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A CONVENIENT SYNTHESIS OF FUNCTIONAL GROUP END-CAPPED THIOPHENE OLIGOMERS

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Summary: A series of α, ω -aldehyde-capped thiophene oligomers with two, four and six thiophene units have been prepared via a convenient, three-step synthesis in good yields. The UV-vis spectral data show that the π -conjugation length in the tetramer is longer than those in the hexamer and in the dimer in various solvents.

Polythiophene, an important electronically conducting polymer, has been investigated extensively for more than a decade.³ However, the applications of polythiophene are limited because of its poor solubility, processibility and mechanical properties. Recently, it was discovered that the oligomeric materials with as few as six thiophene units have many interesting optical, electronic and electrochemical properties similar to polythiophene while maintaining excellent processibility.^{4,5} These thiophene oligomers without functional end-groups were synthesized usually via Grignard coupling reactions.⁴⁻⁷ We envisaged that if the thiophene oligomers with the functional groups (such as aldehyde, hydroxy, carboxylic acid, etc.) as the end-groups could be prepared in a reasonably good yield, we should be able to incorporate these electroactive oligomers into the backbones of conventional polymers (such as polyesters, polyurethanes, polyamides, etc.) through the step-growth polymerization⁸ to afford a novel family of electroactive polymers with good processibility and mechanical properties. Towards this goal, we have developed a simple, three-step synthetic methodology as shown in Scheme I and prepared a series of the thiophene oligomers having both ends capped with aldehyde groups, including 2,2'-bithienyl-5,5'-dicarbaldehyde (**1a**), 2,2':5',2'':5'',2'''-guiterthienyl-5,5'''-dicarbaldehyde (**1c**).

Scheme I



The starting material for the synthesis of 2.2'-bithienyl-5.5'-dicarbaldehyde (1a) was commercially available 5-bromothienvl-2-carboxaldehvde (4a). The bithiophene (2b, m=1) and the terthiophene (2c, m=2) were prepared from the coupling of 2-thienvlmagnesium bromide with 2-bromothiophene and with 2.5dibromothiophene, respectively, catalyzed by [1,3-bis(diphenylphosphinno)propane]nickel(II) chloride.^{6,7} Both 2b and 2c can also be obtained from commercial sources (e.g. Aldrich). The thiophene or its oligomers (2) were treated with phosphorus oxychloride and DMF in dichloroethane⁹ to afford their correspondent mono- α -aldehyde derivatives (3) in good yields. As a typical procedure, to a 50-mL three-necked round bottom flask was added 12 mmol of the bithiophene (2b) or terthiophene (2c), 0.96 g (13 mmol) DMF and 20 mL of 1.2dichloroethane. The solution was cooled to ~0 °C in an ice bath and 2.0 g (13 mmol) POCl₃ was added dropwise with stirring. The solution was then warmed to room temperature followed by refluxing at ~60 °C for 4 h. The reaction mixture was poured slowly into 100 mL saturated sodium acetate aqueous solution that was precooled to ~0 °C. The organic layer was diluted with ether, washed with water and saturated NaHCO₂ aqueous solution, and dried over anhydrous MgSO₄ overnight. Upon evaporation of the solvents, the product 3b or 3c was obtained in 91% or 84% yield, respectively. The α -aldehyde derivatives (3) were then brominated in chloroform in the presence of sodium bicarbonate.^{10,11} Thus, 11 mmol of **3b** or **3c** and 1.0 g sodium bicarbonate were added to a 50-mL three-necked round bottom flask containing 20 mL chloroform. The mixture was brought to reflux followed by a dropwise addition of the solution of 1.92 g (12 mmol) bromine in 10 mL chloroform. After refluxing for 4 h, the mixture was cooled to room temperature and poured into ice water. The organic layer was washed with water and saturated NaHCO₃, and dried over anhydrous MgSO₄. Upon evaporation of the solvent, the solid was purified by recrystallization from THF/methanol (1:2 v/v) to afford 4b (95%) or 4c (89%).

Finally, the α , ω -aldehyde-capped thiophene oligomers (1) were obtained via a coupling reaction of 4 in the presence of zinc, nickel(II) chloride and triphenylphosphine in DMF under nitrogen atmosphere.^{12,13} For a general procedure, to a 100-mL three-necked round bottom flask containing 0.040 g (0.31 mmol) nickel chloride, 0.79 g (3.0 mmol) triphenylphosphine, 0.70 g (10.7 mmol) zinc dust and 20 mL DMF was slowly added 3.0 mmol of **4a**, **4b** or **4c** under N₂. The resulting brown suspension was refluxed under N₂ for 6 h and then was cooled to room temperature followed by filtration. The filtrate was diluted with chloroform and extracted with water and saturated NaHCO₃ followed by drying over anhydrous MgSO₄. Upon evaporation of the solvents, the crude product was recrystallized from THF/methanol (1:2 v/v) to afford compound **1a**, **1b** or **1c**, respectively, in good yield (Table I). It is noteworthy that we have attempted to employ the Grignard coupling^{6,7} in the last step with the aldehyde groups protected by formation of cyclic acetals or thioacetals.^{9,14} However, the desired product **1** was not obtained after the deprotection.

