

Synthesis and Properties of the Longest Oligothiophenes: The Icosamer and Heptacosamer

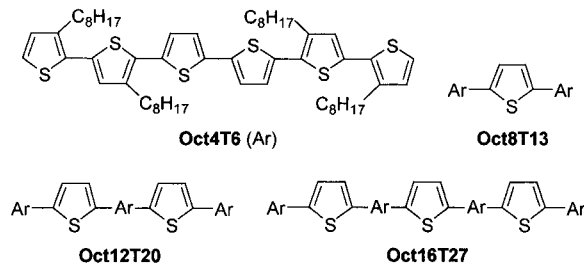
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Recently, well-defined conjugated macromolecules have attracted much attention as useful alternatives to polymer systems.¹ One of the most extensively studied types is that of α -linked oligothiophenes:² an extended series of nonsubstituted oligothiophenes has been intensively prepared, but no homologues higher than the octamer were accessible because of their insolubility.³ Instead, soluble oligothiophenes bearing mostly long alkyl groups have been of current interest, leading to the preparation of further extended members, the 9-mer,^{4,5} 10-mer,⁶ 11-mer,⁴ 12-mer,^{5,7,8} 15-mer,⁵ and 16-mer.⁸ Although the branched alkyl groups have more or less an influence on the conjugation system, such long oligothiophenes give helpful information on the correlation between the chain length and properties. The π - π^* electronic transitions of the oligothiophenes show bathochromic shifts with increasing chain length, and concomitantly, the conductivities increase steadily, approaching those of the corresponding polymers. On the basis of the observation that the absorption spectra and doped conductivities of the 11-mer and 12-mer were very similar to those for polythiophenes, it was claimed that an effective conjugation length for the polythiophene system is not longer than 11 units.^{4,9} Spectroscopic studies of the oxidized oligothiophenes also supported such a limited conjugation length.^{5b,e,10} However, even for the longer 15-mer⁵ and 16-mer,⁸ no complete spectroscopic saturation occurs yet. Thus, for more comprehensive understanding, further longer oligothiophenes are informative. Here, we would like to report

the syntheses and properties of a series of very long oligothiophenes with an interval of tetraoctyl-substituted septithiophene segment, the tridecamer (abbreviated as **Oct8T13**), the icosamer (**Oct12T20**), and the heptacosamer (**Oct16T27**). These compounds are very interesting in terms



of not only the polymer models but also advanced nanoscale molecules (molecular wires); for instance, the molecular size of the heptacosamer has a length of 10.8 nm.

These long oligothiophenes were synthesized according to Scheme 1, which involves a combination of two different types of synthetic reactions, i.e., conventional Ni(II)-catalyzed aryl Grignard cross-coupling for the large-scale preparation of the key intermediate, tetraoctyl-substituted sextithiophene (**Oct4T6**), and Eglinton coupling followed by sodium sulfide-induced 1,3-butadiene cyclization for the elaborate preparation of the further higher oligothiophenes. For the synthesis of such long oligomers, hard work on purification is inevitable. The latter reaction sequence has the advantage of less contamination with analogous oligomeric byproducts.¹¹ First, **Oct4T6** was prepared in high yield via the dioctyl-substituted quaterthiophene (**3**) by double Grignard coupling. Subsequently, bromination of **Oct4T6** with one equimolar NBS led to the formation of the monobromo derivative (**5**) (60% yield), and a coupling reaction of **5** with (trimethylsilyl)acetylene in the presence of Pd(PPh₃)₄ catalyst gave the (trimethylsilyl)ethynyl derivative (**6**) (89% yield), which was then desilylated with potassium hydroxide to the ethynyl derivative (**7**) (90% yield). Alternatively, treatment of **Oct4T6** with two equimolar NBS gave the dibromo derivative (**8**), which was similarly converted to the diethynyl derivative (**10**). An Eglinton coupling reaction using a mixture of **7** and **10** in a 3:1 molar ratio gave a mixture of **11** (50%), **12** (21%), and **13** (14%), which were separated by gel-permeation liquid chromatography. Subsequent treatment of each product with sodium sulfide afforded the desired oligothiophenes **Oct8T13**, **Oct12T20**, and **Oct16T27** in good yields.

The obtained oligothiophenes appear as dark red amorphous solids that are very soluble in common solvents, yielding excellent processability. Their structures were unambiguously characterized by ¹H NMR and MS spectroscopic measurements as well as elemental analyses. The electronic absorption and emission maxima, first oxidation potentials, and doped conductivities of these oligothiophenes, summarized in Table 1, provide definite information on the effective conjugation length. In the electronic absorption spectra, as expected, the π - π^* transitions are progressively shifted to longer wavelengths with increasing chain length up to the 20-mer. It is, however, noticeable that there is no more shift in going from the 20-mer to the 27-mer, though the absorption intensity per thiophene unit still increases. A similar chain length dependence is also observed for their

