Synthesis and Structural Characterization of Alkyl Oligothiophenes—The First Isomerically Pure Dialkylsexithiophene[1]

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Regioselective bromination of alkylated bi- and ter-thiophenes affords key building blocks for the synthesis of higher, isomerically pure alkyl oligothiophenes. For all new compounds, unequivocal structural assignment is based on a detailed analysis of the fully coupled ^{13}C, ^{1}H NMR spectra.

Polythiophenes are among the best investigated conjugated, electrically conducting π-systems. As is the rule with polymers, these materials lack a rigidly defined structural principle, due to statistical chain-length distribution and interruption of the conjugated chain by mislinkages and other defects. The physical properties of such conducting polymers thus cannot be straightforwardly correlated to structural parameters. Oligothiophenes have therefore gained more and more prominence in recent years. By assembling defined oligomers step by step, *via* well understood organic reaction sequences, materials are obtained where both chain and conjugation length are well controlled and rigorously defined.[2]

This painstaking synthetic procedure appears well justified since such oligomers may serve, on one hand, as model compounds for the respective polymers; they are far better soluble as a rule, and thus can be characterized with much higher precision.[3] Some of their physical properties, on the other hand, even surpass those of the polymeric material. For this reason, oligothiophenes have recently been advanced as components for molecular electronic[4] and optical devices.[5] An all-α-linked sexithiophene '6T' has, in fact, been successfully employed as an active component in an organic field-effect transistor.[4] Fully conjugated polyheterocyclic systems are likewise expected to display high non-linear optical effects.[6] Finally, oligothiophenes have been used as starting materials for the electrochemical preparation of polythiophenes.[7]

The series of α-conjugated oligothiophenes has recently been extended to the decamer.[8] Solubility, however, drops drastically with increasing chain length, sexithiophene, for instance, being almost insoluble in organic solvents. Better solubility may be effected by introducing alkyl side chains into the β-positions of the thiophene moieties. Such substituents cause significant steric hindrance, though, resulting in a more or less pronounced twist between adjacent aromatic rings—as demonstrated experimentally by a hypsochromic shift of the longest-wavelength absorption[9] and by a detailed ^{1}H NMR spectroscopic analysis[10a] of both oligothiophenes and the corresponding poly(alkylthiophenes).[11] Theoretical calculations likewise show how the oligomer's conformation changes upon introduction of alkyl substituents in various positions.[10b]

In this context, a series of alkyl-substituted oligothiophenes has recently been synthesized including the dodecamer, the largest oligothiophene definitely characterized so far.[12] Likewise, terthiophenes with one, and sexithiophenes with two solubility enhancing decyl and dodecyl groups, respectively, have been reported.[13] Owing to the synthetic strategy, isomeric mixtures of the various oligomers are expected, though, and the absolute position of the alkyl substituents remains ambiguous. The compounds thus obtained cannot be assigned, even after purification, an unequivocal structure.

Within the scope of our work on functionalized polythiophenes,[14] we have also prepared highly soluble poly(alkylterthiophenes).[15] This communication presents the first rigidly defined synthesis of alkyl oligothiophenes which may serve as model compounds for the respective polymers. The product structure of all compounds synthesized in this series has been characterized unambiguously by a combination of ^{1}H and fully ^{13}C,^{1}H-coupled NMR spectroscopy. Crystallographic analyses for both an alkylterthiophene and a related dialkylsexithiophene could additionally be obtained and support the NMR spectroscopic assignments.[16]

Results and Discussion

Preparation of Alkyl-substituted Oligothiophenes.—α-Conjugated oligothiophenes may be formed either by ring-closure reactions, *e.g.* from diacetylenes[17] or 1,4-diketones,[18] respectively, or by C–C-linkage reactions between thiophenes and/or oligothiophenes. In particular, transition metal-catalysed methods have been developed within the last few years; among these, the nickel-catalysed coupling of Grignard compounds with bromoarenes represents the most direct procedure, besides copper- and palladium-promoted reactions. This so-called Kumada coupling generally affords excellent yields and high purity of products.[19]

All these coupling reactions require the respective monohalo oligothiophenes as starting material. Bromination of thiophenes with molecular bromine gives a mixture of mono- and di-bromothiophenes which can be separated by straightforward fractional distillation.[20] Monobromo oligothiophenes, on the other hand, are not accessible *via* this route. 5-Bromo-2,2′-dithiophene, for instance, was obtained only by a multi-step sequence, employing extensive protecting-group techniques.[21] Direct bromination of oligothiophenes, even under the most selective conditions, always gives some dibromo derivatives which cannot be separated on a preparative scale.[22] Somewhat better results are obtained with *N*-bromosuccinimide (NBS) as brominating agent in chloroform/acetic acid.[23] Bromination of arenes with NBS is known to proceed with especially high selectivity in dipolar-aprotic solvents, *e.g.* dimethylformamide (DMF).[24] We have therefore applied this technique to the bromination of oligothiophenes, and observed a marked increase in selectivity as compared with reactions in either tetrachloromethane or chloroform/acetic acid mixtures.[25]