Table I. Coupling yields and wavelengths of maximum UV absorption (λ_{max}) of the α, ω -aldehyde-capped thiophene oligomers (1)

онс-С______сно

entry	compound		yield (%)	λ_{max} (nm) in			
				СН ₃ ОН	DMF	THF	Hexane
1	la m	m = 0	85	360	370	366	361
2	1 b	m = 1	78	435	440	433	430
3	1 c	m = 2	70	415	397	397	390

All the α, ω -aldehyde-capped thiophene oligomers (1) were characterized by spectroscopic methods and the results support the proposed structures.¹⁵ Electronic absorption spectra of the oligomers 1 were measured on a Lambda 2 UV-vis spectrophotometer in various solvents. As shown in Table I, the λ_{max} of π - π * transition band changes from 360 nm for the dimer (1a) to 435 nm for the tetramer (1b) in methanol, indicating the increase in the conjugation length as expected.⁴⁻⁷ The λ_{max} (415 nm) for the hexamer (1c) is higher than that for the dimer (1a) but lower than that for the tetramer (1b). This trend remains the same regardless of the polarity or the type (i.e. protic or aprotic) of solvents. Therefore, in the α, ω -aldehyde-capped thiophene oligomer series, the π -conjugation may reach its maximum length around the tetramer level. Further increase in the number of thiophene units to six resulted in a decrease in the conjugation length, owing probably to the changes in conformation that disrupt the conjugation system. As the polarity of the solvents is increased, the λ_{max} value increases because of the better solvation and hence the greater degree of coplanarity in these oligomers.

In summary, we have successfully prepared a series of α, ω -aldehyde-capped thiophene oligomers with two, four and six thiophene units through a convenient, three-step synthesis in good yields. The UV-Vis spectral results indicate that the π -conjugation in the tetramer is more extended than those in the hexamer and in the dimer in various solvents. It should be noted that the aldehyde groups can be readily converted to other functional groups (e.g. hydroxymethyl, carboxylic acid, etc.) and all of the α, ω -functional group-capped thiophene oligomers can be used as monomers in the step-growth polymerization. These studies are currently in progress in our laboratory.

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- Characterization results: 2,2'-Bithienyl-5,5'-dicarbaldehyde (1a): m.p.(uncorr.) 214 °C (lit. 215-218 °C, Nakayama, J.; Fujimori, T. *Sulfur Lett.* 1990, *11*, 20); IR (recorded on a Perkin-Elmer Model 1610 FTIR spectrometer; KBr) cm⁻¹, 1655 (C=O), 3099 (Aromatic H-C); ¹H-NMR (recorded on an IBM Bruker WM250 NMR spectrometer in CDCl₃) δ (in ppm) 9.9 (2H), 7.7 (2H), 7.4 (2H); ¹³C-NMR (CDCl₃) δ (in ppm) 183, 145, 144, 138, 128; Anal.: calc. for C₁₀H₆O₂S₂, C 54.04, H 2.72; found C 54.33, H 2.80; MS (recorded on a VG ZAB mass spectrometer) 221.9809 (calc. 221.9809). 2,2':5',2'':5'',2'''-Quaterthienyl-5,5'''-dicarbaldehyde (1b): IR (KBr) cm⁻¹, 1656 (C=O), 3091 (Aromatic H-C); ¹H-NMR (CDCl₃) δ(in ppm) 9.9 (2H), 7.7 (2H), 7.3 (4H), 7.2 (2H); Anal.: calc. for C₁₈H₁₀O₂S₄, C 55.93, H 2.61; found C 55.65, H 2.53; MS 385.9563 (calc. 385.9564). 2,2':5',2''':5''',2''''-Swithienyl-5,5'''-dicarbaldehyde (1c): IR (KBr) cm⁻¹, 1652 (C=O), 3092 (Aromatic H-C); ¹H-NMR (CDCl₃) δ(in ppm) 9.9 (2H), 7.7 (2H), 7.4 (2H), 7.3 (2H), 7.2 (2H), 7.0 (4H); Anal.: calc. for C₂₆H₁₄O₂S₆, C 56.69, H 2.56; found C 56.87, H 2.45.

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