

Substituted 2,2':5',2":5",2''':5''',2''''':5''''',2''''': 5''''',2''''':5''''',2''''':5''''',2''''':5''''',2''''':5''''',2''''':5'''''- undecithiophenes, the longest characterized oligothiophenes

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Chart I

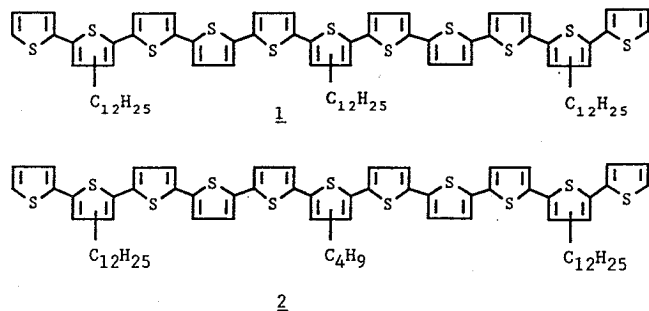


Table I

entry	oligomer ^a	conductivity ^b	λ_{\max} ^c
1	T3 d(2)	<i>d</i>	345
2	T5 b(2)	0.01	412
3	T7 b2(2,6)	0.20	440
4	T9 d(4)	<i>d</i>	455
5	T11 d2(2,10) b(6) 2	20	462
6	T11 d3(2,6,10) 1	462	462
7	poly(3-hexylthiophene)	10–100 ^e	430–440 ^f

^aThe short-hand notation used in the table, for example, T11 d2(2,10) b(6) 2, for entry 5, reads as follows: 11 thiophene units with two dodecyl groups at units 2 and 10 and one butyl group at unit 6. ^bSpecific conductivities (S/cm, four-point method) of thin coherent layers obtained by melting the oligomer on a ceramic plate and doping with iodine at room temperature until saturation. ^cAbsorption maximum of a solution in CHCl_3 . ^dFT-IR and vis absorption spectra after undoping pointed to postpolymerization during doping. ^eReference 5. ^fHotta, S.; Rughooputh, S. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* 1987, 20, 212.

critically on the method of preparation.⁷

We have prepared a number of oligothiophenes carrying a limited number of aliphatic sidechains. The synthetic route leaves no doubt about the ideal all- α,α' linkage of the thiophene units. This series of soluble oligothiophenes enables use to study the dependence of the conjugation length on the chain length.⁸

As a characteristic example of the synthesis of these oligothiophenes, we report here the preparation of the all- α,α' -linked undecithiophenes 1 and 2, which at present constitute the longest known all- α,α' -linked oligothiophenes (Chart I).

Diketone 3⁹ (Scheme I) can be conveniently alkylated with 1-bromobutane and 1-bromododecane, using solid KOH in DMSO.¹⁰ Hydrolysis of the crude reaction product, consisting of a mixture of the alkylated diketone and enol ethers, gives the desired alkylated diketones, which are directly transformed into 3'-butylterthiophene 4 or 3'-dodecylterthiophene 5. Terthiophene 5 is formylated to afford monoaldehyde 6 as a mixture of two isomers (based on ¹H NMR and ¹³C NMR). For the middle sections of 1 and 2, terthiophenes 4 and 5 are converted to the bis-acetylated terthiophenes 7 and 8. These can then be transformed into the amines 9 and 10. Subsequently, 9 and 10 are coupled with 2 equiv of aldehyde 6 (Stetter reaction¹¹) to give the tetraketones 11 and 12, both as mixtures of isomers. Finally, a ring closure with Lawesson's reagent leads to the desired undecithiophenes 1 and 2, as mixtures of isomers. For purification, the undecithiophenes are recrystallized from chlorobenzene after having been filtered over aluminum oxide, hot chlorobenzene being

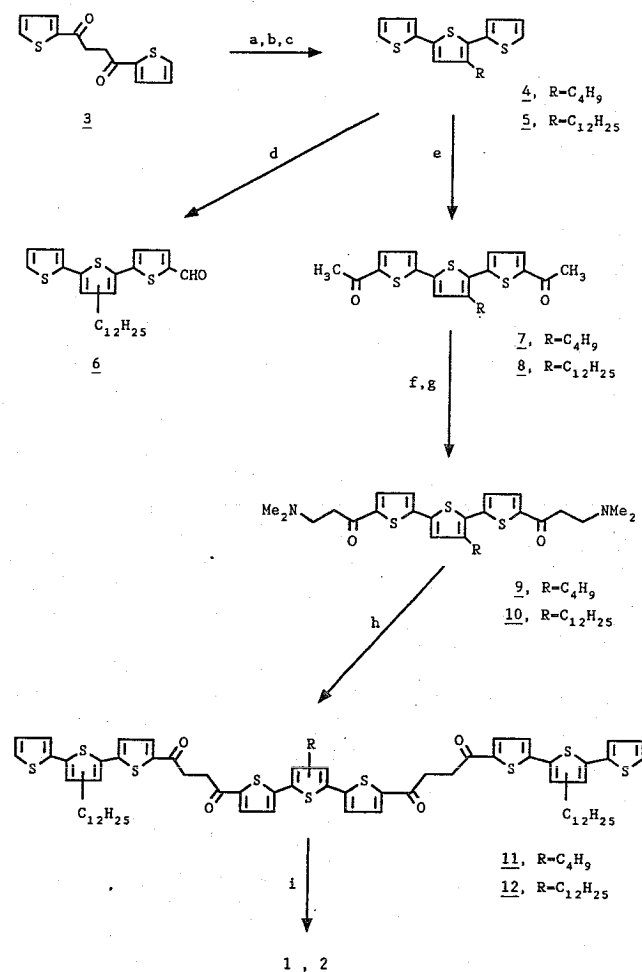
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Scheme I^a