The synthetic route to the various oligothiophenes, first prepared in the course of the present study, is outlined in Schemes 1–6. The central building block in each case is 3-dodecylthiophene **1**, which was obtained *via* Kumada coupling

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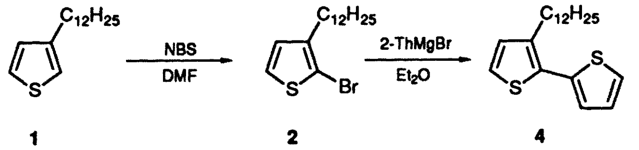
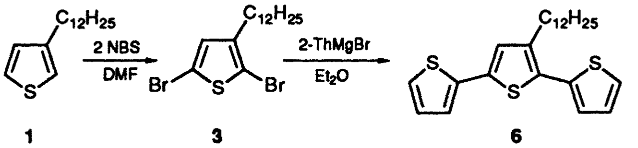
† NMR analyses.

of 3-bromothiophene with dodecylmagnesium bromide.[26] Selective bromination of compound **1** with *one* mole equivalent of NBS in DMF gave 2-bromo-3-dodecylthiophene **2** in 75% yield. By nickel-catalysed coupling of the bromide **2** with 2-thienylmagnesium bromide, 3-dodecyl-2,2′-bithiophene **4** was formed in 85% yield (Scheme 1). Bromination of **1** with *two* mole equivalents of NBS afforded, in a smooth reaction and in 86% yield, 2,5-dibromo-3-dodecylthiophene **3**. This in turn was treated with two mole equivalents of 2-thienylmagnesium bromide, in a nickel-catalysed Grignard coupling, to give 3′-dodecyl-2,2′:5′,2″-terthiophene **6** (Scheme 2). The yield of analytically pure product **6** drops to 31% in this case, however, since tedious chromatographic purification procedures are required.

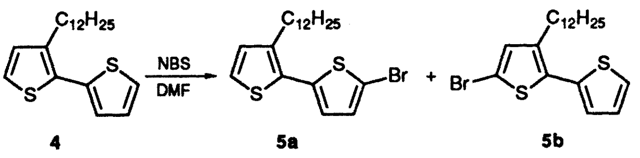


Scheme 1



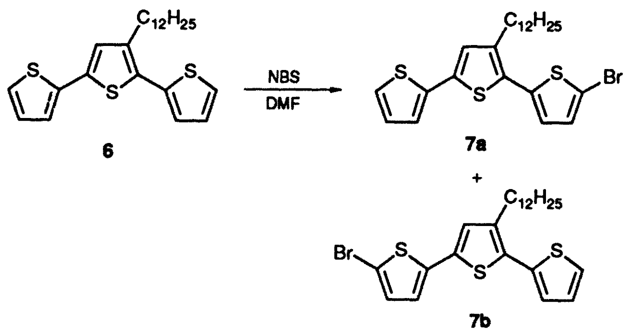
Scheme 2

The physical characteristics of compound **6** have been reported recently, although without either synthetic details or spectroscopic data.[13a,b] Delabouglise *et al.*[13c] have synthesized 3′-decyl-2,2′:5′,2″-terthiophene, homologous with compound **6**, by the same procedure, and further elaborated it, *via* lithiation and subsequent copper-catalysed coupling, to a mixture of isomeric didecylsexithiophenes. Direct metallation of bi- and ter-thiophene with butyllithium, however, is known to give a substantial percentage of dilithiation (in both α-positions).[22b,23c,27] We have therefore tested the selectivity of our NBS/DMF bromination procedure for dodecylbithiophene **4**. At room temperature, compound **4** reacted with one mole equivalent of NBS to give a mixture of the two bromobithiophenes **5a, b** (combined yield 47%), besides an 8% yield of a dibromo derivative, which was smoothly separated by column chromatography (Scheme 3). The structure of the isomers **5a** and **5b** became immediately apparent from the ^{1}H NMR spectra (two AB systems for **5a**; a singlet and an ABC system for **5b**). Surprisingly, the isomer **5a** was formed with high preference (88 : 12, as determined by HPLC and NMR).

