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# Preparation and Oxidative Doping Studies of Dithienyl Polyenes Stabilized by Alkyl Group Substitution

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Dithienyl polyenes with up to 10 double bonds have been synthesized by Wittig condensation. The thienyl end groups were substituted in the β and β' positions with butyl groups, resulting in greatly enhanced polyene solubility in common solvents. Oxidative doping of the polyene series with $SbCl_5$ in methylene dichloride solution produced extremely stable bipolaron-like dications. Preliminary evaluation of the third-order optical nonlinearity of both the neutral and doped species by degenerate four-wave mixing confirms previous predictions of bipolaronic enhancement of $\chi^{(3)}$, the third-order susceptibility.

Over the past 4 years, we have reported several synthetic studies whose stated goal was the preparation of series of stable, processable polyenes whose third-order nonlinear optical properties as a function of conjugation length could be evaluated by such techniques as third harmonic generation or degenerate four-wave mixing.[1–3] Parent α,ω-dithienyl polyenes as well as polyenes terminally substituted in the 5' and 5'' with functionalities such as RO and RS were synthesized and oxidatively doped to bipolaron-like dications (BP). Thus, these systems modelled quite well the formation of spinless bipolarons in oxidatively doped conjugated polymers, such as poly-[2,5-thienylenevinylene].[4] However, the solubility limitations of these series precluded measurement of their third-order nonlinearities either by third harmonic generation (THG) or degenerate four-wave mixing (DFWM). Only in the case of dithienyl polyenes terminally substituted with decylsulfanyl groups, could $\gamma_{THG}$ be evaluated up to the hexaene, albeit with large error bars.[5] It was thought that alkyl substitution in the β and β' positions of each thiophene unit in the dithienyl polyenes would yield solubility enhancement such that long polyene sequencies could be synthesized and for which nonlinear optical susceptibility measurements for well-characterized long conjugation lengths could be made. In addition, bipolaron formation and stabilization in these long conjugation sequences could be studied to determine if self-localization phenomena limited the optical nonlinearity.

*Synthesis of (dibutyl)thienyl polyenes.* We have previously described the syntheses of dithienyl polyenes substituted with alkyl, alkoxy and alkylsulfanyl substituents.[1–3,5] Increased
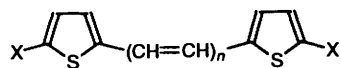


X = Me, MeO, MeS, $C_{10}H_{21}S$

solubility was observed for the $C_{10}H_{21}S$ samples, but still insufficient to obtain accurate $\chi^{(3)}$ values for *n* greater than 4 *via* degenerate four-wave mixing experiments. In the present study, two series of polyenes were synthesized wherein X = H and alkylsulfanyl. In order to balance solubility enhancement with



X = H, BuS

*n* = 3,4,5....

**1**
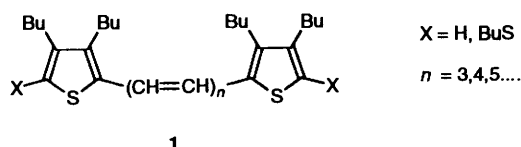
the possibility of side-chain crystallization, an intermediate-length alkyl group, butyl, was selected. In addition, we

attempted to determine how long the polyene sequence could be extended without considerable loss of solubility and polyene environmental stability.

As we have outlined in our previous series of papers,[1–5] a Wittig approach was utilized that yielded a symmetrically substituted polyene series. Similar strategies have been employed by Blanchard-Desce.[6] This approach is outlined in Scheme 1.
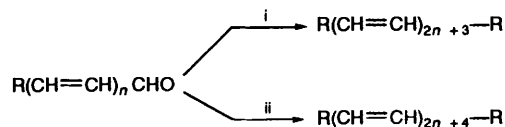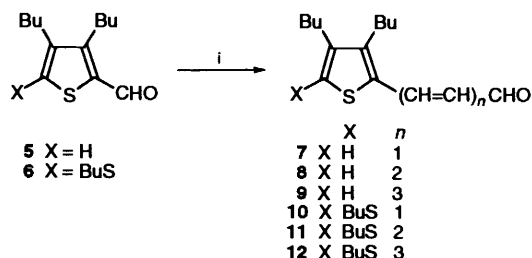


**Scheme 1** *Reagents:* i, $Bu_3\overset{+}{P}CH_2CH=CHCH_2\overset{+}{P}Bu_3$ 2 Cl$^-$, NaOEt, EtOH or DMF; ii, $Bu_3\overset{+}{P}CH_2(CH=CH)_2CH_2\overset{+}{P}Bu_3$ 2 Br$^-$, NaOEt, EtOH or DMF

3,4-Dibutylthiophene was synthesized essentially by the method of Tour and Wu[7] from 3,4-dibromothiophene. A butylsulfanyl substituent was introduced by lithiation of **3** followed by addition of sulfur followed by iodobutane. Finally, formylation of either **3** or **4** was carried out as we have described previously.[1–5] This sequence is illustrated in Scheme 2.



**2**

    3 $R^1 = R^2 = H$
    4 $R^1 = BuS, = R^2 = H$
    6 $R^1 = BuS, = R^2 = CHO$
    5 $R^1 = H, R^2 = CHO$
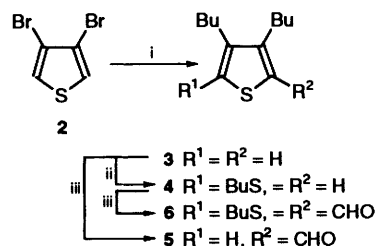
**Scheme 2** *Reagents:* i, BuMgBr[Ni(dppp)Cl₂]; ii, BuLi/TMEDA; S; BuI; iii, BuLi/TMEDA, 25 °C; DMF

Either **5** or **6** could be extended *via* Wittig methodology developed in our laboratory based on an original suggestion by Cresp *et al.*[8,9] illustrated in Scheme 3. All polyenes were then



| | X | n |
|---|---|---|
| 5 X = H | 7 X H | 1 |
| 6 X = BuS | 8 X H | 2 |
| | 9 X H | 3 |
| | 10 X BuS | 1 |
| | 11 X BuS | 2 |
| | 12 X BuS | 3 |

