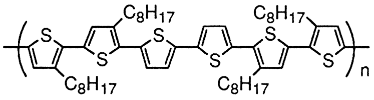
Electrical Conductivities. Since the electrical conductiv-

Table 4. Electrical Conductivities[a)] of Doped Oligothiophenes (***n*****T**)[b)]

Compd	σ/S cm^{-1}		
	$FeCl_3$ doping[c)]	I_2 doping[d)]	Electrochemical doping[e)]
6T	1.2–3.0 (21%)	0.025–0.056 (20%)	0.62 (17%)
13T	5.0–7.7 (23%)	3.2–3.7 (20%)	5.6 (23%)
20T	11–21 (17%)	5.2–8.9 (17%)	9.7 (20%)
27T	13–35 (16%)	12–25 (19%)	28 (22%)
34T	12–36 (21%)	16–38 (—)[f)]	—[g)]
41T	22 (17%)	—[f)]	—[g)]

a) Conductivities were measured on films by a four-probe method. Several measurements for each sample were carried out except for the electrochemically doped samples and the $FeCl_3$ doped sample of **41T**. b) The recovery of the oligothiophenes by reduction of the doped samples with hydrazine hydrate confirmed that no oligomerization or polymerization occurs during the doping. c) Chemical doping by immersing the oligothiophene film in a 0.05 M acetonitrile solution of $FeCl_3$. Values in parentheses indicate doping level per thiophene unit, calculated on the basis of elemental analysis by assuming $FeCl_4^-$ for the counterion. d) Chemical doping by exposure of the oligothiophene film to excess iodine vapor. Values in parentheses indicate doping level per thiophene unit, calculated on the basis of elemental analysis by assuming I_3^- for the counterion. e) Electrochemical doping at 1.0 V in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte. Values in parentheses indicate doping level per thiophene unit, calculated on the basis of elemental analysis by assuming ClO_4^- for the counterion. f) Unmeasurable due to labile dedoping. g) Unmeasurable because of exfoliation of the film from the ITO electrode during doping.

ities of polythiophenes had been pointed out to depend on the thickness and morphology of the measured samples,[24] we examined the relative conductivities of the present oligothiophene series up to **41T** using similar thin films of ca. 100 µm in thickness, which were prepared by casting their carbon disulfide solutions on glass or ITO plates. When chemically oxidized by a treatment with $FeCl_3$ in acetonitrile or by exposure to vaporized iodine or electrochemically oxidized in acetonitrile containing tetrabutylammonium perchlorate as a supporting electrolyte, the oligothiophene films, nearly insulating in the neutral state, became conductive with increasing doping level. Although the iodine-doped conductivity of **41T** could not be measured because of ready dedoping and the electrochemically doped conductivities of **34T** and **41T** because of exfoliation of the film from the ITO electrode during doping, the other measurements, irrespective of the doping method, gave reliable data, except for **6T**, with a deviation of two orders of magnitude, as summarized in Table 4. The full doping levels are ca. 20%, almost independent of the oligothiophene species as well as the doping method. This simply means the distribution of a positive charge per five-thiophene sequence (polaron)[25] in the conjugation system. There is evidently a progressive increase in conductivity from the 6-mer up to approximately the 27-mer. Interestingly, this change resembles the optical and voltammetric changes described above. The relatively low conductivity of the 6-mer is simply ascribable to an insufficient conduction pathway and/or the involvement of only charge carrier species with a limited length, such as polarons or π-dimers.[26] On the other hand, the gradual increases of conductivity from the 6-mer to the 27-mer imply that the extension of the conjugated system is advantageous to charge transport not only among the adjacent oligomeric chains but also along the oligomeric chains. In addition, more spreadable charge carrier species such as two individual polarons on a single chain[27] and bipolarons[28] can participate in the charge-carrier species. It is worth noting that the converged conductivities (12–38 S cm^{-1}) of the long oligothiophenes (**27T**, **34T**, and **41T**) are nearly identical to the values (17 S cm^{-1} for $FeCl_3$ doping and 18 S cm^{-1} for iodine doping) of poly(sexithiophene) (**17**) (Chart 2), which was prepared by nickel-catalyzed reductive polymerization of the dibromosexithiophene (**4**). It is apparent that the charge transport is governed by the effective conjugation length of 20–30 thiophene units. On the other hand, similar $FeCl_3$ oxidation of the oligo(sexithienylene-diethynylene)s **9–11** showed conductivities of the order of 10^{-1} S cm^{-1}, which were similar to that of **6T** and independent of the chain length, in contrast to the oligothiophene series: **9**, 0.44 S cm^{-1}; **10**, 0.073 S cm^{-1}; **11**, 0.095 S cm^{-1}. This can be rationalized in terms of less effective conjugation of the oligo(sexithienylene-diethynylene)s due to the incorporation of diethynylene bridges, which must prevent charge transport along the oligomeric chains and disallow the involvement of the speredable charge carrier species.



