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Synthesis of Oligo(thienylenevinylenes) Substituted with Alkoxy Groups

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ABSTRACT: *Conjugated oligomers based on a combination of thiophene and 3,4-dialkoxythiophene moieties have been synthesized via the Vilsmeier formylation, Wittig-Honer reaction, and McMurry coupling reaction starting from dimethyl 3,4-dihydroxythiophene-2,5-dicarboxylates. Comparison of the optical and electrochemical properties shows that the mixed π-conjugated oligomers of thiophene and 3,4-dialkoxythiophene produces a decrease of the highest occupied molecular orbital–lowest unoccupied molecular orbital gap that is attributed to the electron-donating property of the alkoxy groups.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:414–417, 2001

Linear π-conjugated molecular or polymeric systems are the focus of extensive current research interest for their opt-electronic properties and their potential applications in the field of opt-electronic devices, such as light-emitting diodes [1], field effect transistors [2,3], and nonlinear optics (NLO) [4,5]. More recently, their potential use as molecular wires in molecular electronics has attracted much attention [6]. Oligo(thiophenes) [7,8], oligo(thienylenevinylenes) [9–12], oligo(phenylenevinylene) [13–16], and other related oligomers [17] possessing well-defined conjugated lengths and oligomers [17] possessing well-defined conjugated lengths and structures have been prepared in order to contribute to a better understanding of electronic materials. Roncali and his coworkers constructed extended thienylenevinylene oligomers using 3,4-dihexylthiophene as a building block and found that oligo(thienylenevinylenes) are the most efficient extended molecular wires among the known π-conjugated systems [9–12]. Long alkyl groups such as the hexyl group are required to improve the solubility of the higher oligomers and also serve as electron-donating groups to control the electronic properties of π-conjugated systems. In this article, we report a new type of oligo(thienylenevinylenes) consisted of a mixture of 3,4-dialkoxythiophene and thiophene rings. Since 3,4-dialkoxythiophenes are more electron rich than unsubstituted thiophenes, oligomers linked with such thiophene units are expected to show a narrow highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gap. Furthermore, S···O intramolecular interaction may contribute to reduce the HOMO-LUMO energy gap. Fine tuning of the HOMO and LUMO energies of molecular wires is essential for efficient electron transport over a long distance [18,19]. Alkoxy derivatives have several advantages over the alkyl-substituted ones since alkoxy groups are more effective to raise the HOMO energy level than alkyl groups; the presence of alkoxy groups in place of alkyl substituents decreases the ionization potential of polymers and oligomers. Thus, if the oxygen is directly attached to the ring, the band gap (ΔE) of poly(thio-

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Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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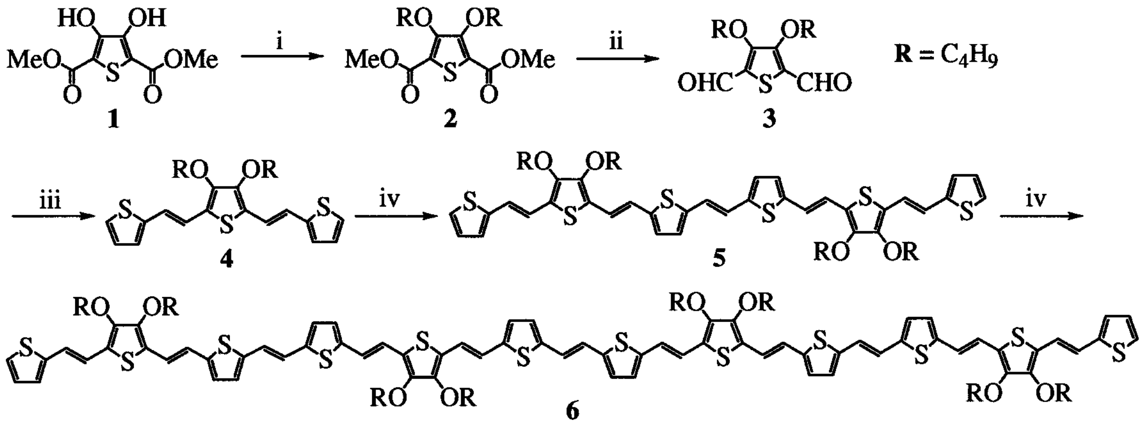

