Preparation and Oxidative Doping Studies of α,ω-Dithienyl Polyenes Stabilized by Long Chain Alkylthio Substituents

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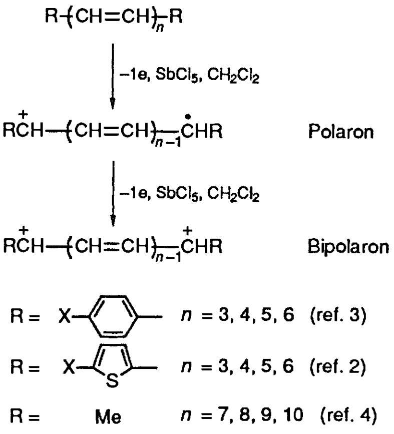
Polyenes containing mesomerically interactive substituent groups can be oxidatively doped with $SbCl_5$ in solution to yield stabilized bipolaron-like charge states. However, in both α,ω-diphenyl and α,ω-dithienyl polyene series, lack of solubility has precluded studies of bipolaron formation for polyenes containing more than six double bonds in the polyene segment. In the present study, the use of long-chain alkylthio substituents to stabilize the bipolaronic charge states has allowed the synthesis of dithienyl polyenes containing up to ten double bonds, and observation of bipolaron formation in the octaene. Models for copolymers containing these bipolaronic repeat units have also been synthesized, and oxidatively doped.

The oxidative doping of polyacetylene chains, or other electroactive polymers with degenerate ground states, are best interpreted in terms of the formation of charged solitons. Polymers with non-degenerate ground states, such as polythiophene or poly(2,5-thienylene-*co*-vinylene) (PTV) have been shown to be dominated by spinless bipolarons in their doped states.

In several recent publications we have outlined the synthesis of α,ω-diphenyl and α,ω-dithienyl polyenes containing up to six double bonds by Wittig methodology and have studied their oxidative doping behaviour as models for polyacetylene.[1,2] Surprisingly, although it is probable that the initial oxidative doping involves the polyene chains, the identity of the end groups is not insignificant, nor is the profound mesomeric interaction of end group substituents. Thus polaron-like and bipolaron-like charge states in these polyene systems can be formed by oxidative doping with $SbCl_5$ in solution, with the bipolaron (BP) dominating in all cases.[2–4] Mesomerically interactive electron-donating groups stabilize these species in solution for up to several days in contact with moist air under normal laboratory conditions.[3,4] We have observed similar behaviour in the oligomeric series related to poly(*p*-phenylene-*co*-vinylene)[5] and poly(2,5-thienylene-*co*-vinylene),[6] and while we realise that radical-ion and di-ion formation in the small model polyenes and oligomers is fundamentally different from polaron and bipolaron formation in a polymer lattice, we will refer to these as polarons and bipolarons for the sake of simplicity in the following discussions. However, up to the present time, we have not been able to study bipolaron formation in longer conjugation sequences owing to the lack of polyene solubility beyond the hexaene. Since the longer polyenes are generated most efficiently by a bis-Wittig condensation, a further difficulty arises in the attempted preparation of a longer conjugation sequence, that is the lack of solubility of partially condensed (mono condensation) materials (Scheme 1). An exception is the α,ω-dimethyl polyene series where the decaene and decaene–BP have been described, however, the terminal alkyl groups do not provide adequate stabilization.[4]