17

Chart 2.

Conclusion

In order to investigate the effect of chain length on the extent of conjugation, we have succeeded in the synthesis of a series of well-characterized oligothiophenes up to the 48-mer. Among them, the higher members are of the longest class in fully conjugated nanoscale molecules and are long enough to belong to monodisperse polymers. From studies of their electronic spectra, cyclic voltammograms, and doped conductivities, it has been concluded that the effective conjugation length of the oligothiophene systems is extended to a wide range of approximately 20–30 conjugated repeat units, much longer than that previously described, which has control over the optical and electroconductive properties of long oligothiophenes and polythiophenes.

Experimental

General. All melting points are uncorrected. All chemicals and solvents were of reagent grade. NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in deuteriochloroform with tetramethylsilane as an internal standard. MS spectra were measured with a JEOL JMS-SX 102A (FAB) spectrometer using a 3-nitrobenzyl alcohol matrix or a Shimadzu KOMPACT-MALDI PROBE (MALDI-TOF) using a dithranol matrix.[29] Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Emission spectra were taken on a Shimadzu RF-5000 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator.

5,5‴-Dibromo-3,3‴-dioctyl-2,2′:5′,2″:5″,2‴-quaterthiophene (1). A solution of NBS (2.7 g, 15.6 mmol) in DMF (10 mL) was added into a mixture of **4T**[16] (4.3 g, 7.8 mmol), DMF (40 mL), and carbon disulfide (50 mL) with ice-cooling. The mixture was stirred at room temperature for 5 h and treated with satd. aq. sodium hydrogencarbonate (100 mL). After the insoluble materials were removed by filtration through a celite pad, the organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and the extract were combined, washed successively with brine and water, and dried (MgSO$_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane) followed by recrystallization from hexane to give yellow leaflets of **1** (4.5 g, 81%): mp 54–55 °C (Ref. 16, mp 61–63 °C); MS (FAB) *m/z* 710, 712, 714 (M^{+}); ^{1}H NMR δ 0.87 (t, J = 6.8 Hz, 6H), 1.29 (m, 20H), 1.63 (m, 4H), 2.70 (t, J = 6.8 Hz, 4H), 6.90 (s, 2H), 6.95 (d, J = 3.9 Hz, 2H), 7.10 (d, J = 3.9 Hz, 2H); Anal. Calcd for $C_{32}H_{40}Br_2S_4$: C, 53.92; H, 5.67%. Found: C, 53.90; H, 5.65%.