**Scheme 3** *Reagents:* i, $\overline{OCH_2CH_2O}CH-CH_2\overset{+}{P}Bu_3$, Br$^-$, DMF, 90 °C; 10% aq. HCl, THF

**Table 1**  Absorption spectra for neutral polymers and bipolaron-like dications (BP)

| Compd. | $\pi$-$\pi$* [$\lambda$/nm ($\varepsilon_{max}$/10$^4$ (dm$^3$ mol$^{-1}$ m$^{-1}$))][a] | BP [$\lambda$/nm ($\varepsilon_{max}$/10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)][a] |
|---|---|---|
| 1a | 422, **399**, 380 (5.3) | **655**, 593 |
| 1b | 443, **418**, 396 (8.8) | **661**, 600 |
| 1c | 462, **435**, 412 (6.2) | **715**, 679 |
| 1d | 480, **450**, 426 (9.1) | **809**, 719 |
| 1e | 496, **464**, 439 (14.6) | **849**, 790 |
| 1f | 510, **477**, 450 (16.8) | **914**, 855 |
| 1g | 521, **489**, 461 (15.5) | **971**, 892 |
| 1h | 534, **499**, 471 (13.6) | **1022**, 950 |
| 1i | 424 (3.1) | 643 (6.4) |
| 1j | 439 (4.3) | 657 (5.6) |
| 1k | 451 (4.8) | 705 (6.2) |
| 1l | 466 (4.8) | 754 (5.6) |
| 1m | 476 (15.9) | 801 (15.6) |
| 1n | 488 (21.2) | 849 (20.0) |
| 1o | 501 (23.4) | 867 (44.4) |
| 1p | b | — |
| 1q | b | — |

[a] 10$^{-5}$ mol dm$^{-3}$ CH$_2$Cl$_2$; peak of maximum intensity in bold. [b] Polyene decomposes rapidly.

synthesized from either **5, 6** or their extended counterparts. All polyenes were obtained by Wittig reaction, as shown in Scheme 1, and are illustrated in Scheme 4. Oxidative doping was carried
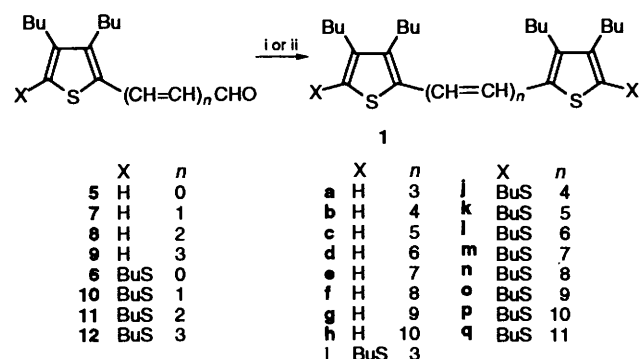


**Scheme 4**  *Reagents:* i, Bu$_3\overset{+}{P}$CH$_2$CH=CHCH$_2\overset{+}{P}$Bu$_3$ 2 Cl$^-$, NaOEt or DMF; ii, Bu$_3\overset{+}{P}$CH$_2$(CH=CH)$_2$CH$_2\overset{+}{P}$Bu$_3$, 2 Br$^-$, NaOEt, EtOH or DMF

out in CH$_2$Cl$_2$ solution by careful addition of a known amount of SbCl$_5$ in CH$_2$Cl$_2$. In all cases, an excess of dopant was present. The bipolaron-like dications formed from the neutral polymers are extremely stable under ambient laboratory conditions (*e.g.* solutions are in contact with air with no special precautions to protect them from normal humidity). Some solutions were monitored periodically, and showed little evidence of change, as determined by comparison of optical absorption over several months. The UV–VIS–NIR absorptions for both neutral and oxidized (doped) species are displayed in Table 1.

## Results and Discussion

The question of conjugation length dependence of both $\beta$ and $\gamma$, the nonlinear hyperpolarizabilities, has been of interest for some time, particularly from the perspective of whether some length limitation of electron delocalization may effectively limit any further increases in the nonlinearity. Prasad, for example, has clearly shown for series of electroactive oligomers that $\gamma$ may be related to delocalization which is less than the perceived, or formula, conjugation length owing to steric or conformational effects that may cause twisting out of planarity and loss of orbital overlap.[10,11] Thus, in poly(3-dodecylthiophene) delocalization may occur over as many as 10 repeat units, while in
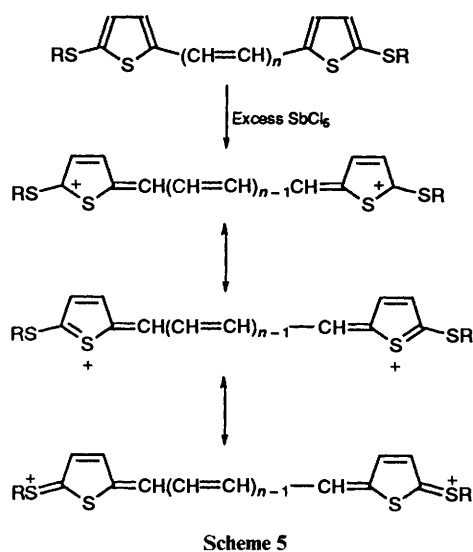
p-phenylene oligomers, effective conjugation occurs only up to the terphenyl level.

We have shown in our previous studies on the formation of bipolaron-like dications in a variety of systems that delocalization occurs effectively over the length of the oligomer, particularly if electron-donating substituents in the terminal aromatic rings provide mesomeric stabilization of the developing positive charges. With thienyl end groups, additional stabilization is provided by the ring sulfurs. When this is coupled with the additional mesomeric stabilization associated with the highly polarizable RS substituents, it comes as no surprise that the bipolaronic charge generation and stabilization observed in the dithienyl polyene systems is particularly favoured, as illustrated in Scheme 5. When the identity of the R group in question is Bu or greater, and additional substituents in the 3 and 4 positions add both increased solubility and inductive electron-release, we should expect both highly processable and stable bipolaronic species. This is, in fact, what is observed. Not only are the oxidized species exceedingly stable, they are also extremely soluble in a variety of solvents. For example, all of the components listed in Table 1 up to the octaene level are soluble to the extent of 10$^{-3}$–10$^{-2}$ mol dm$^{-3}$ in both hexane and methylene dichloride. This is in marked contrast to previous polyene series, for which 10$^{-6}$ mol dm$^{-3}$ solutions at the hexaene level was the upper limit of solubility. Since degenerate four-wave mixing studies either slightly on or off resonance usually require concentration levels of 1% or better, the present series of polyenes represents the first series with sufficient solubility to be capable of providing a conjugation length versus nonlinearity evaluation for both neutral and doped species.