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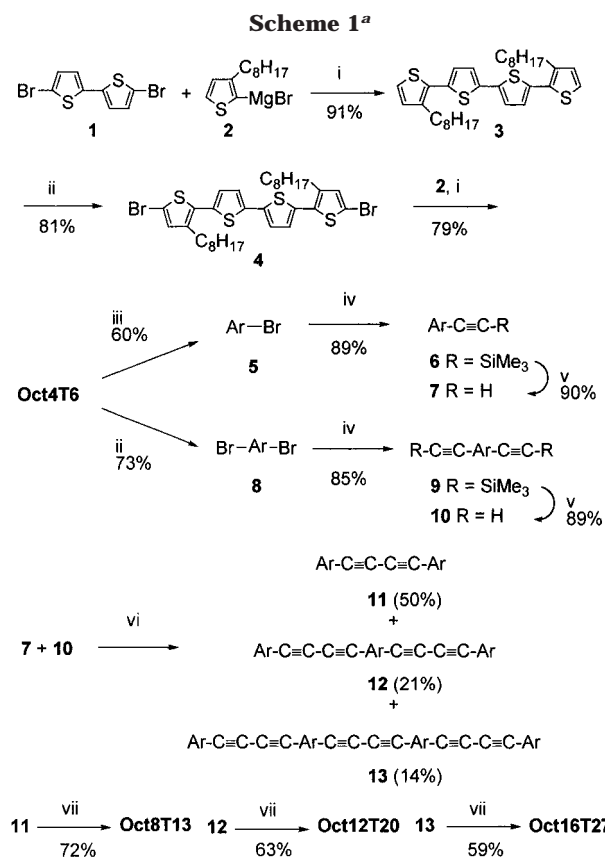
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Table 1. Electronic Absorption and Emission Spectra,^a Oxidation Potentials,^b and Doped Conductivities^c of Oligothiophenes

compd	λ_{\max} (abs, nm)	ϵ^d ($M^{-1} \text{ cm}^{-1}$)	λ_{\max} (emis, nm)	E_{pa}^e (V)	σ^f ($S \text{ cm}^{-1}$)	σ^g ($S \text{ cm}^{-1}$)
Oct4T6	413	41 500 (6917)	509	0.85	0.62 (17%)	0.041 (20%)
Oct8T13	453	93 700 (7208)	554	0.66	5.6 (23%)	3.5 (20%)
Oct12T20	461	151 700 (7585)	559	0.57	9.7 (20%)	7.1 (17%)
Oct16T27	461	211 400 (7830)	560	0.54	28 (22%)	18.5 (19%)

^a Absorption and emission spectra were measured in tetrahydrofuran. ^b Cyclic voltammetry was measured at scan rate 100 mV s⁻¹ in benzonitrile containing 0.1 M Bu₄NClO₄ using an Ag/AgCl standard electrode and Pt working electrode. ^c Conductivities were measured with a four-probe method. ^d Values in parentheses indicate absorption intensity per thiophene unit. ^e The first oxidation peak. ^f Electrical doping with perchlorate; values in parentheses indicate doping level per thiophene unit, calculated on the basis of elemental analyses. ^g Doping with iodine; values in parentheses indicate doping level per thiophene unit, calculated on the basis of elemental analyses by assuming I₃⁻ for the counterion.



^a Reagents and conditions: (i) Ni(dppp)Cl₂, ether–benzene–THF, reflux, 3 h; (ii) 2 equiv NBS, DMF–CS₂, rt, 5 h; (iii) 1 equiv NBS, DMF–CS₂, rt, 5 h; (iv) Me₃SiC≡CH, Pd(PPh₃)₄, CuI, triethylamine, 70 °C, 3 h; (v) KOH, benzene–MeOH, rt, 3 h; (vi) Cu(OAc)₂, pyridine, 40 °C, 10 h; (vii) Na₂S·9H₂O, KOH, dioxane, reflux, 20 h.

emission spectra. This means that a certain limitation on the extensive conjugation occurs at around the 20-mer.

The cyclic voltammogram of **Oct4T6** shows two oxidation waves at 0.85 and 0.95 V, while those of the longer oligothiophenes have a poorly resolved cluster of multiple oxidation waves in the range of 0.5–1.2 V. The potentials of the first oxidation peak decrease along the oligomer series. Apparently there is an appreciable difference between the oxidation potentials of the 20-mer and the 27-mer, in contrast to the above electronic spectra. This indicates a more extensive charge delocalization for the cationic species of the oligothiophenes.

Since the electrical conductivities of polythiophenes had been pointed out to depend on the thickness and morphology of the measured samples,¹² we examined relative conductivities using the similarly prepared cast films of the oligothiophenes. The electrochemical oxidation of the films, nearly insulating in the neutral state, led to an increase of the conductivities depending on doping degree and the

highest value at the maximum doping level of ca. 20%, which are summarized in Table 1. Similar conductivities were also observed on exposure to vaporized iodine. Evidently, a progressive increase in conductivity continues from the 6-mer up to the 27-mer. Although there are some documents on the involvement of polarons^{5,13} and spinless π -dimers¹⁴ in the conduction mechanism of polythiophenes, bipolarons are generally accepted to be the principal charge carriers.¹⁵ The maximum doping level of ca. 20% for any of the present oligothiophenes simply indicates the distribution of a radical cation (polaron) over approximately five thiophene units or a dication (bipolaron) over 10 thiophene units in the conjugation system. The relatively low conductivities (10^{-1} – $10^{-2} \text{ S cm}^{-1}$) of the 6-mer are ascribable to the involvement of only polarons in the conduction mechanism. On the other hand, a marked increase of the conductivity by 1 or 2 orders of magnitude in going from the 6-mer to the 13-mer presumably indicates contribution of bipolarons. Further gradual conductivity increase from the 13-mer up to the 27-mer implies that the extension of the conjugated system to the 27-mer is advantageous to charge hopping between the adjacent oligomeric chains. Finally, it is worth noting that the conductivities (28 S cm⁻¹ for electrochemical doping and 18.5 S cm⁻¹ for iodine doping) of the 27-mer are very close to the respective values (33 S cm⁻¹ and 17.5 S cm⁻¹) of poly-(sexithiophene) prepared by nickel-catalyzed reductive polymerization of the dibromosexithiophene (**8**).

In summary, we have succeeded in the synthesis of a series of the longest class of oligothiophenes and found that their spectral properties and doped conductivities varied progressively with increasing chain length up to around the 20-mer.

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Supporting Information Available: Experimental details and compound characterization data (5 pages).

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