Electroactive polymers and oligomers have been shown by several research groups to exhibit enhanced non-linear optical (NLO) properties.[7–10] In all of these studies γ, the third-order hyperpolarizability, increases with increasing conjugation length. However, Prasad and co-workers have shown that the effective conjugation length giving rise to the non-linear optical response may be 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] DeMelo and Silbey have recently postulated that enhancement of γ_{xxxx} or γ^{π} may be possible by incorporating delocalized charge states in the pi-conjugation sequence.[12,13] The consequences of this in the design of new NLO oligomers and polymers have been reviewed by Spangler and Havelka.[14,15] In essence, deMelo and Silbey have predicted that γ_{xxxx} would not saturate up to $N \sim 20$, where N is the number of polyene repeat units. Their data fits a power series aN^b for both the neutral polyene and bipolaronic charge states, where γ_{xxxx} has the following calculated relationship: neutral, $a = 52.0$, $b = 4.25$; bipolaron, $a = 0.247$, $b = 6.04$. The power-law dependence for neutral polyenes is in accord with experiment.[10] Owing to the larger power dependence, long bipolaronic charge sequences may lead to significant enhancement of γ_{xxxx}. Thus, in order to test the above predictions, it will be necessary to synthesize stable, processable bipolarons of sufficient length. To date, this has not been possible owing to either a lack of solubility in the longer polyenes,[1,2] or a lack of stability.[4]



Scheme 1 Polaron and bipolaron formation in polyacetylene oligomers with alkyl, phenyl and thienyl end groups

The lack of solubility in electroactive polymers has been addressed by a variety of approaches, but the inclusion of long- or branched-chain alkyl groups is synthetically attractive since the solubilising alkyl group can be combined with the mesomerically interactive bipolaron stabilizing group (*i.e.* RO–, RS–, R_2N–). We have most recently shown that exceptionally stable

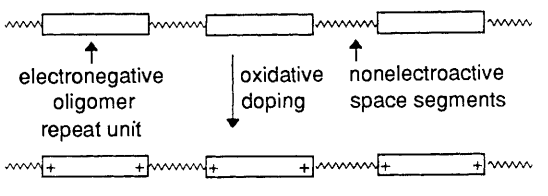
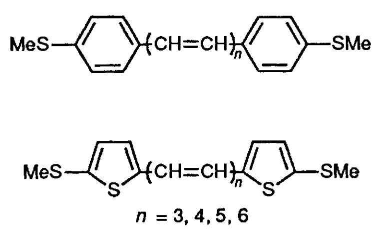
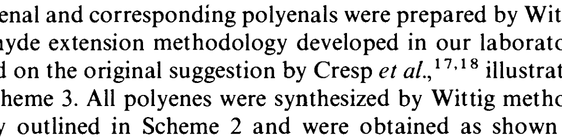


Fig. 1 Potential incorporation of bipolaronic charge states in formal copolymer structures

bipolarons exhibiting large red shifts in the absorption spectra can be formed when MeS substituents are utilized in both α,ω-diphenyl polyene and α,ω-dithienyl polyene series. However, lack of solubility again precludes studies of bipolaron formation beyond $n = 6$. Therefore, we decided to examine the efficacy of using long-chain alkylthio groups to address both the solubility and BP stability problems in the dithienyl polyene series which is, in general, more soluble than the diphenyl polyene series.



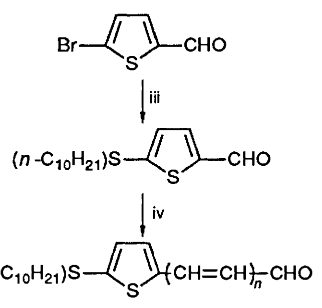
Synthesis of Bis-substituted Polyenes.—As stated above, we have outlined a general approach to the synthesis of symmetrically substituted polyenes *via* Wittig methodology in several publications.[1,2] Similar synthetic strategies have been employed by Blanchard-Desce.[16] This approach is illustrated in Scheme 2. Decylthiobenzaldehyde was prepared directly by nucleophilic substitution on commercially available 5-bromothiophene-2-carbaldehyde (Aldrich). 3-(5-Decylthio-2-thienyl)-propenal and corresponding polyenals were prepared by Wittig aldehyde extension methodology developed in our laboratory based on the original suggestion by Cresp *et al.*,[17,18] illustrated in Scheme 3. All polyenes were synthesized by Wittig methodology outlined in Scheme 2 and were obtained as shown in Scheme 4.