DeMelo and Silbey postulated that enhancement of $\gamma$ may be possible by incorporation of either polaronic or bipolaronic charge states in the $\pi$-conjugation sequence.[12,13] Birge and co-workers have refined the original calculations and also confirm the prediction of bipolaronic enhancement of $\gamma$.[14] When one couples the observation that in electroactive polymers the bipolaron states are confined with the prediction that third-order NLO response is proportional to 1/Eg$^6$, where Eg is the band gap,[15,16] it is germane to determine if bipolaronic charge delocalizes over the whole oligomer length when that length is systematically increased one unit at a time. Brédas and co-workers have recently reviewed both theoretical and experimental aspects of bipolaronic enhancement and have correctly indicated that conflicting evidence exists in the literature.[17] We have recently reported a two-order magnitude increase in the oxidative doping in dianthracenyl polyenes, however, these

**Table 2** $\chi^{(3)}$ Values for neutral and doped dithienyl polyenes (X = H) by degenerate four-wave mixing

| $n$ | $\lambda$/nm | $\chi^{(3)}$ neutral/$10^{-13}$ esu$^a$ | $\chi^{(3)}$ doped/$10^{-13}$ esu$^a$ |
|---|---|---|---|
| 5 | 532 | 2.7 | 7.8 |
| 7 | 532 | 43.0 | 11 |
| 8 | 532 | 258 | 14 |
| 5 | 1064 | 0.54 | 1.4 |
| 7 | 1064 | 0.85 | 3.2 |
| 8 | 1064 | 0.66 | 2.7 |

$^a$ All solutions corrected to $10^{-3}$ mol dm$^{-3}$.

**Table 3** $\chi^{(3)}$ Values for neutral bis-thienyl polyenes (X = BuS) by degenerate four-wave mixing at 532 nm

| $n$ | $\chi^{(3)}$ neutral/$10^{-13}$ esu$^a$ |
|---|---|
| 3 | 1.3 |
| 4 | 9.5 |
| 5 | 48 |
| 6 | 170 |
| 7 | 300 |
| 8 | 1000 |

$^a$ All solutions corrected to $10^{-3}$ mol dm$^{-3}$.



**Scheme 5**

materials have severe solubility limitations which preclude any length-dependence studies.[18,19]

One notable trend in the UV–VIS–NIR spectra of both dithienyl polyene series shown in Table 1 is the remarkable shift in oscillator strength upon doping. In addition, the dramatic red shifts between series members is still maintained at the decaene level, implying that delocalization over the oligomer length is maintained. For **1h**, this would imply delocalization over 28 atoms, comparable to delocalization in polyacetylene and ladder polymers such as POL and PTL.[20] The decreasing band gap associated with this delocalization should be manifested by enhanced optical nonlinearity. We have previously reported preliminary $\chi^{(3)}$ results for selected members of the X = H series.[21] Measurements were conducted at both 532 and 1064 nm by degenerate four-wave mixing in conventional back-beam geometry. These results are shown in Table 2.

Given the fixed irradiation wavelengths utilized in this study, the question of bipolaronic enhancement is difficult to settle conclusively. Only for the $n = 5$ substrate can the neutral and doped results be compared without one or the other measurement being significantly resonance enhanced. For this sample, bipolaronic enhancement, by a factor of 2.6–2.8 is observed. For $n = 7$ and 8, $\chi^{(3)}$ neutral shows increasing resonance enhancement at 532 nm as would be expected from examination of the absorption spectra. The extent to which $\chi^{(3)}$ neutral can display resonance enhancement is seen in the X = BuS series, as seen in Table 3. In this series, both $n = 7$ and 8 have leading edge absorption at 532 nm. It is significant that the butylsulfanyl substituents enhance $\chi^{(3)}$ neutral for comparable $n$. Meyers and Brédas have recently calculated that push-push (donor–donor) polyenes should demonstrate increasing $\langle\gamma\rangle$ as a function of chain length compared to push-pull, which

dominate at lower chain length ($n = 2,3$).[22] This data clearly confirms dramatic donor group enhancement (factor of 18) of $\chi^{(3)}$ for $n = 5$. Comparison of higher series members is difficult due to differing degrees of resonance enhancement, as can be seen from the absorption spectra (Table 1).

In our previous studies, polyene segment lengths were limited by the solubility of both Wittig intermediates and the final products. This is not the case for the polyenes prepared in this study. For example, in both the X = H and X = BuS series, solubility is still quite good up to the decaene level. However, when longer polyene syntheses were attempted, the products became increasingly unstable and decomposed during either recrystallization or chromatographic purification, even at room temperature. Comparison of absorption spectra before and after silica gel chromatography of the X = BuS decaene showed dramatic changes, primarily loss of low-energy absorption. This may be indicative of oxidative cross-linking of polyene sequences once the polyene segments attain a certain length. Similar results were oserved for the X = H, $n = 11$ and 12 oligomers. We are currently attempting to address these issues by further addition of stabilizing groups.

*Conclusions.*—In this study, we have demonstrated that long polyene oligomers can be synthesized and stabilized up to the decaene limit. Attempts to prepare even longer sequences have not been successful owing to polyene instability rather than the solubility limitations encountered in previous studies. Bipolaron-like dications for all of the samples synthesized in this study can be formed by oxidation with SbCl$_5$ in CH$_2$Cl$_2$ solution, and are exceptionally stable. Preliminary evaluation of the third-order nonlinearity of both the neutral and doped species were carried out at 532 and 1064 nm by degenerate four-wave mixing and provided further evidence for bipolaronic enhancement of $\chi^{(3)}$. Since it is difficult to compare $\chi^{(3)}$ results for a complete series at these wavelengths without encountering resonance enhancement for some of our samples, it is clear that $\chi^{(3)}$ measurements by third harmonic generation using irradiation at 1.9 or 2.1 μm are necessary to evaluate fully whether $\gamma$ is still increasing for the longer conjugation lengths. However, it is certain that both the neutral and oxidized polyenes reported in this study are among the most non-linear small molecules yet studied, and deserve much more detailed spectroscopic evaluation.