3,4′,3⁗,3′′′′′-Tetraoctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene (6T). Into a stirred mixture of **1** (6.0 g, 8.4 mmol) and Ni(dppp)Cl$_2$ (100 mg, 0.18 mmol) in dry ether (60 mL) was added the Grignard reagent (**2**) freshly prepared from 2-bromo-3-octylthiophene[17] (7.0 g, 25.2 mmol) and magnesium (674 mg, 27.8 mmol) in dry ether (40 mL). The mixture was refluxed for 5 h, then cooled to 0 °C, and quenched with satd. aq ammonium chloride (100 mL). After the insoluble materials were removed by filtration through a celite pad, the organic layer was separated, and the aqueous layer was extracted with chloroform (50 mL × 3). The organic layer and the extract were combined and washed successively with satd. aq sodium hydrogencarbonate (200 mL), brine (200 mL), and water (200 mL). After dryness (MgSO$_4$), the solvent was evaporated, and the residue was purified by column chromatography (silica gel, hexane) followed by recrystallization from hexane to give red crystals of **6T** (6.6 g, 84%); mp 41–42 °C; ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 12H), 1.31 (m, 40H), 1.66 (m, 8H), 2.78 (t, J = 7.6 Hz, 8H), 6.93 (d, J = 5.1 Hz, 2H), 6.95 (s, 2H), 7.05 (d, J = 3.9 Hz, 2H), 7.13 (d, J = 3.9 Hz, 2H), 7.17 (d, J = 5.1 Hz, 2H); ^{13}C NMR δ 14.10, 22.67, 29.43, 29.55, 30.53, 30.69, 31.90, 123.66, 123.89, 126.34, 128.76, 130.11, 130.16, 130.42, 134.39, 135.05, 136.75, 139.72, 140.03; Anal. Calcd for $C_{56}H_{78}S_6$: C, 71.27; H, 8.35%. Found: C, 71.18; H, 8.30%.

5-Bromo-3,4′,3⁗,3′′′′′-tetraoctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene (3). A solution of NBS (265 mg, 1.5 mmol) in DMF (10 mL) was added into a mixture of **6T** (1.4 g, 1.5 mmol), DMF (50 mL), and carbon disulfide (30 mL) with ice-cooling. The mixture was stirred at room temperature for 5 h and then treated with satd. aq sodium hydrogencarbonate (40 mL). After the insoluble materials were removed by filtration through a celite pad, the organic layer was separated, and the aqueous layer was extracted with chloroform (50 mL × 3). The organic layer and the extract were combined, washed with water (100 mL × 2), and dried (MgSO$_4$). After evaporation of the solvent, the residue was a product mixture of **3**, **4**, and **6T**, which was purified by column chromatography (silica gel, hexane) to give an orange oil of **3** (900 mg, 60%); MS (FAB) *m/z* 1020, 1022 (M^{+}); ^{1}H NMR δ 0.88 (m, 12H), 1.30 (m, 40H), 1.66 (m, 8H), 2.71 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 6H), 6.88 (s, 1H), 6.89 (s, 1H), 6.93 (d, J = 5.1 Hz, 1H), 6.95 (s, 1H), 7.04 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.9 Hz, 1H), 7.13 (d, J = 3.9 Hz, 1H), 7.14 (d, J = 3.9 Hz, 1H), 7.17 (d, J = 5.1 Hz, 1H); ^{13}C NMR δ 14.13, 22.69, 29.25, 29.29, 29.38, 29.43, 29.55, 30.54, 30.69, 31.90, 110.37, 123.69, 123.91, 123.98, 126.35, 126.54, 128.78, 129.13, 130.13, 130.41, 130.73, 131.95, 132.74, 132.96, 134.43, 134.70, 135.16, 136.63, 137.00, 139.75, 140.08, 140.30; Anal. Calcd for $C_{56}H_{77}BrS_6$: C, 65.76; H, 7.80%. Found: C, 65.66; H, 7.75%.

5,5′′′′′-Dibromo-3,4′,3⁗,3′′′′′-tetraoctyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene (4). Compound **4** was obtained in 73% yield by the treatment of **6T** with two equimolar NBS in a similar manner as described for **3**: orange fine crystals from hexane; mp 40–41.5 °C; MS (FAB) *m/z* 1098, 1100, 1102 (M^{+}); ^{1}H NMR δ 0.88 (t, J = 7.0 Hz, 12H), 1.30 (m, 40H), 1.66 (m, 8H), 2.71 (t, J = 8.0 Hz, 4H), 2.77 (t, J = 8.0 Hz, 4H), 6.88 (s, 2H), 6.89 (s, 2H), 7.04 (d, J = 3.9 Hz, 2H), 7.14 (d, J = 3.9 Hz, 2H); ^{13}C NMR δ 14.10, 22.67, 29.23, 29.26, 29.37, 29.41, 29.52, 30.50, 30.53, 31.88, 110.38, 123.96, 126.51, 129.10, 130.68, 132.72, 132.97, 134.80, 136.86, 140.08, 140.28; Anal. Calcd for $C_{56}H_{76}Br_2S_6$: C, 61.09; H, 6.97%. Found: C, 61.26; H, 6.96%.