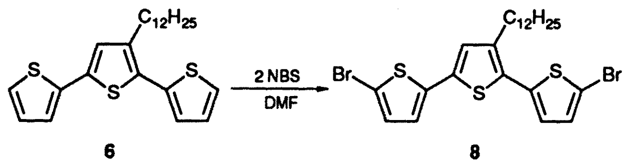


Scheme 3

Reaction of the alkylterthiophene **6** with one mole equivalent of NBS at −20 °C gave the monobromo products **7** (36%), besides a little of the dibromo compound **8** (4%). At room temperature, the yield of the monobromo terthiophenes **7** went up to 56%, but with a slight increase in the percentage of the side product **8** (9%) (Scheme 4). The dibromo product **8** may be prepared independently, in 66% yield, by reaction of **6** with two mole equivalents of NBS (Scheme 5). At lower temperatures, the two possible α-bromo terthiophenes are formed almost exclusively; the isomer ratio **7a**/**7b** was found, by both ^{1}H NMR and HPLC analysis to be 90:10. Repetitive recrystallization afforded the isomer **7a** in 97% purity, in 26% total yield. The definitive structural assignment of **7a**, which relies mainly on 2D correlation spectra, is detailed below. This unexpected high selectivity in either bromination reaction must be attributed to a better stabilization of the σ-complex intermediates leading to **5a**/**7a** where the positive charge can be formulated at the alkyl-substituted carbon. This is not the case for the alternative attack of bromine at the alkylated ring.

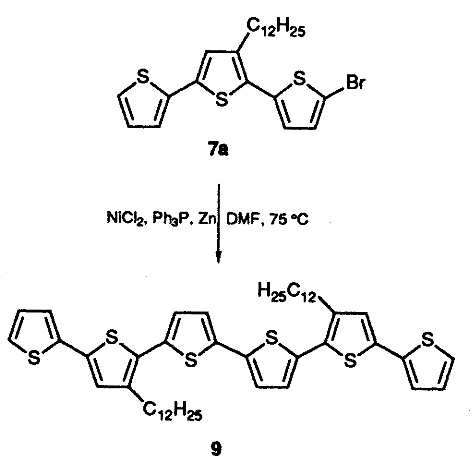


Scheme 4



Scheme 5

The isomerically pure bromo(dodecyl)terthiophene **7a** is the key intermediate for the ensuing synthesis of rigidly defined higher oligomers. It cannot be dimerized to the respective didodecylsexithiophene **9**, however, by a Grignard coupling reaction; in fact, **7a** does not react to give, even in the presence of entrainers, any Grignard compound. We therefore employed a method developed by Colon and Kelsey for the coupling of chloroarenes,[28] where the catalyst is prepared *in situ* from nickel dichloride, triphenylphosphine, and zinc. This procedure has already been extended to the synthesis of α-sexithiophene from α-bromoterthiophene.[2,23a] Under the conditions given in Scheme 6 (75 °C; DMF), the bromoterthiophene **7a** was indeed dimerized to the isomerically pure didodecylsexithiophene **9** in 33% yield (Scheme 6). As expected, the melting point of our product **9** (110–111 °C) was distinctly higher than that reported by Havinga *et al.* for their isomeric mixture (80–84 °C).[13a,b] Compared with unsubstituted α-sexithienyl, **9** is excellently



Scheme 6

soluble in organic solvents; thus, its physical properties can be characterized extensively. Both electrochemical and spectroelectrochemical investigations, which will be reported separately,[29] establish the well defined chemical character of our didodecylsexithiophene **9**. The structural assignment of compound **9** is also unequivocal, resting on NMR as well as on crystallographic data.

NMR Spectroscopic Structural Assignment.—Only a few ^{1}H and even fewer ^{13}C NMR data of alkyl[10a] and bromo[23c,30a] oligothiophenes have been published. In particular, the assignments of ^{13}C resonances in these compounds[10a,23c,30] have not been confirmed in all cases. NMR data of the decyl and dodecyl derivative of terthiophene **6** and sexithiophene **9** which would be comparable to our compounds are either not given[13a,b] in the respective publications, or are simply listed without any assignment.[13c] We now report ^{1}H NMR data for all new compounds, and definitive ^{13}C NMR data for representative members of the series. In particular, in the case of the key building block **7a**, 2D correlation spectra (COSY, HX-COSY) and fully ^{13}C, ^{1}H-coupled spectra were required. Furthermore, 2-bromothiophene and 5,5′-dibromo-2,2′-bithiophene had to be included for comparison.