## Experimental

Mps were obtained with an electrothermal apparatus and are uncorrected. C,H,N analyses were carried out in our laboratory with a Perkin-Elmer Model 240 analyzer by Paulanne Rider. UV–VIS–NIR spectra were recorded with Hitachi Model 200 and Guided Wave Model 200-25 spectrometers as CH$_2$Cl$_2$ solutions. $^1$H NMR spectra were determined as solutions in CDCl$_3$ unless otherwise noted (Me$_4$Si internal reference, $J$ values are given in Hz) on an IBM WP-200 spectrometer. Solutions of pure polyenes ($10^{-5}$ mol dm$^{-3}$) were oxidized in a

controlled manner so that an excess of oxidizing agent was present. All doping studies were carried out in a 1 cm path length silica cell, and absorption spectral changes recorded in the range 400–1600 nm with a Guided Wave spectrometer via a fibre-optic cable link to a remote sample cell at a scan rate of 7 nm s$^{-1}$. Scans were repeated over a 24 h period to determine the relative stabilities of the BPs produced. In all cases very rapid bleaching of the original $\pi$–$\pi$* transition was observed (less than 30 s after mixing) simultaneously with the appearance of the BP absorption. The following abbreviations have been used: DMF (N,N-dimethylformamide); TMEDA (N,N,N,N-tetramethylethylenediamine).

3,4-Dibutylthiophene 3.—A solution of butylmagnesium chloride (2 mol dm$^{-3}$ solution in diethyl ether; 0.33 mol, 165 cm$^3$) was added dropwise to a solution of 3,4-dibromothiophene[13] and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.5 g) in diethyl ether (400 cm$^3$) at 0 °C. The solution was warmed slowly to 50 °C and held at this temperature for 16 h. Water (50 cm$^3$) containing a few drops of conc. HCl was then added dropwise to the reaction mixture with ice-bath cooling. After filtration to remove solid impurities, the liquid was further extracted with diethyl ether (3 × 100 cm$^3$). The combined extracts were washed with brine and dried (MgSO$_4$). After removal of the drying agent, vacuum distillation yielded pure 3 (25.7 g, 92%), bp (1 Torr) 92–94 °C; $\delta_H$ 0.91 (t, 6 H, J 11, CH$_3$), 1.34–1.68 (m, 8 H, CH$_2$), 2.51 (t, 4 H, J 6, CH$_2$) and 6.87 (s, 2 H, ring $\alpha$-H); $\delta_C$ 13.96, 22.63, 28.43, 31.82, 119.87 and 141.98 Hz.

3,4-Dibutylthiophene-2-carbaldehyde 5.—A solution of butyllithium (1.6 mol dm$^{-3}$ solution in hexanes; 0.10 mol, 62.5 cm$^3$) was added dropwise to a solution of 3 (19.6 g, 0.1 mol) and TMEDA (11.6 g, 0.1 mol) in THF (100 cm$^3$). The resulting mixture was then refluxed for 2 h, cooled to room temperature and treated dropwise with DMF (40 cm$^3$). After the addition was complete, the mixture was again refluxed for 0.5 h, after which it was cooled to room temperature, acidified by dropwise addition of 3 mol dm$^{-3}$ HCl solution (150 cm$^3$) and refluxed for 0.5 h. After being poured into cold water, the mixture was extracted with diethyl ether (3 × 100 cm$^3$). The combined extracts were washed with brine, dried (MgSO$_4$) and evaporated. The title compound 5 was obtained by vacuum distillation of the residue (15.6 g, 70%), bp 125–127 °C (1 Torr); $\delta_H$ 0.90 (m, 6 H, CH$_3$), 1.4–1.7 (m, 8 H, CH$_2$), 2.5 (t, 2 H, J 11, CH$_2$), 2.9 (t, 2 H, J 11, CH$_2$), 2.9 (t, 2 H, J 11, CH$_2$), 7.3 (s, 1 H) and 10.0 (s, H, CHO). The product was used directly without further purification.

3,4-Dibutyl-5-butylsulfanylthiophene 4.—A solution of butyllithium (1.6 mol dm$^{-3}$ solution in hexanes; 0.375 mol, 150 cm$^3$) was added dropwise to a solution of 3 (71.2 g, 0.36 mol) and TMEDA (54.5 cm$^3$, 0.35 mol) in THF (250 cm$^3$) at room temperature. The resulting mixture was refluxed for 0.5 h, cooled in an ice-bath, and powdered sulfur (12.0 g, 0.375 mol) added carefully. After the resulting mixture had become clear, iodobutane (45.4 cm$^3$, 0.40 mol) was added dropwise. It was then stirred at room temperature overnight, poured into cold water and extracted with ethyl ether (3 × 150 cm$^3$). The combined extracts were washed with brine, dried (MgSO$_4$) and evaporated. The title compound 4 was obtained by vacuum distillation (64.4 g, 62%), bp 140–141 °C (1 Torr); $\delta_H$ 0.96 (m, 9 H, CH$_3$), 1.29–1.76 (m, 12 H, CH$_2$), 2.50 (t, 2 H, J 9, CH$_2$), 2.9 (t, 2 H, J 11, CH$_2$), 2.64 (t, 2 H, J 7.5, CH$_2$), 2.74 (1 t, 2 H, J 7.5, CH$_2$) and 6.91 (s, 1 H, ring $\alpha$-H) (Found: C, 67.6; H, 9.9; S, 22.4. Calc. for C$_{16}$H$_{28}$S$_2$: C, 67.60; H, 9.86; S, 22.54%).

3,4-Dibutyl-5-butylsulfanylthiophene-2-carbaldehyde 6.—A solution of butyllithium (2.5 mol dm$^{-3}$ solution in hexanes; 0.25

mol, 100 cm$^3$) was added dropwise to a solution of 4 (64.4 g, 0.23 mol) and TMEDA (34 cm$^3$, 0.22 mol) in THF (200 cm$^3$). Reaction with DMF (25 cm$^3$) and subsequent work-up was identical with that described above for 5. The crude product obtained after solvent removal was purified by column chromatography over silica gel, eluting with 5% ethyl acetate in hexane to give 6 (65.9 g, 93%), $\delta_H$ 0.98 (m, 9 H, CH$_3$), 1.30–1.78 (m, 12 H, CH$_2$), 2.55 (t, 2 H, J 7.4, CH$_2$) and 9.89 (s, 1 H, CHO); $\delta_C$ 13.50, 13.81, 22.78, 27.00, 27.12, 31.95, 34.37, 36.24, 136.37, 142.46, 145.76, 152.16 and 180.71 (Found: C, 65.6; H, 9.1; S, 20.3. Calc. for C$_{17}$H$_{28}$S$_2$O: C, 65.38; H, 8.97; S, 20.51%).