3,4′,3⁗,3′′′′′-Tetraoctyl-5-(trimethylsilylethynyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene (5). Into a solution of **3** (350 mg, 0.338 mmol), [Pd(Ph$_3$P)$_4$] (100 mg, 0.0858 mmol), and copper(I) iodide (30 mg, 0.158 mmol) in triethylamine (12 mL) heated to 70 °C was added trimethylsilyl acetylene (0.3 mL, 2.13 mmol); the resulting mixture was stirred at the temperature for 5 h. After being cooled to room temperature, the mixture was poured into 5 M hydrochloric acid (50 mL) with ice-cooling. After the insoluble materials were removed by filtration through a celite, the filtrate was extracted with chloroform (30 mL × 3). The extract was successively washed with satd. aq sodium hydrogencarbonate (30 mL) and water (30 mL × 2), and dried (MgSO$_4$). After evaporation, column chromatography of the residue (silica gel, hexane) gave an orange oil of **5** (338 mg, 95%): MS (FAB) *m/z* 1038 (M^{+}); ^{1}H NMR δ 0.25 (s, 9H), 0.88 (m, 12H), 1.28 (m, 40H), 1.67 (m, 8H), 2.75 (m, 8H), 6.93 (d, J = 5.1 Hz, 1H), 6.94 (s, 1H), 6.95 (s, 1H), 7.04 (d, J = 3.9 Hz, 2H), 7.05 (s, 1H), 7.13 (d, J = 3.9 Hz, 1H), 7.14 (d, J = 3.9 Hz, 1H), 7.17 (d, J = 5.1 Hz, 1H); ^{13}C NMR δ -0.12, 14.12, 22.69, 29.26, 29.29, 29.40, 29.44, 29.56, 30.41, 30.50, 30.54, 30.70, 31.90, 97.58, 99.75, 120.68, 123.69, 123.91, 123.99, 126.35, 126.54, 128.78, 129.11, 130.13, 130.13, 130.41, 130.78, 132.40, 133.40, 134.43, 134.74, 135.16, 135.71, 136.64, 136.99, 139.29, 139.75, 140.07, 140.13; IR (neat) 2143 cm^{-1} (C$\equiv$C); Anal. Calcd for $C_{61}H_{86}S_6Si$: C, 70.45; H, 8.35%. Found: C, 70.57; H, 8.44%.

3,4′,3′′′′,3′′′′′-Tetraoctyl-5,5′′′′′-bis(trimethylsilylethynyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (6). Compound **6** was obtained in 93% yield from **4** in a similar manner as described for **5**: red leaflets from hexane; mp 38 °C; MS (FAB) *m*/*z* 1134 (M$^+$); ^{1}H NMR δ 0.25 (s, 18H), 0.88 (m, 12H), 1.27 (m, 40H), 1.65 (m, 8H), 2.72 (t, *J* = 8.0 Hz, 4H), 2.77 (t, *J* = 8.0 Hz, 4H), 6.95 (s, 2H), 7.05 (d, *J* = 3.9 Hz, 2H), 7.06 (s, 2H), 7.14 (d, *J* = 3.9 Hz, 2H); ^{13}C NMR δ −0.12, 14.13, 22.69, 29.25, 29.27, 29.38, 29.43, 29.54, 30.40, 30.49, 31.89, 97.57, 99.76, 120.68, 123.99, 126.53, 129.11, 130.73, 132.38, 133.42, 134.83, 135.71, 136.87, 139.29, 140.14; IR (neat) 2145 cm^{-1} (C≡C); Anal. Calcd for $C_{66}H_{94}S_6Si_2$: C, 69.77; H, 8.36%. Found: C, 69.68; H, 8.26%.