In Table 1, the ^{13}C chemical shift data and all relevant ^{13}C, ^{1}H coupling constants are collected for 2-bromothiophene and 3-dodecylthiophene **1**, for the dimers 5,5′-dibromo- and 5-bromo-3′-dodecyl-2,2′-bithiophene **5a**, and for the 5-bromo-3′-dodecyl-2,2′:5′,2″-terthiophene **7a** in question. The chemical shifts and C,H coupling constants in Table 1 are arranged in such a manner that analogy between homologous and thence directly comparable positions in the various thienyl structures becomes immediately apparent. Assignment of all the NMR data compiled in Table 1 is definitive; it is based mainly on the analysis of selectively decoupled and C,H-correlated spectra. The substituent pattern of the terthiophene is established unequivocally as 5-bromo-3′-dodecyl-2,2′:5′,2″-terthiophene **7a** from the following arguments:

(i) In the first place, the four chemical shifts for C-2 to C-5, *i.e.* for the bromo-substituted thienyl ring, are more or less identical for **5a** and **7a**; all coupling constants, resolved in the fully coupled spectra, likewise are numerically identical.

(ii) The dodecyl-substituted carbon in **7a** has about the same chemical shift as has that in **5a**. The most prominent coupling for this carbon in the bithiophene **5a** is to the 5′-proton ($^{3}J_{trans}$ 9.4 Hz). This larger long-range coupling is missing from the coupling pattern of the respective dodecyl-substituted carbon in **7a**. Consequently, both respective α-positions (2′,5′) are blocked by a thienyl ring.

(iii) C-2 in **7a** displays no coupling into the middle ring, as does the C-2 carbon resonance in the dibromobithiophene: ^{3}J(C-2,3′-H) 2.2 Hz.

(iv) The C-2′ and C-3′ chemical shifts are more or less identical for **5a** and **7a**, *i.e.* the partial structures of both compounds on the 'right hand side' of the molecule must be identical.

Taken together, these arguments are compatible only with a structure which has both the bromo substituent on the outer, and the dodecyl group on the middle ring, in the same hemisphere of the terthiophene backbone. This assignment is further strengthened by the X-ray data obtained for the sexithiophene **9**, which clearly indicate the same structural features.[16] A detailed description of all ^{1}H and ^{13}C NMR data and assignments will be published separately.

Experimental

^{1}H and ^{13}C NMR spectra: Bruker ACF 250 spectrometer (^{1}H, 250 MHz; ^{13}C, 63 MHz), solvent $CDCl_3$, shifts in ppm (*vs.* $SiMe_4$ as internal standard), multiplicity, coupling constant(s) in Hz, assignment. M.p.s: Elektrotherm 9100; the m.p.s are not corrected. Preparative column chromatograph: glass columns of different sizes, packed with silica gel A 60, grain size 0.032–0.063 mm (Riedel de Haen). HPLC: Shimadzu LC-9A pump and SPD-M6A detector, Knauer Nucleosil NO_2 5 μm columns. GLC: Carlo Erba Auto-HRGC, detector FID EL 580, integrator Spectra-Physics DP 700, 20 m OV 1701 glass column, temperature program 100–300 °C, 16°/min, carrier gas hydrogen. All experiments were performed under nitrogen as inert gas with 'absolute' solvents. Elemental analysis data of all new compounds are collected in Table 2.

3-*Dodecylthiophene* **1**.—The synthesis was performed in a slightly changed procedure from that given in ref. 26. 1-Bromodecane (149.54 g, 0.6 mol) was slowly added dropwise to a suspension of magnesium turnings (iodine etched) (14.59 g, 0.6 mol) in diethyl ether (60 cm^3), and the reaction mixture was heated to reflux for 2 h. The Grignard solution was transferred to the dropping funnel of a second apparatus *via* canula and was added dropwise, through a frit, to an ice-cooled solution of 3-bromothiophene (83.03 g, 0.5 mol) and Ni(dppp)Cl_2 (0.271 g, 0.05 mol) in diethyl ether (340 cm^3). The mixture was refluxed for 20 h, cooled to room temperature, and hydrolysed with 1 mol dm^{-3} HCl. The ether phase was separated, neutralized, washed with water, dried over sodium sulfate, and evaporated. The residue was fractionated under reduced pressure (b.p. 112 °C/10^{-2} mmHg). 3-Dodecylthiophene **1** (109.39 g, 87%) was obtained as a liquid (t_R 6.12 min).