SCHEME 1 Reagents and conditions: (i) n-C_4H_9Br, K_2CO_3, DMF, 60°C; (ii) $LiAlH_4$, THF, 0°C, tetrapropylammonium perruthenate(VII), *N*-methylmorpholine *N*-oxide, CH_2Cl_2, 4Å MS, r.t.; (iii) diethyl (2-thienylmethyl)phosphonate, *t*-BuOK, THF, 0°C; (iv) $POCl_3$, DMF, 1,2-$C_2H_4Cl_2$, reflux, $TiCl_4$, Zn, THF.

phenes) [20] or poly(thienylenevinylenes) [21–22] can be reduced by a substantial amount and the conducting states of the polymer are stabilized. Polythiophenes fused with pyrazine and ethylenedioxy rings in an alternate way have an extremely narrow bandgap (0.36 eV) [23]. In addition, the side alkoxy chains can act as molecular recognition units for chemical sensing.

Oligomers **4**, **5**, and **6** were prepared according to the procedures summarized in Scheme 1, in which 3, 6, and 12 thiophene rings were connected with 2, 5, and 11 double bonds, respectively. The requisite 3,4-dialkoxythiophene-2,5-dicarbaldehyde **3** was prepared from dimethyl 3,4-dihydroxythiophene-2,5-dicarboxylate **2**. The reduction of **2** with $LiALH_4$ followed by oxidation with tetrapropylammonium perruthnenate (TPAP) and *N*-methylmorpholine *N*-oxide (NMO) gave **3** in good yield. Because the alcohol intermediate derived from **2** was unstable under acidic conditions, the oxidation with other reagents such as pyridinium chlorochromate or activated dimethyl sulfoxide (DMSO) (Swern oxidation) gave **3** in poor yield. The thiophene **3** can be alternatively prepared by formylation of 3,4-dibutoxythiophene, but the present method is better for the preparation of **3** with various functional groups. The Wittig-Honer reaction, Vilsmeier formylation, and subsequent McMurry coupling reaction gave the desired oligo(thienylenevinylenes), **4**, **5**, and **6**.

The electronic absorption spectra of **4**, **5**, and **6** are shown in Figure 1 and Table 1. Chain extension leads to a red shift of the absorption maximum (λ_{max}) and to intensification of the absorption. The λ_{max} values for **5** and **6** (556 and 596 nm) are a little longer than those reported for the corresponding alkyl-substituted oligo(thienylenevinylenes), namely, 548 and 595 nm [10]. The HOMO-LUMO gap (ΔE) estimated from the absorption edge is 1.62 eV for **6**. The dependence of ΔE versus the reciprocal number of carbons (1/Cn) in the conjugated chain leads to a straight line with a similar slope observed for alkyl substituted oligo(thienylnevinylenes) [6]. Extrapolation to 1/Cn = 0 gives a ΔE of 1.41 eV for an infinite poly(thienylenevinylene) with alkoxy groups. This value is in good agreement with those reported for the bandgap of poly(thienylenevinylene) with alkoxy groups (1.2–1.4 eV) [20–22].

The cyclic voltammetry (CV) data of **4**, **5**, and **6** are summarized in Table 1, and the CV data of **6** is shown in Figure 2. Chain extension leads to a negative shift of the redox potentials (E_{pa}) and to an increase in the number of redox states. Thus, oxidation

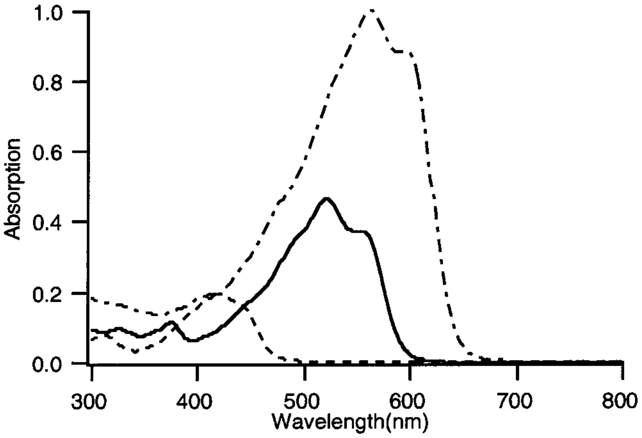

FIGURE 1 UV–vis absorption spectra of **4**, **5**, and **6** (10^{-5} mol·dm^{-3} in CH_2Cl_2).