5-Ethynyl-3,4′,3′′′′,3′′′′′-tetraoctyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (7). Into a solution of **6** (250 mg, 0.24 mmol) in benzene (15 mL) and methanol (12 mL) was added potassium hydroxide (60 mg, 1.07 mmol), and the mixture was stirred at rt for 8 h. After water (50 mL) had been added, the mixture was extracted with benzene (30 mL × 2), and the extract was washed successively with satd. aq ammonium chloride (50 mL) and water (50 mL) and dried ($MgSO_4$). After evaporation, the residue was purified by column chromatography (silica gel, hexane) to give an orange oil of **7** (232 mg, quant): MS (FAB) *m*/*z* 966 (M$^+$); ^{1}H NMR δ 0.88 (t, *J* = 7.0 Hz, 12H), 1.30 (m, 40H), 1.66 (m, 8H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 6H), 3.38 (s, 1H), 6.93 (d, *J* = 5.1 Hz, 1H), 6.95 (s, 1H), 6.96 (s, 1H), 7.04 (d, *J* = 3.9 Hz, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 7.10 (s, 1H), 7.14 (d, *J* = 3.9 Hz, 2H), 7.16 (d, *J* = 5.1 Hz, 1H); IR (neat) 3310 (≡C–H), 2101 cm^{-1} (C≡C); Anal. Calcd for $C_{58}H_{78}S_6$: C, 71.98; H, 8.14%. Found: 72.08; H, 8.34%.

5,5′′′′′-Diethynyl-3,4′,3′′′′,3′′′′′-tetraoctyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (8). Compound **8** was obtained as an orange oil in a quantitative yield from **6** in a similar manner as described for **7**: MS (FAB) *m*/*z* 990 (M$^+$); ^{1}H NMR δ 0.88 (m, 12H), 1.27 (m, 40H), 1.65 (m, 8H), 2.73 (t, *J* = 7.8 Hz, 4H), 2.78 (t, *J* = 7.8 Hz, 4H), 3.39 (s, 2H), 6.96 (s, 2H), 7.06 (d, *J* = 3.8 Hz, 2H), 7.11 (s, 2H), 7.15 (d, *J* = 3.8 Hz, 2H); IR (neat) 3308 (≡C–H), 2101 cm^{-1} (C≡C); Anal. Calcd for $C_{60}H_{78}S_6$: C, 72.61; H, 7.94%. Found: C, 72.66; H, 8.16%.

Eglinton Homo-Coupling Reaction of 7 to Bis(sexithienyl)diacetylene (9). A mixture of **7** (690 mg, 0.72 mmol) and copper(II) acetate hydrate (1.2 g, 6.0 mmol) in pyridine (40 mL) was stirred with at 40 °C for 5 h and then treated with 5 M hydrochloric acid (20 mL) with ice-cooling. The insoluble materials were removed by filtration through a celite pad, and the filtrate was extracted with carbon disulfide (100 mL × 2). The extract was washed successively with satd. aq sodium hydrogencarbonate (150 mL) and water (150 mL × 2) and dried ($MgSO_4$). After evaporation, the residue was purified by column chromatography (silica gel, carbon disulfide) to give a dark red viscous oil of **9** (630 mg, 92%); ^{1}H NMR δ 0.88 (m, 24H), 1.28 (m, 80H), 1.66 (m, 16H), 2.77 (m, 16H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 2H), 7.05 (d, *J* = 3.9 Hz, 2H), 7.07 (d, *J* = 3.9 Hz, 2H), 7.15 (d, *J* = 3.9 Hz, 4H), 7.16 (d, *J* = 5.1 Hz, 2H), 7.17 (s, 2H); IR (neat) 2188, 2136 cm^{-1} (C≡C); Anal. Calcd for $C_{116}H_{154}S_{12}$: C, 72.06; H, 8.04%. Found: C, 72.17; H, 8.02%.