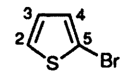
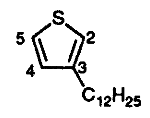
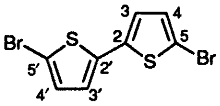
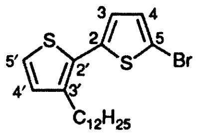
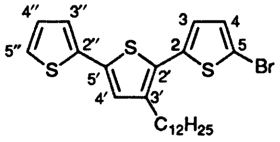
2-*Bromo*-3-*dodecylthiophene* **2**.—In the absence of light, a solution of NBS (8.49 g, 48.0 mmol) in DMF (40 cm^3) was slowly added dropwise to a solution of **1** (10.95 g, 43.0 mmol) in DMF (35 cm^3), and the mixture was stirred for 40 h, poured onto ice, and extracted several times with diethyl ether. The organic phases were combined, washed with water, and dried over sodium sulfate. Evaporation of the solvent and distillation under reduced pressure yielded **2** (11.52 g, 80.9%) as a slightly yellow liquid (GLC > 95%). Subsequent fractionated distillation afforded **2** (10.68 g, 75%) in >98% purity (t_R 10.35 min); δ_H(250 MHz; $CDCl_3$) 7.18 (1 H, d, $^{3}J_{5,4}$ 5.6, 5-H), 6.79 (1 H, d, $^{3}J_{4,5}$ 5.6, 4-H), 2.56 (2 H, t, $^{3}J_{1',2'}$ 7.6, 1′-H_2), 1.40 (20 H, 2′–11′-H_2) and 0.88 (3 H, t, *J* 6.5, 12′-H_3).

2,5-*Dibromo*-3-*dodecylthiophene* **3**.—Compound **1** (30 g, 0.12 mol) and NBS (42.6 g, 0.24 mol) in DMF (450 cm^3) are allowed to react under the conditions given for the synthesis of **2**. After a reaction time of 3 h at 40 °C, compound **3** (42.76 g, 86%) was obtained as a yellowish liquid (b.p. 150–160 °C/10^{-3} mmHg; GLC > 96%; t_R 11.73 min); δ_H(250 MHz; $CDCl_3$) 6.77 (1 H, s, 4-H), 2.50 (2 H, t, $^{3}J_{1',2'}$ 7.6, 1′-H_2), 1.53 (2 H, m, 2′-H_2), 1.27 (18 H, 3′–11′-H_2) and 0.88 (3 H, t, *J* 6.6, 12′-H_3).

3-*Dodecyl*-2,2′-*bithiophene* **4**.—From 2-bromothiophene (2.31 g, 14.2 mmol) and magnesium turnings (0.38 g, 15.6 mmol) in diethyl ether (50 cm^3), the corresponding Grignard reagent was prepared and coupled with bromide **2** (3.7 g, 11.2 mmol) and Ni(dppp)Cl_2 (0.147 g, 0.27 mmol) in diethyl ether (30 cm^3), according to the procedure for the synthesis of **1**. The bithiophene **4** (3.18 g, 85%) was isolated after distillation under reduced pressure as a slightly yellow liquid (b.p. 175–180 °C/5 × 10^{-3} mmHg), m.p. 0–10 °C, GLC > 96% (t_R 13.27 min); δ_H(250 MHz; $CDCl_3$) 7.27 (1 H, dd, $^{3}J_{5',4'}$ 5.1, $^{4}J_{5',3'}$ 1.2, 5′-H), 7.14 (1 H, d, $^{3}J_{5,4}$ 5.4, 5-H), 7.09 (1 H, dd, $^{3}J_{3',4'}$ 3.7, $^{4}J_{3',5'}$ 1.2, 3′-H), 7.04 (1 H, dd, $^{3}J_{4',5'}$ 5.2, $^{3}J_{4',3'}$ 3.7, 4′-H), 6.91 (1 H, d, $^{3}J_{4,5}$ 5.3, 4-H), 2.65 (2 H, t, *J* 7.8, 1″-H_2), 1.54 (2 H, m, 2″-H_2) 1.25 (18 H, 3″–11″-H_2) and 0.80 (3 H, t, *J* 6.6, 12″-H_3).

3′-*Dodecyl*-2,2′:5′,2″-*terthiophene* **6**.—From 2-bromothio-

Table 1 ^{13}C chemical shifts and ^{13}C, ^{1}H coupling constants of selected bromo-, alkyl- and alkyl(bromo)-thiophenes