^a(a) RBr, KOH, DMSO, room temperature; (b) HCl, acetone-water, reflux; (c) Lawesson's reagent, toluene, reflux (4, 77%; 5, 58%); (d) DMF-POCl₃, 100 °C (85%); (e) acetic anhydride, phosphoric acid, 100 °C, 10 min (7, 34%; 8, 57%); (f) paraformaldehyde, dimethylamine, HCl, DMF, 100 °C; (g) NaOH, water, toluene, room temperature (9, 70%; 10, 65%); (h) 6 (2 equiv), NaCN, DMF, room temperature; (i) Lawesson's reagent, toluene, reflux (1, 45%; 2, 44%; last two steps).

used as the eluent.¹² Using this synthetic strategy, we have synthesized a series of oligothiophenes with different chain lengths and numbers (and sites) of substituents.

The conductivity of iodine-doped oligothiophenes and the optical properties of a selected number of oligomers are given in Table I. The conductivity data of the iodine-doped oligomers increases steadily with chain length. The value for 2, 20 S/cm, is of the same order of magnitude as that for doped polythiophenes. Hence, the effective conjugation length for doped polythiophenes is not much longer than 11 units. The wavelength of the maximum absorbance of CHCl_3 solutions of the oligothiophenes, being a rather direct measure of the conjugation length, increases steadily with chain length and seems to approach saturation (at 11 units) without actually reaching it. The conjugation length of 1 and 2 exceeds that of poly(3-alkylthiophene) (see Table I), due to a decreased steric interaction of side groups which are more widely spaced. Absorption spectra of solid films of both 1 and 2 and

(12) Elemental analysis for 1 and 2 (calculated values within parentheses). 1 (mp 140–142 °C): C, 67.91 (68.13); H, 6.89 (6.86); S, 24.77 (25.01). 2 (mp 150–161 °C): C, 66.26 (66.62); H, 6.23 (6.21); S, 26.74 (27.17). Due to the low solubility of 1 and 2 in organic solvents (insoluble in DMSO at room temperature; the solubility in hot chlorobenzene is about 1 g/50 mL), we were unable to obtain suitable NMR spectra (DMSO-*d*₆, 100 °C). IR (KBr) for 1: 3065 (w), 2956 (m), 2924 (s), 2853 (m), 1640 (w, br), 1492 (m), 1460 (m, br), 1261 (m), 1100–1030 (m, br), 870 (m), 832 (m), 804 (s), 788 (s), 687 (m). The IR spectrum of 2 is virtually identical with the spectrum of 1.

poly(3-alkylthiophenes), however, are much alike, with maxima at higher wavelength (520 nm), indicating a much larger conjugation length in the solid state.^{8b} Recently, the third-order nonlinear optical susceptibilities of some of the oligomers have been measured in poled PMMA solutions, and in this case saturation sets in at 7-8 thiophene units, thus indicating the sensitivity of planarity of these oligomers to matrix composition.^{8a}

Comprehensive studies on the properties of these undecithiophenes and lower homologues as well as a full account of the synthesis of all these oligothiophenes will be published elsewhere.^{8,13}

In conclusion, two oligothiophenes of unprecedented length have been prepared through a solid route. Moreover, these undecithiophenes bridge the gap that exists between the well-characterized lower oligothiophenes (up to sexithiophene) and the vaguely characterized polythiophenes.

(13) Ten Hoeve, W.; Wynberg, H., to be published.

Aluminum and Gallium Oxide Pillared MoO₃

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It has been shown that microporous or zeolite-like structures can be constructed by intercalating large clusters between the layers of two-dimensional structures. These "pillaring" reactions were first reported for aluminosilicate clays.¹ They have not been extended to many simple transition-metal oxide hosts, other than titanium,² due to the difficulty in opening up the layers sufficiently to allow introduction of a large guest species. There is obvious interest in this approach as a route to developing and/or modifying metal oxides with specific properties. MoO₃, in particular, is a multifunctional material which has attracted considerable attention as a partial methane oxidation catalyst³ and as a potentially viable cathode in secondary batteries.⁴ The search for other polytypes of the layered structure of α -MoO₃ has led to two new phases,^{5,6} but neither are microporous. We report here the first examples of pillaring of α -MoO₃ by the incorporation of Al₁₃O₄(OH)₂₄(H₂O)₁₂⁷⁺ ("Al₁₃") to give rise to a microporous molybdenum oxide with a high surface area. The layers have also been pillared with a new oxy-gallium cluster which is analogous to the Al₁₃ oligomer. Remarkably well-ordered materials are obtained which enables the first direct determination of the orientation of the guest Al₁₃ cluster by 1-D Fourier analysis.