Eglinton Cross-Coupling Reaction of 7 and 8 to a Series of Oligo(sexithienylene-diethynylene)s. A mixture of **7** (56 mg, 0.058 mmol) and **8** (57 mg, 0.057 mmol) in pyridine (12 mL) was stirred with copper(II) acetate hydrate (230 mg, 1.15 mmol) at 40 °C for 8 h and then treated with 5 M hydrochloric acid (5 mL) with ice-cooling. The insoluble materials were removed by filtration through a celite pad, and the filtrate was extracted with carbon disulfide (30 mL × 2). The extract was washed successively with satd. aq sodium hydrogencarbonate (50 mL) and water (50 mL × 2) and dried ($MgSO_4$). After evaporation, the residue was purified by column chromatography (silica gel, carbon disulfide) to give a mixture of the oligo(sexithienylene-diethynylene)s, which were separated by preparative gel permeation liquid chromatography (JAIGEL 3H/4H) with chloroform eluent and eluted in the order of **16** (retention volume 211 mL, 2.1 mg, 3%), **15** (214 mL, 2.8 mg, 4%), **14** (219 mL, 4.0 mg, 5%), **13** (224 mL, 4.5 mg, 5%), **12** (228 mL, 7.3 mg, 8%), **11** (236 mL, 9.3 mg, 8%), **10** (245 mL, 14.3 mg, 17%), and **9** (257 mL, 18.1 mg, 32%).

A similar Eglinton cross-coupling reaction of **7** (75 mg, 0.078 mmol) and **8** (25 mg, 0.025 mmol) gave a mixture of **9** (36.8 mg, 49%), **10** (17.2 mg, 23%), and **11** (8.6 mg, 17%) together with negligible amounts of the higher oligomers.

10: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 36H), 1.28 (m, 120H), 1.68 (m, 24H), 2.77 (m, 24H), 6.92 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 4H), 7.04 (d, *J* = 3.9 Hz, 2H), 7.06 (d, *J* = 3.9 Hz, 2H), 7.07 (d, *J* = 3.9 Hz, 2H), 7.15 (d, *J* = 3.9 Hz, 4H) 7.16 (d, *J* = 3.9 Hz, 2H), 7.17 (d, *J* = 5.1 Hz, 2H,), 7.17 (s, 4H); IR (neat) 2188, 2136 cm^{-1} (C≡C); Anal. Calcd for $C_{176}H_{230}S_{18}$: C, 72.31; H, 7.95%. Found: C, 72.11; H, 8.05%.

11: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 48H), 1.28 (m, 160H), 1.68 (m, 32H), 2.77 (m, 32H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 6H), 7.04 (d, *J* = 3.9 Hz, 2H), 7.06 (d, *J* = 3.9 Hz, 2H), 7.07 (d, *J* = 3.9 Hz, 4H), 7.15 (d, *J* = 3.9 Hz, 4H), 7.16 (d, *J* = 3.9 Hz, 4H), 7.17 (d, *J* = 5.1 Hz, 2H), 7.17 (s, 6H); IR (neat) 2188, 2136 cm^{-1} (C≡C); Anal. Calcd for $C_{236}H_{306}S_{24}$: C, 72.44; H, 7.89%. Found: C, 72.60; H, 8.10%.

12: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 60H), 1.28 (m, 200H), 1.67 (m, 40H), 2.76 (m, 40H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 8H), 7.05 (d, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 3.7 Hz, 6H), 7.15 (d, *J* = 3.7 Hz, 4H), 7.16 (d, *J* = 3.7 Hz, 6H), 7.17 (s, 8H), 7.17 (d, *J* = 5.1 Hz, 2H); IR (neat) 2188, 2136 cm^{-1} (C≡C); Anal. Calcd for $C_{296}H_{382}S_{30}$: C, 72.53; H, 7.85%. Found: C, 72.53; H, 7.85%.

13: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 72H), 1.28 (m, 240H), 1.67 (m, 48H), 2.77 (m, 48H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 10H), 7.05 (d, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 3.7 Hz, 8H), 7.15 (d, *J* = 3.7 Hz, 4H), 7.16 (d, *J* = 3.7 Hz, 8H), 7.17 (s, 10H), 7.17 (d, *J* = 5.1 Hz, 2H); IR (neat) 2188, 2136 cm^{-1} (C≡C); Anal. Calcd for $C_{356}H_{458}S_{36}$: C, 72.58; H, 7.84%. Found: C, 72.31; H, 7.95%.