			 1				 5a		 7a	
C-2	126.82				137.80		137.80		137.42	
	^1J(C-2, 2-H)	184.6								
	^2J(C-2, 3-H)	4.9			^2J(C-2, 3-H)	5.2	^2J(C-2, 3-H)	5.4	^2J(C-2, 3-H)	5.1
	^3J(C-2, 4-H)	11.4			^3J(C-2, 4-H)	11.0	^3J(C-2, 4-H)	9.1	^3J(C-2, 4-H)	10.5
					^3J(C-2, 3′-H)	2.2				
							^4J(C-2, 5′-H)	1.9		
C-3	127.51				124.16		126.21		126.06	
	^1J(C-3, 3-H)	169.1			^1J(C-3, 3-H)	169.3	^1J(C-3, 3-H)	169.3	^1J(C-3, 3-H)	169.3
	^2J(C-3, 4-H)	4.5			^2J(C-3, 4-H)	4.7	^2J(C-3, 4-H)	4.7	^2J(C-3, 4-H)	4.7
C-4	129.71				130.67		130.13		130.23	
	^1J(C-4, 4-H)	172.6			^1J(C-4, 4-H)	173.5	^1J(C-4, 4-H)	172.9	^1J(C-4, 4-H)	168.6
	^2J(C-4, 3-H)	5.7			^2J(C-4, 3-H)	4.9	^2J(C-4, 3-H)	5.2	^2J(C-4, 3-H)	5.1
	^3J(C-4, 2-H)	8.6								
C-5	112.04				111.54		111.74		111.84	
	^2J(C-5, 4-H)	2.2			^2J(C-5, 4-H)	1.6	^2J(C-5, 4-H)	1.5	^2J(C-5, 4-H)	1.7
	^3J(C-5, 3-H)	14.0			^3J(C-5, 3-H)	14.8	^3J(C-5, 3-H)	14.9	^3J(C-5, 3-H)	15.0
	^3J(C-5, 2-H)	7.6								
C-2′			119.73				129.55		128.47	
			^1J(C-2′, 2′-H)	182.6			[a]		[a]	
			^3J(C-2′, 4′-H)	9.6						
			^3J(C-2′, 5′-H)	5.4						
			^3J(C-2′, α-CH$_2$)	5.4						
C-3′			143.24				140.24		140.91	
			^2J(C-3′, 4′-H)	5.4			^2J(C-3′, 4′-H)	5.4	^2J(C-3′, 4′-H)	3.7
			^2J(C-3′, 2′-H)	3.8			^3J(C-3′, 5′-H)	9.4	^2J(C-3′, α-CH$_2$)	1.8
			^3J(C-3′, 5′-H)	9.2						
C-4′			128.26				129.88		126.45	
			^1J(C-4′, 4′-H)	165.2			^1J(C-4′, 4′-H)	165.9	^1J(C-4′, 4′-H)	164.8
			^2J(C-4′, 5′-H)	4.0			^2J(C-4′, 5′-H)	4.6		
			^3J(C-4′, 2′-H)	13.0						
			^3J(C-4′, α-CH$_2$)	9.2			^3J(C-3′, α-CH$_2$)	8.3	^3J(C-4′, α-CH$_2$)	5.0
C-5′			124.99				124.21		135.67	
			^1J(C-5′, 5′-H)	185.3			^1J(C-5′, 5′-H)	186.4		
			^2J(C-5′, 4′-H)	5.2			^2J(C-5′, 4′-H)	6.3	^2J(C-5′, 4′-H)	3.1
			^3J(C-5′, 2′-H)	7.0					^3J(C-5′, 3″-H)	5.0
									^4J(C-5′, α-CH$_2$)	1.3
C-2″									136.98	
									^2J(C-2″, 3″-H)	4.3
									^3J(C-2″, 4″-H)	10.1
									^3J(C-2″, 5″-H)	6.5
C-3″									123.78	
									^1J(C-3″, 3″-H)	166.8
									^2J(C-3″, 4″-H)	3.6
									^3J(C-3″, 5″-H)	9.2
C-4″									127.88	
									^1J(C-4″, 4″-H)	168.6
									^2J(C-4″, 3″-H)	3.6
									^2J(C-4″, 5″-H)	5.1
C-5″									124.56	
									^1J(C-5″, 5″-H)	187.1
									^2J(C-5″, 4″-H)	6.9
									^3J(C-5″, 3″-H)	10.7

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[a] Couplings not resolved.

Table 2 Elemental analytical data for the thiophenes **2**–**9**

Compound	Formula (molar mass)	M.p./b.p. (°C/ mmHg)	Requires (%) Found (%)			
			C	H	Br	S
2	$C_{16}H_{27}BrS$	122–125	58.00	8.21	24.11	9.68
	(331.4)	0.001	57.9	8.3	24.3	9.5
3	$C_{16}H_{26}Br_2S$	150–160	46.84	6.39	38.95	7.82
	(410.2)	0.001	47.1	6.5	38.9	7.95
4	$C_{20}H_{30}S_2$	175–178	71.80	9.04		19.17
	(334.6)	0.005	71.9	9.0		19.1
5a	$C_{20}H_{29}BrS_2$	185–190	58.10	7.07	19.32	15.51
	(413.5)	0.005	58.2	7.2	19.6	15.55
6	$C_{24}H_{32}S_3$	39–40	69.18	7.74		23.08
	(416.7)		69.2	7.8		23.0
7a	$C_{24}H_{31}BrS_3$	43–43.5	58.16	6.31	16.12	19.41
	(495.6)		58.3	6.4	16.2	19.2
8	$C_{24}H_{30}Br_2S_3$	48–49	50.18	5.26	27.82	16.75
	(574.5)		50.1	5.3	27.9	16.5
9	$C_{48}H_{62}S_6$	110–111	69.43	7.40		23.17
	(830.4)		69.5	7.5		22.9