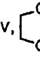
Scheme 2 *Reagents:* i, $Bu_3P^+CH_2CH{=}CHCH_2P^+Bu_3$, $2Cl^-$, NaOEt, EtOH or DMF; ii, $Bu_3P^+CH_2(CH{=}CH)_2CH_2P^+Bu_3$, $2Br^-$, NaOEt, EtOH or DMF

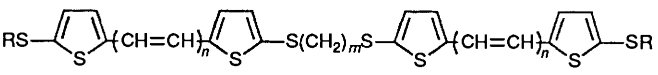
Results and Discussion

If organic charge state formation, either polaronic or bipolaronic, is eventually found to be a general phenomenon for the enhancement of non-linear optical response, then it is essential that we probe the limitation, if any, to the charge delocalization. As stated above, the calculations of DeMelo and Silbey predict a power-law dependence on the number of repeat units for both P and BP. However, in electroactive polymers, it is generally recognised that both P and BP states are confined.[19–21] It has also been shown that third-order NLO response is proportional to $1/E_g$,[6] where E_g is the band gap.[22] Thus it is germane to determine if electrons delocalise over the whole length of oligomers whose length is systematically increased one repeat unit at a time. This is particularly important if one envisions oligomer (and oligomer bipolaron) incorporation in formal copolymers,[14,15] as shown in Fig. 1:



3; $n = 1$
4; $n = 2$
5; $n = 3$
6; $n = 4$

Scheme 3 *Reagents and conditions* iii, KOH, n-$C_{10}H_{21}Br$, EtOH, 80 °C; iv,  $-CH_2\overset{+}{P}Bu_3,Br^-$, DMF, 90 °C; 10% H_3O^+, THF.

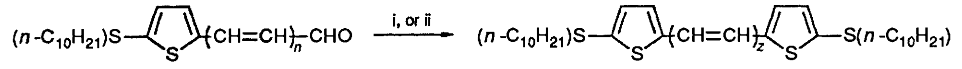


R = n-$C_{10}H_{21}$

15; $n = 4, m = 6$
16; $n = 5, m = 6$
17; $n = 5, m = 10$

If bipolarons in these copolymer structures are delocalised as indicated by model compound studies, then not only the absorption characteristics, but also the magnitude of the NLO response should be predictable. To this end, we have also prepared a model of such a polymer incorporating alkylthiothienyl end groups, a polyene segment containing four or five C=C units, and variable length spacer segments. Both the α,ω-bis(5-decylthio-2-thienyl)polyenes and the above copolymer models were oxidatively doped, under identical conditions, with $SbCl_5$ in CH_2Cl_2. These results are shown in Tables 1 and 2.

The incorporation of the long-chain alkylthio groups increases the solubility of the bis(thiothienyl)polyenes significantly compared to our previous studies with MeO and MeS substituents.[23] This solubility enhancement allows for bis-Wittig condensation to yield polyenes with up to ten double



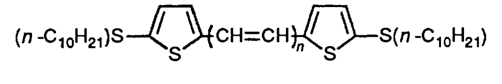
3; $n = 1$
4; $n = 2$
5; $n = 3$
6; $n = 4$

7; $z = 3$
8; $z = 4$
9; $z = 5$
10; $z = 6$
11; $z = 7$
12; $z = 8$
13; $z = 9$
14; $z = 10$