14: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 84H), 1.28 (m, 280H), 1.68 (m, 56H), 2.77 (m, 56H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 12H), 7.05 (d, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 3.7 Hz, 10H), 7.15 (d, *J* = 3.7 Hz, 4H), 7.16 (d, *J* = 3.7 Hz, 10H), 7.17 (s, 12H), 7.17 (d, *J* = 5.1 Hz, 2H); IR (KBr) 2186, 2134 cm^{-1} (C≡C); Anal. Calcd for $C_{416}H_{534}S_{42}$: C, 72.61; H, 7.82%. Found: C, 72.63; H, 7.86%.

15: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 96H), 1.28 (m, 320H), 1.67 (m, 64H), 2.77 (m, 64H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 14H), 7.05 (d, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 3.7 Hz, 12H), 7.15 (d, *J* = 3.7 Hz, 4H), 7.16 (d, *J* = 3.7 Hz, 12H), 7.17 (s, 14H), 7.17 (d, *J* = 5.1 Hz, 2H); IR (KBr) 2134 cm^{-1} (C≡C); Anal. Calcd for $C_{476}H_{610}S_{48}$: C, 72.64; H, 7.81%. Found: C, 72.62; H, 8.11%.

16: a dark red viscous oil; ^{1}H NMR δ 0.88 (m, 108H), 1.28 (m, 360H), 1.67 (m, 72H), 2.77 (m, 72H), 6.93 (d, *J* = 5.1 Hz, 2H), 6.95 (s, 2H), 6.99 (s, 16H), 7.05 (d, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 3.7 Hz, 14H), 7.15 (d, *J* = 3.7 Hz, 4H), 7.16 (d, *J* = 3.7 Hz, 14H), 7.17 (s, 16H), 7.17 (d, *J* = 5.1 Hz, 2H);

IR (neat) 2134 $\mathrm{cm^{-1}}$ (C≡C); Anal. Calcd for $C_{536}H_{686}S_{54}$: C, 72.66; H, 7.80%. Found: C, 72.48; H, 7.79%.

Preparations of the Long Oligothiophenes. A typical procedure is described concerning the preparation of **13T**. A mixture of **9** (150 mg, 0.077 mmol), $Na_2S{\cdot}9H_2O$ (75 mg, 0.31 mmol), and KOH (10 mg) in dioxane (40 mL) was refluxed for 20 h. After water (100 mL) was added, the mixture was extracted with chloroform (30 mL × 3), and the extract was dried ($MgSO_4$). After evaporation, the residue was purified by column chromatography (silica gel, carbon disulfide) and then preparative gel permeation liquid chromatography (JAIGEL 3H/4H, chloroform) to give a dark-red amorphous solid of **13T** (100 mg, 72%): ^{1}H NMR δ 0.88 (m, 24H), 1.28 (m, 80H), 1.66 (m, 16H), 2.77 (m, 16H), 6.92 (d, J = 5.1 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 2H), 7.01 (s, 2H), 7.05 (d, J = 3.9 Hz, 2H), 7.06 (d, J = 3.9 Hz, 2H), 7.07 (s, 2H), 7.15 (d, J = 3.9 Hz, 4H), 7.17 (d, J = 5.1 Hz, 2H); ^{13}C NMR δ 14.44, 23.00, 29.61, 29.75, 29.88, 30.78, 30.84, 31.00, 32.22, 123.98, 124.22 (× 2), 124.54, 126.64, 126.67, 129.96, 128.92, 129.06, 130.02, 130.43, 130.45, 130.66, 130.72, 134.21, 134.70, 134.96, 135.23, 135.40, 136.27, 136.99, 137.13, 140.03, 140.33, 140.41, 140.75; Anal. Calcd for $C_{116}H_{156}S_{13}$: C, 70.81; H, 8.01%. Found: C, 70.84; H, 8.09%.