phene (48.6 g, 0.298 mol) and magnesium turnings (7.9 g, 0.3 mol) in diethyl ether (100 cm^3), the corresponding Grignard reagent was prepared and coupled with dibromide **3** (42.76 g, 0.103 mol) and Ni(dppp)Cl_2 (0.275 g, 0.5 mmol) in diethyl ether (100 cm^3), according to the procedure for the synthesis of **1**. The reaction mixture in this case was extracted with dichloromethane, and the crude product was purified by chromatography on silica gel [eluent hexane–dichloromethane (40 : 1)]. Recrystallization from methanol gave the terthiophene **6** (13.3 g, 31%) as yellow solid, m.p. 39–40 °C; GLC > 98%; t_R 23.25 min; δ_H(250 MHz; $CDCl_3$) 7.31 (1 H, dd, $^{3}J_{5',4'}$ 4.9, $^{4}J_{5',3'}$ 1.2, 5-H), 7.21 (1 H, dd, $^{3}J_{5'',4''}$ 5.1, $^{4}J_{5'',3''}$ 1.2, 5″-H), 7.16 (1 H, dd, $^{3}J_{3'',4''}$ 3.6, $^{4}J_{3'',5''}$ 1.2, 3″-H), 7.13 (1 H, dd, $^{3}J_{3,4}$ 3.7, $^{3}J_{3,5}$ 1.2, 3-H), 7.07 (1 H, dd, $^{3}J_{4,5}$ 4.9, $^{3}J_{4,3}$ 3.7, 4-H), 7.02 (1 H, dd, $^{3}J_{4'',5''}$ 5.1, $^{3}J_{4'',3''}$ 3.6, 4″-H), 7.02 (1 H, s, 4′-H), 2.65 (2 H, t, *J* 7.8, 1‴-H_2), 1.58 (2 H, m, 2‴-H_2), 1.25 (18 H, 3‴–11‴-H_2) and 0.81 (3 H, t, $^{3}J_{11''',12'''}$ 6.5, 12‴-H_2).

5-*Bromo*-3′-*dodecyl*-2,2′-*bithiophene* **5a**.—Compound **4** (1.5 g, 4.5 mmol) and NBS (0.8 g, 4.5 mmol) in DMF (15 cm^3) were allowed to react as described for the synthesis of **2**. The NBS was added over a period of 90 min, and the reaction mixture was subsequently stirred for 5 h. After the usual work-up, the product mixture (containing **4**, **5a**/**b** and the dibromo compound) was purified by chromatography on silica gel (eluent hexane), to afford **5a**/**b** (88 : 12) (0.87 g, 47%) as a pale yellow oil, b.p. 185–190 °C/5 × 10^{-3} mmHg; m.p. 5–10 °C; GLC > 99%; t_R 13.30 min; δ_H(250 MHz; $CDCl_3$) 7.17 (1 H, d, $^{3}J_{5',4'}$ 5.2, 5′-H), 7.00 (1 H, d, $^{3}J_{3,4}$ 3.8, 3-H), 6.91 (1 H, d, $^{3}J_{4',5'}$ 5.2, 4′-H), 6.84 (1 H, d, $^{3}J_{4,3}$ 3.8, 4-H), 2.69 (2 H, t, *J* 7.8, 1″-H_2), 1.60 (2 H, m, 2″-H_2), 1.25 (18 H, 3″–11″-H_2) and 0.88 (3 H, t, *J* 6.6, 12″-H_2).