3-(3',4'-Dibutyl-2'-thienyl)prop-2-enal 7.—A solution of sodium ethoxide (1 mol dm$^{-3}$; 0.20 mol, 200 cm$^3$) in ethanol was added dropwise to a solution of 6 (15.6 g, 0.07 mol) and tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (1.2 mol dm$^{-3}$; 0.13 mol, 111 cm$^3$) in ethanol (300 cm$^3$) at 90 °C. The resulting mixture was stirred under an atmosphere of N$_2$ at 90 °C for 12.0 h after which it was cooled to room temperature. Aqueous HCl (3 mol dm$^{-3}$; 200 cm$^3$) was then added dropwise to the mixture which was then stirred for 1 h. After this it was poured into cold water (500 cm$^3$) and extracted with diethyl ether (3 × 200 cm$^3$). The combined extracts were washed with saturated aqueous Na$_2$CO$_3$ and brine, dried (MgSO$_4$) and evaporated. The residue was purified by column chromatography over silica gel, eluting with 5% ethyl acetate in hexane to yield the title compound 7 (15.8 g, 91%), $\delta_H$ 0.92 (m, 6 H, CH$_3$), 1.30–1.71 (m, 8 H, CH$_2$), 2.53 (t, 2 H, J 6.0, CH$_2$), 2.90 (t, 2 H, J 6.0, CH$_2$), 6.48 (dd, 1 H$_b$, J$_{ab}$ 9.5, J$_{bc}$ 18.1, =CHCHO), 6.91 (s, 1 H, $\alpha$-ring H), 7.67 (d, 1 H$_c$, J 18.1, vinyl) and 9.6 (d, 1 H$_a$, J 9.5, CHO).

5-(3',4'-Dibutyl-2'-thienyl)penta-2,4-dienal 8. Compound 8 was prepared from 7 (15.8 g, 0.063 mol), tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (1.2 mol dm$^{-3}$; 0.11 mol, 95 cm$^3$) and sodium ethoxide (1 mol dm$^{-3}$; 0.18 mol, 180 cm$^3$) as described above for the preparation of 7. The crude product was purified by column chromatography over silica gel, eluting with 5–7% ethyl acetate in hexane to yield 8 (10.7 g, 60%) mp 62–64 °C; $\delta_H$ 0.91 (m, 6 H, CH$_3$), 1.29–1.70 (m, 8 H, CH$_2$), 2.50 (t, 2 H, J 6.5, CH$_2$), 2.63 (t, 2 H, J 6.9, CH$_2$), 6.94 (t, 2 H, J 6.9, CH$_2$), 6.23 (dd; 1 H, J$_{ab}$ 8.1, J$_{bc}$ 10.0, vinyl), 6.75 (dd, 1 H, J 10.0, 19.9, vinyl), 6.95 (S, 1 H, $\alpha$-ring H), 7.14–7.32 (m, 2 H, vinyl) and 9.6 (d, 1 H, J 8.1, CHO); $\delta_C$ 13.84, 22.48, 22.72, 26.73, 28.45, 31.71, 33.23, 121.99, 124.33, 130.19, 133.89, 135.40, 143.65, 144.22, 152.16 and 193.17.

7-(3',4'-Dibutyl-2'-thienyl)hepta-2,4,6-trienal 9. Compound 9 was prepared from 8 (6.0 g, 0.022 mol), tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (1.2 mol dm$^{-3}$; 0.041 mol, 36 cm$^3$) and sodium ethoxide (1 mol dm$^{-3}$; 0.075, 75 cm$^3$) as described above for the preparation of 7. The crude product was purified by column chromatography over silica gel, eluting with 10% ethyl acetate in hexane to yield 9 (2.9 g, 44%); $\delta_H$ 0.94 (m, 6 H, CH$_3$), 1.28–1.70 (m, 8 H, CH$_2$), 2.49 (t, 2 H, J 6.85, CH$_2$), 2.59 (t, 2 H, J 6.7, CH$_2$), 6.29 (dd, 1 H, J 6.4, 12.8, vinyl), 6.44–7.28 (m, 6 H, vinyl, ring $\alpha$-H) and 9.64 (d, 1 H, J 8, CHO).

3-(3',4'-Dibutyl-5'-butylsulfanyl-2'-thienyl)prop-2-enal 10. Compound 10 was prepared from 6 (26.0 g, 0.083 mol), tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (1.2 mol dm$^{-3}$; 0.14 mol, 123 cm$^3$) and sodium ethoxide (1 mol dm$^{-3}$; 0.185 mol, 185 cm$^3$) as described above for the preparation of 7. The crude product was purified by column chromatography over silica gel, eluting with 5% ethyl acetate in hexane to yield 10 (25.8 g, 92%); $\delta_H$ 0.98 (m, 9 H, CH$_3$), 1.30–1.78 (m, 12 H, CH$_2$), 2.61 (t, 4 H, CH$_2$), 2.91 (t, 2 H, J 8.3, CH$_2$), 6.38 (dd, 1 H, J 7.7, 15.4, vinyl), 7.59 (d, 1 H, J 15.4, vinyl) and 9.61 (d, 1 H, J 7.7, CHO); $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 379 (14 800) (Found: C, 67.7; H, 9.0; S, 18.8. Calc. for C$_{19}$H$_{30}$S$_2$O: C, 67.46; H, 8.88; S, 18.93%).

*5-(3′,4′-Dibutyl-5′-butylsulfanyl-2′-thienyl)penta-2,4-dienal*
**11.** Compound **11** was prepared from **10** (25 g, 0.074 mol), tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (0.114 mol, 1.2 mol dm$^{-3}$, 95 cm$^3$) and sodium ethoxide (0.134 mol, 1 mol dm$^{-3}$, 134 cm$^3$) as described above for the preparation of **7**. The crude product was purified by column chromatography over silica gel, eluting with 5–7% ethyl acetate in hexane to yield **11** (15 g, 56%), $\delta_H$ 0.99 (m, 9 H, CH$_3$), 1.29–1.69 (m, 12 H, CH$_2$), 2.59 (m, 4 H, CH$_2$), 2.86 (t, 2 H, *J* 5.6, CH$_2$), 6.22 (dd, 1 H, *J* 6.6, 13.3, vinyl), 6.65 (dd, 1 H, *J* 8.6, 7.1, vinyl), 7.15 (m, 2 H, vinyl) and 9.60 (d, 1 H, *J* 7.7, CHO); $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 396 (14 100) (Found: C, 69.0; H, 9.0; S, 17.8. Calc. for C$_{21}$H$_{32}$S$_2$O: C, 69.23; H, 8.79; S, 17.79%).