TABLE 1 Electrochemical and Optical Data of **4**, **5**, and **6**

	λ_{max}/nm (ε)[a]	ΔE/eV[b]	E_{pa1}[c]	E_{pa2}	E_{pa3}	E_{pa4}	Conductivity[d]/Scm^{-1}
4	420 (49,400) 442 (42,000)	2.30	0.61	0.89	—	—	—
5	521 (132,000) 556 (106,000)	1.82	0.47	0.60	1.08	—	1.10×10^{-1}
6	560 (280,000) 596 (248,000)	1.62	0.11	0.22	0.50	0.88	1.33×10^{-1}

[a] In CH_2Cl_2.
[b] Estimated from the absorption edge.
[c] 10^{-4} mol-dm^{-3} substrate in 10^{-1} mol-dm^{-3} NBu_4PF_6 in CH_2Cl_2, scan rate 100 mV-s^{-1}, Pt electrodes, reference Ag/AgNO$_3$ (E in V).
[d] Doped with I_2, measured by a four-probe method.

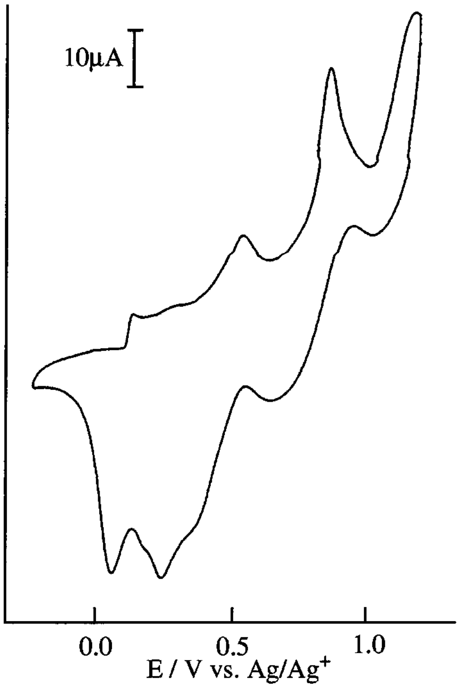

FIGURE 2 Cyclic voltammogram of **6**, 10^{-4} mol dm^{-3} in 10^{-1} mol dm^{-3} NBu_4PF_6-CH_2Cl_2, scan rate 100 mV/s.

peaks for **6**, E_{pa1}, E_{pa2}, E_{pa3}, and E_{pa4} were 0.11, 0.22, 0.55, and 0.86 V (vs. Ag/AgNO$_3$), respectively. The oxidation potentials of the corresponding 12-mer of thienylenevinylene with alkyl groups are reported to be 0.42, 0.59, and 0.97 V (vs. SCE) [7–12]. Evidently, oligo(thienylenevinylenes) with alkoxy groups like **6** are more readily oxidized than the alkyl derivatives. Oligomers **5** and **6** were rapidly oxidized to doped states by the exposure to iodine, whose conductivity was about 10^{-1} Scm^{-1}. New absorption peaks of doped states are observed by oxidation of **5** (λ_{max} 1120 nm) and **6** (λ_{max} 1590 nm). These states are very stable under aerobic conditions at room temperature. The conductivity of these oligomers is the same as that of poly(thienyenevinylenes) with alkoxy groups that were prepared by treatment of **3** with $TiCl_4$–Zn [24]. The oxidation potentials and HOMO-LUMO gaps are steadily reduced with chain extension as observed in pure alkyl derivatives. However, the synthesis of the higher oligomers consisting of alkoxythiophenes (donor) and electron-deficient thiophenes (acceptor) is necessary in order to discuss the difference between alkyl and alkoxy derivatives concerning the efficiency of a given oligomeric system for use as molecular wires.

EXPERIMENTAL

3,4-Dibutoxythiophene-2,5-dicarbaldehyde **3**

This compound was prepared from the corresponding ester **2**. The requisite ester was prepared by alkylation of 3,4-dihydroxy thiophene **1** with butyl bromide according to the method in the literature [25]. To a stirred solution of **2** (1.38 g, 4 mmol) in tetrahydrofuran (THF) (20 mL) was added $LiAlH_4$ (1.0 g, 28 mmol) slowly at 0°C, and the resulting mixture was stirred at 0°C for 1.5 hours. The reaction mixture was poured into water and extracted with diethyl ether. The extract was dried with anhydrous magnesium sulfate and concentrated to give the corresponding alcohol. The alcohol was dissolved in CH_2Cl_2 (10 mL) and NMO (2.32 g, 16 mmol), and molecular sieve 4Å (1.5 g) and TPAP (0.032 g, 0.1 mmol) were added to the reaction solution. The resulting mixture was stirred for 1.5 hours at room temperature. Filtration followed by concentration gave the crude **3**, which was purified by column chromatography (silica gel, $CHCl_3$) to give pure **3** (57.5%): ^{1}H NMR ($CDCl_3$) δ 10.1 (s, 2H), 4.28 (t, J = 6.4 Hz, 4H), 1.80 (m, 4H), 1.51 (m, 4H), 0.99 (t, J = 7.3 Hz, 6H); IR (NaCl) 1676, 1429, 1377, 1186, 1065 cm^{-1}; MS *m/z* (EI) 284 (M$^+$, 16), 228 (22), 172 (100). Anal. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09; Found: C, 59.35; H, 6.99.