Scheme 4

bonds. However, the nonaene and decaene were extremely difficult to purify and did not have sufficient solubility in CH_2Cl_2 to study bipolaron formation. Consequently, we have studied bipolaron formation for the triene–octaene series. As can be seen from Table 1, we observe a continuous red shift both in the polyene π–π* and in the bipolaron spectra as conjugation increases. Thus we conclude that delocalization extends over the oligomer length and shows no sign of saturation. The delocalization length in **12** compares quite favourably with those observed in electroactive polymers. For example, Dalton has shown that intrinsic defect delocalization in polyacetylene is of the order of 15 atoms by ENDOR and ESE spectroscopies.[24] Similarly, Kamiya and Tanaka[25] have shown that polaron formation in polyacetylene is localised over 15–20 atoms. Fichou and co-workers[26,27] have modelled delocalization in doped polythiophene by studying charge delocalization in a series of oligomers up to the hexamer (24 atoms) and most recently Guay and co-workers have shown that charge is delocalized over the whole length of a solubilized polythiophene octamer (32 atoms).[28] These results agree quite well with the 'effective conjugation lengths' of poly(*p*-phenylene) (3 repeat units, 12 atoms) and polythiophene (6–10 repeat units, 24–40 atoms) as determined by Prasad and co-workers by degenerate four-wave mixing studies.[10,11] This is encouraging for the potential application of bipolaronic charge states for NLO purposes wherein $\chi^{(3)}$ is related to this shift in oscillator strength. The BP absorptions show little if any decline after several hours. When these absorptions are compared with the model copolymers with identical conjugation length (*e.g.* compound **8** with compounds **15** and **17**), we find identical oxidation behaviour, *i.e.*, a complete disappearance of the original π–π* absorption along with the appearance of the red-shifted BP absorption. This confirms, for the polymer models, that each electroactive segment can be independently oxidised to a bipolaronic segment. Thus, in the copolymer formulation, one can have *only* bipolaronic absorption, in contrast to a fully conjugated electroactive polymer where both oxidised and unoxidised segments coexist upon doping leading to extremely broad absorption behaviour. The copolymer formulation, on the other hand, has narrow absorption bands whose position and intensity can be predicted with small molecule studies, as we have discussed in general in previous papers.[14,15]

Table 1 Bipolaron absorption spectra for α,ω-bis(5-decylthio-2-thienyl)polyenes



Compound	*n*	π–π*,[a] (λ/nm)	BP [λ/nm ($\varepsilon_{max}/10^4$)]
7	3	**402**, 421	620 (10.9)
8	4	**418**, 443	673 (9.8)
9	5	**435**, 462	726 (13.5)
10	6	**452**, 479	779 (19.4)
11	7	**462**, 493	834 (8.6)
12	8	**475**, 507[b]	884 (8.8)
13	9	**481**, 514[c]	*d*
14	10	**491**, 524[c]	*d*

[a] 10^{-5} mol dm^{-3} CH_2Cl_2; peak of maximum intensity in bold. [b] Polyene solubility 2.5×10^{-6} mol dm^{-3} in CH_2Cl_2. [c] Polyene solubility less than 10^{-6} mol dm^{-3}. [d] Polyene solubility too low in CH_2Cl_2 to measure accurately BP absorption.

Conclusions

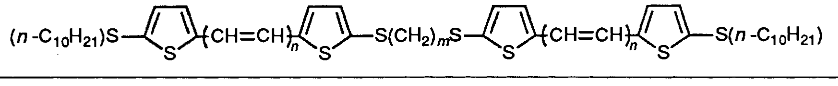
We have shown in this study that the use of solubilising substituents can enhance the formation of soluble stable bipolarons. We have also shown that bipolarons stabilized with alkylthio substituents still have not shown absorption saturation at the octaene level and that delocalisation lengths longer than 26 atoms should be achievable. Finally, we have demonstrated that when alkylthio substituted thienyl polyene segments are incorporated in a formal copolymer structure with saturated hydrocarbon spacers, each polyene segment can be oxidised to similar bipolaronic states. Thus it should be possible eventually to compare copolymers wherein the electroactive segments are either wholly neutral or wholly bipolaronic, and thus obtain an unambiguous comparison of the enhancement of NLO polymer response by bipolaronic states.