*7-(3′,4′-Dibutyl-5′-butylsulfanyl-2′-thienyl)hepta-2,4,6-trienal*
**12.** Compound **12** was prepared from **11** (15 g, 0.041 mol), tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide (1.1 mol dm$^{-3}$; 0.065 mol, 60 cm$^3$) and sodium ethoxide (1 mol dm$^{-3}$; 0.097 mol, 97 cm$^3$) as described above for the preparation of **7**. The crude product was purified by column chromatography, eluting with 10% ethyl acetate in hexane to yield pure **12** (7 g, 44%), $\delta_H$ 0.97 (m, 9 H, CH$_3$), 1.30–1.69 (m, 12 H, CH$_2$), 2.56 (m, 4 H, CH$_2$), 2.82 (t, 2 H, *J* 6.8, CH$_2$), 6.15–7.23 (m, 6 H, vinyl) and 9.58 (d, 1 H, *J* 7.7, CHO); $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 421 (26 100) (Found: C, 70.8; H, 8.9; S, 16.6. Calc. for C$_{23}$H$_{34}$S$_2$O: C, 70.76; H, 8.72; S, 16.41).

*General Procedure for Polyene Synthesis via Wittig Condensation.*—For polyenes with an odd number of double bonds, a solution of sodium ethoxide (1.0 equiv.) in ethanol (1 mol dm$^{-3}$) was added dropwise to a solution of the aldehyde (0.5–1.0 equiv.) and (*E*)-but-2-ene-1,4-diylbis(tributylphosphonium) dichloride **14** (0.5 equiv.) in either ethanol or DMF. The reaction mixture was stirred for 60 h at 100 °C under nitrogen and then poured into ice–water (200 cm$^3$). The crude product was either extracted with diethyl ether (triene) and purified by column chromatography or isolated by vacuum distillation (pentaene to nonaene). For polyenes with an even number of double bonds, (E,E)-hexa-2,4-diene-1,6-diyl(tributylphosphonium)dibromide **15** was used in place of **14**.

*1,6-Bis(3′,4′-dibutyl-2′-thienyl)hexa-1,3,5-triene* **1a.** Reaction of **14** (7.5 mmol), **5** (15 mmol) and sodium ethoxide (21 mmol) in ethanol (80 cm$^3$) gave crude **1a.** Column chromatography, eluting with 5% ethyl acetate in hexane gave pure **1a** (1.5 g, 46%), mp 84–86 °C, $\delta_H$ 0.95 (t, 0.95, 12 H, *J* 5.3, CH$_3$), 1.25–1.65 (m, 16 H, CH$_2$), 2.47 (t, 8 H, *J* 5.5, CH$_2$), 6.45–6.69 (m, 6 H, vinyl) and 6.74 (s, 2 H, ring α-H); $\delta_C$ 13.93, 22.61, 22.81, 26.66, 28.6, 31.84, 33.21, 118.35, 124.22, 128.06, 132.70, 137.15, 140.04 and 143.28; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 398.5 (53 400) (Found: C, 77.0; H, 9.5; S, 13.5. Calc. for C$_{30}$H$_{44}$S$_2$: C, 76.92; H, 9.40; S, 13.68).

*1,8-Bis(3′,4′-dibutyl-2′-thienyl)octa-1,3,5,7-tetraene* **1b.** Reaction of **15** (7.5 mmol), **5** (15 mmol) and sodium ethoxide (21 mmol) in ethanol (80 cm$^3$) gave crude **1b.** Column chromatography, eluting with 5% ethyl acetate in hexane, gave pure **1b** (1.2 g, 34%), mp 105–106 °C, $\delta_H$ 0.95 (t, 12 H, *J* 5.4, CH$_3$), 1.29–1.70 (m, 16 H, CH$_2$), 2.47 (m, 8 H, CH$_2$), 6.37–6.68 (m, 8 H, vinyl) and 6.75 (s, 2 H, ring α-H); $\delta_C$ 13.94, 22.61, 22.82, 26.67, 28.67, 31.84, 33.21, 118.44, 124.39, 128.11, 132.67, 133.12, 137.16, 140.09 and 143.23; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 417.5 (88 300) (Found: C, 77.7; H, 9.5; S, 12.6. Calc. for C$_{32}$H$_{46}$S$_2$: C, 77.73; H, 9.31; S, 12.96%).

*1,10-Bis(3′,4′-dibutyl-2′-thienyl)deca-1,3,5,7,9-pentaene* **1c.** Reaction of **14** (8.5 mmol), **7** (17.8 mmol) and sodium ethoxide (35 mmol) in ethanol (80 cm$^3$) gave crude **1c.** Recrystallization from hexane gave pure **1c** (1.3 g, 28%), mp 126–128 °C, $\delta_H$ 0.94 (t, 12 H, *J* 5.4, CH$_3$), 1.27–1.69 (m, 16 H, CH$_2$), 2.46 (m, 8 H, CH$_2$), 6.38–6.68 (m, 10 H, vinyl) and 6.75 (s, 2 H, ring α-H); $\delta_C$ 13.96, 22.61, 22.82, 26.67, 28.66, 31.81, 33.21, 118.5, 124.48,

128.09, 132.77, 133.13, 133.34, 137.15, 140.16 and 143.26; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 434.5 (61 500) (Found: C, 78.6; H, 9.4; S, 12.4. Calc. for C$_{34}$H$_{48}$S$_2$: C, 78.46; H, 9.23; S, 12.3%).

*1,12-Bis(3′,4′-dibutyl-2′-thienyl)dodeca-1,3,5,7,9,11-hexaene* **1d.** Reaction of **15** (13 mmol), **7** (18 mmol) and sodium ethoxide (35 mmol) in DMF (35 cm$^3$) gave crude **1d.** Recrystallization from hexane gave pure **1d** (1.5 g, 31%), mp 158–160 °C, $\delta_H$ 0.95 (t, 12 H, *J* 5.5, CH$_3$), 1.29–1.71 (m, 16 H, CH$_2$), 2.48 (m, 8 H, CH$_2$), 6.35–6.68 (m, 12 H, vinyl) and 6.75 (s, 2 H, ring α-H); $\delta_C$ 13.93, 22.59, 22.79, 26.65, 28.64, 31.81, 33.19, 118.54, 124.54, 128.08, 132.75, 133.20, 133.33, 133.44, 137.13, 140.19 and 142.25; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 450 (90 700) (Found: C, 79.0; H, 9.4; S, 11.9. Calc. for C$_{36}$H$_{50}$S$_2$: C, 79.12; H, 9.16; S, 11.72%).