3,4-Dibutoxy-2,5-bis(2′-thienylvinyl)thiophene **4**

To a solution of **3** (3.48 g, 12.3 mmol) and diethyl (2-thienylmethyl)phosphonate (7.2 g, 61.5 mmol) in THF (70 mL) was added *t*-BuOK (8.2 g, 73.8 mmol) at 0°C. The resulting mixture was stirred for 2.5 hours at room temperature and poured into water. Extraction with $CHCl_3$ followed by washing with water, drying with anhydrous magnesium sulfate, and concentration gave crude **4**, which was purified by column chromatography (silica gel, ethyl acetate-hexane), and gave pure **4** (yellow oil) in 30.2% yield: ^{1}H NMR ($CDCl_3$) δ 7.17 (d, J = 4.6 Hz, 2H), 7.04 (d, J = 20.5 Hz, 2H), 6.97–7.02 (m, 4H), 6.94 (d, J = 20.5 Hz, 2H), 4.06 (t, J = 6.4 Hz, 4H), 1.75 (5, J = 7.3 Hz, 4H), 1.53 (6, J = 7.3 Hz, 4H), 1.00 (t, J = 7.3

Hz, 6H); MS *m/z* (EI) 444 (M^+, 100) 387 (15), 332 (20). Anal. Calcd. for $C_{24}H_{28}O_2S_3$: C, 64.82; H. 6.35; Found: C, 64.59; H, 6.54.

Oligomer **5**

Formylation of **4** was carried out according to the literature procedure [12]. Namely, to a solution of **3** (0.44 g, 1 mmol) and DMF (0.077 mL, 1 mmol) in 1,2-dichloroethane (5 mL) was added $POCl_3$ (0.091 mL, 1 mmol) slowly at 0°C under Ar. The reaction mixture was stirred at 85°C for 2.5 hours. After the mixture had been cooled to room temperature, 1 M sodium acetate was added to neutralization, and the mixture was stirred for 1 hour. The solution was extracted with CH_2Cl_2, and the organic phase was dried over sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, ethyl acetate-hexane). The product was converted into **5** by the McMurry coupling reaction. To a stirred mixture of Zn (0.197 g, 3 mmol) and $TiCl_4$ (0.165 mL, 1.5 mmol) in THF (12 mL) was added slowly a solution of the previously mentioned aldehyde (0.352 g, 0.75 mmol) in THF (8 mL) at 0°C. The resulting mixture was heated at 65°C for 1.5 hours and then poured into water. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate) to give pure **5** in 47% yield: m.p. 134–136°C, ^1H NMR ($CDCl_3$) δ 7.17 (d, $J = 4.6$ Hz, 2H,), 6.84–7.08 (m, 18H), 4.08 (t, $J = 6.4$ Hz, 4H), 4.06 (t, $J = 6.4$ Hz, 4H), 1.70–1.79 (m, 8H), 1.50–11.58 (m, 8H), 1.02 (t, $J = 7.3$ Hz, 6H), 1.00 (t, $J = 7.3$ Hz, 6H); MS *m/z* (EI) 912 (M^+, 100), 855 (40). Anal. Calcd for $C_{50}H_{56}O_4S_6$:C, 65.75; H, 6.18; Found: C, 65.55; H, 6.15.

Oligomer **6**

Oligomer **6** was prepared in 37.5% yield by a similar procedure to that described in the preparation of **5**: m.p. 176–178°C, ^1H NMR ($CDCl_3$) δ 7.17–7.31 (m, 18H), 6.84–7.08 (m, 22H), 4.04–4.10 (m, 16H), 1.72–1.80 (m, 16H), 1.54–1.60 (m, 16H), 0.97–1.05 (m, 24H); MS *m/z* (FAB) 1850 (M^+). Anal Calcd for $C_{102}H_{112}O_8S_{12}$: C, 66.19; H, 6.10; Found: C, 66.34; H, 6.05.

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