5-*Bromo*-3′-*dodecyl*-2,2′:5′,2″-*terthiophene* **7a**.—Compound **6** (4 g, 9.6 mmol) and NBS (3.4 g, 19.2 mmol) in DMF (80 cm^3) were allowed to react as described for the synthesis of **2**. The NBS was added over a period of 30 min, and the mixture was subsequently stirred for 12 h. After the usual work-up, the product mixture (containing **6**, **7** and **8**) was purified by chromatography on silica gel [eluent hexane–dichloromethane (30 : 1)] to afford crude regioisomers **7a**/**b** (2.68 g, 56%, 96.5 : 3.5) as a pale yellow oil. Repeated recrystallization from ethanol yielded **7a** (1.25 g, 26%) as a yellow solid, m.p. 43–43.5 °C; HPLC > 98%; δ_H(250 MHz; $CDCl_3$) 7.24 (1 H, dd, $^{3}J_{5'',4''}$ 5.0, $^{4}J_{5'',3''}$ 1.1, 5″-H), 7.18 (1 H, dd, $^{3}J_{3'',4''}$ 3.6, $^{4}J_{3'',5''}$ 1.1, 3″-H), 7.04 (1 H, dd, $^{3}J_{4'',3''}$ 3.6, $^{3}J_{4'',5''}$ 5.0, 4″-H), 7.04 (1 H, d, $^{3}J_{4,3}$ 3.8, 4-H), 7.02 (1 H, s, 4′-H), 6.89 (1 H, d, $^{3}J_{3,4}$ 3.8, 3-H), 2.68 (2 H, t, $^{3}J_{1''',2'''}$ 7.8, 1‴-H_2), 1.65 (2 H, m, 2‴-H_2), 1.25 (18 H, 3‴–11‴-H_2) and 0.88 (3 H, t, *J* 6.6, 12‴-H_3). Additionally, pure dibromo derivative **8** (0.53 g, 9.4%) was isolated by chromatography as a separate fraction.

5,5″-*Dibromo*-3′-*dodecyl*-2,2′:5′,2″-*terthiophene* **8**.—Compound **6** (2 g, 4.8 mmol) and NBS (2.76 g, 15 mmol) in DMF (70 cm^3) were allowed to react as described for the synthesis of **2**. The NBS was added over a period of 30 min and the mixture was subsequently stirred for 40 h, to yield compound **8** (1.84 g, 66%) as a yellow solid, m.p. 48–49 °C; δ_H(250 MHz; $CDCl_3$) 7.00 (1 H, d, $^{3}J_{4,3}$ 3.9, 4-H), 6.99 (1 H, d, $^{3}J_{4'',3''}$ 3.9, 4″-H), 6.90 (1 H, s, 4′-H), 6.87 (1 H, d, $^{3}J_{3'',4''}$ 3.9, 3″-H), 6.84 (1 H, d, $^{3}J_{3,4}$ 3.9, 3-H), 2.65 (2 H, t, $^{3}J_{1',2'}$ 7.8, 1‴-H), 1.60 (2 H, m, 2‴-H_2), 1.25 (18 H, 3‴–11‴-H_2) and 0.88 (3 H, t, *J* 6.59, 12‴-H_3). Additionally, the monobromo derivatives **7** (0.23 g, 9.6%) were isolated by chromatography as a separate fraction.

4′,3⁗′-*Didodecyl*-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-*sexithiophene* **9**.—Anhydrous nickel dichloride (25.3 mg, 0.2 mmol), zinc (0.33 g, 5 mmol), and triphenylphosphine (0.33 g, 1.26 mmol) were heated to 70 °C in DMF (5 cm^3) for 1 h. The reddish-brown solution turned green upon addition of alkyl(bromo)thiophene **7a** (0.8 g, 1.6 mmol). The reaction mixture was heated to 70 °C for 7 h, and filtered while hot. The product precipitated upon cooling. Successive chromatography on silica gel [eluent hexane–dichloromethane (3 : 1)] afforded the pure sexithienyl **9** (0.23 g, 33%) as orange microcrystals, m.p. 110–111 °C; δ_H(250 MHz; $CDCl_3$) 7.22 [2 H, dd, $^{3}J_{5,4(5''''',4''''')}$ 5.0, $^{4}J_{5,3(5''''',3''''')}$ 1.1, 5- and 5⁗′-H], 7.17 [2 H, dd, $^{3}J_{3,4(3''''',4''''')}$ 3.6, $^{4}J_{3,5(3''''',5''''')}$ 1.1, 3- and 3⁗′-H], 7.13 [2 H, dd, $^{3}J_{3'',4''(4''',3''')}$ 3.8, $^{3}J_{3,5}$ 1.2, 3″- and 4‴-H], 7.04 [2 H, dd, $^{3}J_{4'',3''(3''',4''')}$ 3.8, 4″- and 3‴-H], 7.02 [2 H, dd, $^{3}J_{4,5(4''''',5''''')}$ 5.0, $^{3}J_{4,3(4''''',3''''')}$ 3.6, 4- and 4⁗′-H], 7.02 (2 H, 3′ and 4⁗-H), 2.77 (4 H, t, *J* 7.8, $CH_2C_{11}H_{23}$), 1.68 (4 H, m, $CH_2CH_2C_{10}H_{21}$), 1.25 (36 H, $CH_2CH_2[CH_2]_9Me$) and 0.88 (6 H, t, *J* 6.6, 2 × Me).

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