20T: a dark-red amorphous solid (63% yield): ^{1}H NMR δ 0.88 (m, 36H), 1.28 (m, 120H), 1.68 (m, 24H), 2.77 (m, 24H), 6.93 (d, J = 5.1 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 4H), 7.00 (s, 4H), 7.04 (d, J = 3.9 Hz, 2H), 7.05 (d, J = 3.9 Hz, 4H), 7.06 (s, 4H), 7.14 (d, J = 3.9 Hz, 4H), 7.15 (d, J = 3.9 Hz, 2H), 7.16 (d, J = 5.1 Hz, 2H); Anal. Calcd for $C_{176}H_{234}S_{20}$: C, 70.66; H, 7.90%. Found: C, 70.63; H, 7.96%.

27T: a dark-red amorphous solid (59% yield): ^{1}H NMR δ 0.88 (m, 48H), 1.28 (m, 160H), 1.68 (m, 32H), 2.77 (m, 32H), 6.93 (d, J = 5.1 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 6H), 7.01 (s, 6H), 7.04 (d, J = 3.9 Hz, 2H), 7.06 (d, J = 3.9 Hz, 4H), 7.07 (d, J = 3.9 Hz, 2H), 7.07 (s, 6H), 7.14 (d, J = 3.9 Hz, 4H), 7.15 (d, J = 3.9 Hz, 4H), 7.16 (d, J = 5.1 Hz, 2H); Anal. Calcd for $C_{236}H_{312}S_{27}$: C, 70.60; H, 7.85%. Found: C, 70.68; H, 7.84%.

34T: a deep-purple amorphous solid (29% yield); ^{1}H NMR δ 0.88 (m, 60H), 1.28 (m, 200H), 1.67 (m, 40H), 2.79 (m, 40H), 6.93 (d, J = 5.4 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 8H), 7.01 (s, 8H), 7.05 (d, J = 3.6 Hz, 2H), 7.06 (d, J = 3.6 Hz, 4H), 7.07 (d, J = 3.6 Hz, 4H), 7.07 (s, 8H), 7.15 (d, J = 3.6 Hz, 4H), 7.16 (d, J = 3.6 Hz, 6H), 7.17 (d, J = 5.4 Hz, 2H); Anal. Calcd for $C_{296}H_{390}S_{34}$: C, 70.56; H, 7.80%. Found: C, 70.33; H, 7.79%.

41T: a deep-purple amorphous solid (13% yield); ^{1}H NMR δ 0.88 (m, 72H), 1.28 (m, 240H), 1.67 (m, 48H), 2.79 (m, 48H), 6.93 (d, J = 5.4 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 10H), 7.02 (s, 10H), 7.05 (d, J = 3.9 Hz, 2H), 7.06 (d, J = 3.5 Hz, 4H), 7.07 (d, J = 3.1 Hz, 6H), 7.07 (s, 10H), 7.15 (d, J = 3.6 Hz, 4H), 7.16 (d, J = 3.4 Hz, 8H), 7.17 (d, J = 5.4 Hz, 2H); Anal. Calcd for $C_{356}H_{468}S_{41}$: C, 70.54; H, 7.78%. Found: C, 70.57; H, 7.84%.

48T: a deep-purple amorphous solid (5% yield); ^{1}H NMR δ 0.89 (m, 84H), 1.27–1.28 (m, 280H), 1.67 (m, 56H), 2.79 (m, 56H), 6.93 (d, J = 5.4 Hz, 2H), 6.95 (s, 2H), 6.98 (s, 12H), 7.02 (s, 12H), 7.05 (d, J = 3.6 Hz, 2H), 7.06 (d, J = 3.4 Hz, 4H), 7.07 (d, J = 3.4 Hz, 8H), 7.07 (s, 12H), 7.15 (d, J = 3.6 Hz, 4H), 7.16 (d, J = 3.4 Hz, 10H), 7.17 (d, J = 5.4 Hz, 2H); Anal. Calcd for $C_{416}H_{546}S_{48}$: C, 70.52; H, 7.77%. Found: C, 70.63; H, 7.76%.

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