We prepared our pillared compounds by combining a solution of the guest cation species with a dispersion of the alkali-layered oxide. Na_xMoO₃(H₂O)_y or Li_xMoO₃(H₂O)₇ was colloiddally dispersed in water. We find that Li_xMoO₃ (x = 0.25) spontaneously exfoliates in water to give very stable dispersions of the MoO₃²⁻ layers. The layers are then reassembled with inclusion of the pillars. This restructuring method was first demonstrated in the pillaring of TaS₂⁸ with Fe₆S₈(PEt₃)₆²⁺ and has recently been

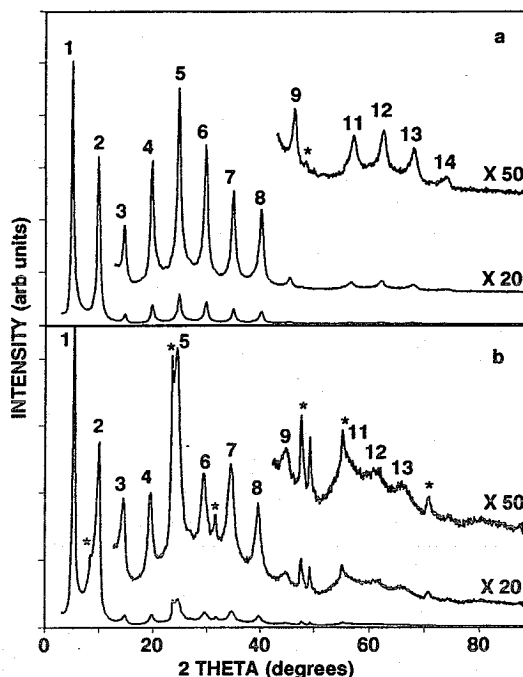


Figure 1. X-ray diffraction pattern (Cu K α radiation) of oriented films of (a) [(Al₁₃)_{0.047}(Na)_{0.003}]MoO₃ and (b) the 18-Å phase of gallium-pillared MoO₃ [(Ga₁₃)_{0.032}(Na)_{0.09}]MoO₃. Reflections arising from residual [Na(H₂O)_{2.025}]MoO₃ ($d_{0k0} = 11.39$ Å)⁷ are marked with an (*). The intensity has been expanded by a factor of 20 and 50 in the upper traces in the figures; the integers indicate the (0k0) indices.

used to intercalate organic molecules in MoS₂.⁹ The sodium compound also forms a dispersion, but our observations and recent TEM studies indicate that extensive exfoliation does not occur. This is in accordance with the lower solvation energy of the sodium cation compared to lithium. However, we find that Na_xMoO₃ undergoes sufficient swelling to permit direct exchange of the Na⁺ for the polyoxycation. Solutions containing the pillaring agents were prepared by OH⁻ hydrolysis of AlCl₃¹⁰ or Ga(NO₃)₃ solutions.

The X-ray diffraction pattern of the oriented thin film obtained from a Na_xMoO₃ dispersion flocculated with Al₁₃ is shown in Figure 1a. The Li_xMoO₃-derived pattern was very similar. An average d spacing of 17.94 Å was calculated from the 14 0k0 (00l) reflections. The large number of reflections, together with the small variation in their d_{0k0} value (± 0.03 Å) indicates that there is a high degree of order along the axis perpendicular to the layers. The interlayer expansion of 10.8 Å on pillaring is consistent with that observed for intercalation of Al₁₃ in smectite clays (9.6 Å)¹ and also corresponds to the van der Waals diameter of Al₁₃ (~10.5 Å). The degree of expansion is, to a certain extent, dependent on the topology of the layered surface and on the siting of the Al₁₃ cations in the interlamellar gap. Chemical (Al, Mo, Na) and thermal gravimetric analysis of the as-prepared material gave the composition [(Al₁₃)_{0.047}(Na)_{0.003}(H₂O)_{1.0}]MoO₃, showing that virtually complete ion exchange of the interlayer alkali cations has occurred. The films were extremely stable, showing no change in the XRD pattern after several days at ambient conditions. Drying the films in air at 100 °C for 2 days resulted in a decrease in the d spacing to 17.35 Å (14 sharp 0k0 reflections, as before). Calcination at higher temperatures shows that a layered structure ($d = 15.2$ Å) is still present up to 350-400 °C but that interlayer collapse begins to occur at higher temperatures. The surface area [BET (N₂)] of the calcined material (200-250 °C) was 107 m²/g. The surface area of the unpillared material (5 m²/g) was negligible by comparison. Analysis of the pore size distribution showed that both micro and meso pores were present, with the surface area

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