*1,14-Bis(3′,4′-dibutyl-2′-thienyl)tetradeca-1,3,5,7,9,11,13-heptaene* **1e.** Reaction of **14** (3 mmol), **8** (4 mmol) and sodium ethoxide (9 mmol) in DMF (40 cm$^3$) gave **1e.** Recrystallization from ethyl acetate–hexane (20:80) gave pure **1e** (32%), mp 170–171 °C; $\delta_H$ 0.93 (t, 12 H, *J* 5.4, CH$_3$), 1.29–1.70 (m, 16 H, CH$_2$), 2.47 (m, 8 H, CH$_2$), 6.33–6.68 (m, 14 H, vinyl) and 6.75 (s, 2 H, α-ring H); $\delta_C$ 13.95, 22.60, 22.82, 26.68, 28.66, 31.84, 33.22, 118.58, 124.61, 128.09, 132.78, 133.22, 133.46, 137.16, 140.25 and 143.29; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 464 (146 000). (Found: C, 79.5; H, 9.1; S, 11.1. Calc. for C$_{38}$H$_{52}$S$_2$: C, 79.72; H, 9.09; S, 11.19%).

*1,16-Bis(3′,4′-dibutyl-2′-thienyl)hexadeca-1,3,5,7,9,11,13,15-octaene* **1f.** Reaction of **15** (3 mmol), **8** (4 mmol) and sodium ethoxide (9 mmol) in DMF (60 cm$^3$) gave crude **1f.** Recrystallization from ethyl acetate–hexane (20:80) gave pure **1f** (0.7 g, 27%), mp 178–179 °C, $\delta_H$ 0.95 (t, 12 H, *J* 5.6, CH$_3$), 1.30–1.72 (m, 16 H, CH$_2$), 2.46 (m, 4 H, CH$_2$), 6.32–6.68 (m, 16 H, vinyl) and 6.75 (s, 2 H, ring α-H); $\delta_C$ 13.96, 22.63, 22.84, 26.69, 28.67, 31.84, 33.33, 118.60, 124.64, 128.09, 132.78, 133.23, 137.16, 140.25 and 143.29; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 476 (168 000) (Found: C, 80.3; H, 9.1; S, 10.9. Calc. for C$_{40}$H$_{54}$S$_2$: C, 80.27; H, 9.03; S, 10.70%).

*1,18-Bis(3′,4′-dibutyl-2′-thienyl)octadeca-1,3,5,7,9,11,13,15,17-nonaene* **1g.** Reaction of **14** (6.7 mmol), **9** (8.7 mmol) and sodium ethoxide (14 mmol) in DMF (80 cm$^3$) gave crude **1g.** Recrystallization from ethyl acetate–hexane (20:80) gave pure **1g** (1.2 g, 22%), mp 203–205 °C, $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 486.5 (155 000) (Found: C, 80.4; H, 9.2; S, 10.3. Calc. for C$_{42}$H$_{56}$S$_2$: C, 80.77; H, 8.97; S, 10.26%).

*1,20-Bis(3′,4′-dibutyl-2′-thienyl)icosa-1,3,5,7,9,11,13,15,17,19-decaene* **1h.** Reaction of **15** (3 mmol), **9** (4 mmol) and sodium ethoxide (10 mmol) in DMF (50 cm$^3$) gave crude **1h.** Recrystallization from ethyl acetate–hexane (20:80) gave pure **1h**, mp 260–262 °C, $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 496 (136 000) Found: C, 81.1; H, 8.8; S, 9.6. Calc. for C$_{44}$H$_{58}$S$_2$: C, 81.23; H, 8.92; S, 9.85%).

*1,6-Bis(3′,4′-dibutyl-5′-butylsulfanyl-2′-thienyl)hexa-1,3,5-triene* **1i.** Reaction of **14** (10 mmol), **6** (12.8 mmol) and sodium ethoxide (20 mmol) in DMF (50 cm$^3$) gave crude **1i** as a sticky semi-solid which was purified by column chromatography eluting with hexane (1.5 g, 36%), $\delta_H$ 0.98 (m, 18 H, CH$_3$), 1.30–1.64 (m, 24 H, CH$_2$), 2.34 (m, 8 H, CH$_2$), 2.78 (t, 4 H, *J* 8.2, CH$_2$) and 6.64 (m, 6 H, vinyl); $\delta_C$ 13.60, 13.90, 21.76, 22.87, 27.34, 27.63, 31.63, 32.96, 33.52, 38.23, 123.64, 128.14, 132.89, 138.5, 140.49 and 146.64; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 424 (30 500) (Found: C, 71.0; H, 9.5; S, 19.9. Calc. for C$_{38}$H$_{60}$S$_4$: C, 70.81; H, 9.32; S, 19.88%).

*1,8-Bis(3′,4′-dibutyl-5′-butylsulfanyl-2′-thienyl)octa-1,3,5,7-tetraene* **1j.** Reaction of **15** (11.6 mmol), **6** (12.8 mmol) and sodium ethoxide (20 mmol) in DMF (30 cm$^3$) gave crude **1j** as a sticky semi-solid which was purified by column chromatography eluting with 5% ethyl acetate in hexane (1.5 g, 35%), $\delta_H$ 0.97 (m, 18 H, CH$_3$), 1.20–1.65 (m, 24 H, CH$_2$), 2.35 (m, 8 H, CH$_2$), 2.78 (t, 4 H, *J* 8.1, CH$_2$) and 6.37–6.64 (m, 8 H, vinyl); $\delta_C$ 13.60, 13.90, 21.77, 22.88, 27.36, 27.66, 31.66, 32.97, 33.54,

38.22, 123.78, 128.34, 128.49, 132.97, 133.19, 138.58, 140.56 and 146.58; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 439 (43 200) (Found: C, 71.3; H, 9.2; S, 19.0. Calc. for $C_{40}H_{62}S_4$: C, 71.54; H, 9.25; S, 19.10%).

1,10-*Bis*(3',4'-*dibutyl*-5'-*butylsulfanyl*-2'-*thienyl*)*deca*-1,3,5,7, 9-*pentaene* **1k**. Reaction of **14** (6.6 mmol), **10** (10 mmol) and sodium ethoxide in ethanol (60 cm$^3$) and DMF (30 cm$^3$) gave crude **1k** as a sticky semi-solid which was purified by column chromatography eluting with 5% ethyl acetate in hexane (2.6 g, 74%), $\delta_H$ 0.97 (m, 18 H, CH$_3$), 1.29–1.67 (m, 24 H, CH$_2$), 2.57 (m, 8 H, CH$_2$), 2.78 (t, 4 H, J 8.2, CH$_2$) and 6.36–6.70 (m, 10 H, vinyl); $\delta_C$ 13.61, 13.91, 21.78, 22.88, 27.37, 27.67, 31.67, 32.97, 33.55, 38.22, 123.83, 128.51, 133.09, 133.32, 138.60, 140.59 and 146.58; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 451.5 (47 800) (Found: C, 72.6; H, 9.5; S, 18.0. Calc. for $C_{42}H_{64}S_4$: C, 72.41; H, 9.20; S, 18.39%).

1,12-*Bis*(3',4'-*dibutyl*-5'-*butylsulfanyl*-2'-*thienyl*)*dodeca*-1,3,5, 7,9,11-*hexaene* **1l**. Reaction of **15** (9 mmol), **10** (10 mmol) and sodium ethoxide (20 mmol) in ethanol (60 cm$^3$) and DMF (24 cm$^3$) gave crude **1l** as a sticky semi-solid which was purified by column chromatography eluting with 5% ethyl acetate in hexane (2.1 g, 58%), $\delta_H$ 0.98 (m, 18 H, CH$_3$), 1.28–1.68 (m, 24 H, CH$_2$), 2.58 (m, 8 H, CH$_2$), 2.80 (t, 4 H, J 7.9 Hz, CH$_2$) and 6.34–6.72 (m, 12 H, vinyl); $\delta_C$ 13.62, 13.94, 21.78, 22.88, 27.36, 27.67, 31.67, 32.98, 33.55, 38.23, 123.84, 128.57, 133.04, 133.34, 138.60, 140.60 and 146.59; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 466.5 (48 000) (Found: C, 73.3; H, 9.1; S, 17.8. Calc. for $C_{44}H_{66}S_4$: C, 73.13; H, 9.14; S, 17.73%).

1,14-*Bis*(3',4'-*dibutyl*-5'-*butylsulfanyl*)-2'-*thienyl*)*tetradeca*-1,3,5,7,9,11,13-*heptaene* **1m**. Reaction of **14** (6 mmol), **11** (8.2 mmol) and sodium ethoxide (25 mmol) in DMF (70 cm$^3$) gave crude **1m** as a sticky semi-solid which was purified by column chromatography eluting with 5% ethyl acetate in hexane (1.3 g, 34%), $\delta_H$ 0.96 (m, 18 H, CH$_3$), 1.29–1.67 (m, 24 H, CH$_2$), 2.59 (m, 8 H, CH$_2$), 2.79 (t, 4 H, J 7.7, CH$_2$) and 6.35–6.67 (m, 14 H, vinyl); $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 479.5 (159 000) (Found: C, 73.7; H, 9.3; S, 17.2. Calc. for $C_{46}H_{68}S_4$: C, 73.79; H, 9.09; S, 17.11%).

1,16-*Bis*(3',4'-*dibutyl*-5'-*butylsulfanyl*-2'-*thienyl*)*hexadeca*-1, 3,5,7,9,11,13,15-*octaene* **1n**. Reaction of **15** (11 mmol), **11** (13.7 mmol) and sodium ethoxide (23 mmol) in DMF (80 cm$^3$) gave crude **1n** as a sticky semi-solid which was purified by column chromatography eluting with 5% ethyl acetate in hexane (1.9 g, 36%), $\delta_H$ 0.97 (m, 18 H, CH$_3$), 1.28–1.67 (m, 24 H, CH$_2$), 2.54 (br d, m, 8 H, CH$_2$), 2.78 (t, 4 H, J 8.1, CH$_2$) and 6.33–6.63 (m, 16 H, vinyl); $\delta_C$ 13.63, 13.96, 22.36, 27.68, 31.66, 32.97, 33.59, 38.25, 123.90, 128.58, 133.00, 133.43, 138.74, 140.71 and 146.60; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 490 (211 600) (Found: C, 74.4; H, 9.3; S, 16.5. Calc. for $C_{48}H_{70}S_4$: C, 74.38; H, 9.25; S, 16.51%).

1,18-*Bis*(3',4'-*dibutyl*-5'-*butylsulfanyl*-2'-*thienyl*)*octadeca*-1, 3,5,7,9,11,13,15,17-*nonaene* **1p**. Reaction of **14** (5.7 mmol), **12** (7.7 mmol) and sodium ethoxide (11 mmol) in DMF (70 cm$^3$) gave crude **1p** as a sticky semi-solid which was purified by column chromatography eluting with 5% ethyl acetate in hexane (1.5 g, 49%), $\delta_H$ 0.98 (m, 18 H, CH$_3$), 1.27–1.70 (m, 24 H, CH$_2$), 2.54 (br d, m, 8 H, CH$_2$), 2.79 (t, 4 H, J 8.3, CH$_2$) and 6.33–6.63 (br d, m, 18 H, vinyl); $\delta_C$ 13.62, 13.95, 22.89, 27.68, 31.67, 32.96, 33.57, 38.26, 123.91, 128.58, 133.02, 133.46, 138.72, 140.70 and 146.70; $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 501 (234 000) (Found: C, 74.9; H, 9.1; S, 15.9. Calc. for $C_{50}H_{72}S_4$: C, 74.94; H, 9.06; S, 16.00%).

1,20-*Bis*(3',4'-*dibutyl*-5'-*butylsulfanyl*-2'-*thienyl*)*icosa*-1,3,5,-7,9,11,13,15,17,19-*decaene* **1q**.—Reaction of **15** (5.7 mmol),

**12** (7.7 mmol) and sodium ethoxide (10 mmol) in DMF (50 cm$^3$) gave **1q** as a sticky semi-solid. Attempts to purify **1q** by column chromatography resulted in decomposition. The crude product had $\lambda_{max}$/nm 507.5, however all chromatography fractions absorbed at significantly lower wavelengths.

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