Experimental

M.p.s 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 analyser by Paulanne Rider. UV–VIS–NIR spectra were recorded with Varian Model 2290 and Guided Wave Model 200-25 spectrometers as CH_2Cl_2 solutions. ^1H NMR spectra were determined as solutions in $CDCl_3$ unless otherwise noted (Me_4Si internal reference, *J*-values are given in Hz) on an IBM WP-200 spectrometer. 5-Bromothiophene-2-carbaldehyde and decyl bromide were obtained from Aldrich Chemical Co. and used without further purification. Solutions of pure polyenes (10^{-5} mol dm^{-3}) were oxidised in a controlled manner so that an excess of oxidising 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 the 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 5–10 times to determine the relative stability of the BP states, and long-term scans with hourly repeat intervals were carried out for several hours. In all cases very rapid bleaching of the original π–π* transition was observed (less than 30 s, after mixing), simultaneous with the appearance of the BP band.

5-Decylthiothiophene-2-carbaldehyde (**2**). A reaction mixture containing KOH (16.8 g, 0.3 mol) decane-1-thiol (42.5 g, 0.3 mol) and 5-bromothiophene-2-carbaldehyde (53.5 g, 0.28 mol) was stirred at 20 °C for 48 h. After vacuum filtration the precipitated

Table 2 Bipolaron formation in model copolymers



Compound	*m*	*n*	π–π*,[a] (λ/nm)	BP [λ/nm ($\varepsilon_{max}/10^4$)]
15	6	4	**420**, 445	676 (8.4)
16	6	5	**435**, 463	724 (10.0)
17	10	4	**420**, 444	675 (6.0)

[a] 10^{-5} mol dm^{-3} CH_2Cl_2; peak of maximum intensity in bold.

solid was washed with pentane (50 cm^3). The combined organic solution was concentrated by rotary evaporation, and the crude product purified by column chromatography over silica gel eluting with 5% ethyl acetate in hexane yielding **2** (36 g, 66%), δ_H 0.8–1.8 (m, 19 H), 3.01 (t, 2 H, *J* 7, Ar–S–CH$_2$–R), 7.00 (d, 1 H$_a$, J_{ab} 4, aromatic), 7.61 (d, 1 H$_b$, J_{ab} 4, aromatic), 9.85 (s, 1 H, CHO); δ_C 14.04, 22.59, 28.27, 28.55, 28.68, 29.01, 29.21, 29.40, 31.81, 36.97, 128.35, 136.86, 143.03, 150.98, 181.42, 191.73 (Found: C, 63.1; H, 8.65. Calc. for $C_{15}H_{24}OS_2$: C, 63.38; H, 8.45).

3-(5-*Decylthio*-2-*thienyl*)*prop*-2-*enal* (**3**). A solution of sodium ethoxide (0.22 mol, 1 mol dm^{-3}, 220 cm^3) in ethanol was added dropwise to a solution of **2** (30 g, 0.11 mol) and (1,3-dioxolan-2-ylmethyl)tributylphosphonium bromide (0.18 mol, 1.2 mol dm^{-3}, 148 cm^3) in dimethylformamide (DMF) (500 cm^3). The resulting mixture was stirred under a N_2 atmosphere for 36 h at 110 °C. The reaction mixture was poured into ice water (600 cm^3) and extracted with diethyl ether (3 × 200 cm^3). The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The liquid product was dissolved in THF (200 cm^3) and acidified with aq. HCl (3 mol dm^{-3}, 150 cm^3). The mixture was then poured into ice water (500 cm^3) and the product extracted with diethyl ether (3 × 200 cm^3). The organic layer was washed, dried and concentrated as before. The crude product was purified by column chromatography over silica gel, eluting with 5% ethyl acetate in hexane to give **3** (26 g, 78%), m.p. 28–29 °C, δ_H 0.8–1.7 (m, 19 H), 2.93 (t, 2 H, *J* 7.3, Ar–S–CH$_2$–R), 6.40 (dd, 1 H$_b$, J_{ab} 7.7, J_{bc} 15.5, =C*H*–CHO), 7.01 (d, 1 H$_d$, J_{de} 4), 7.20 (d, 1 H$_e$, J_{de} 4) 7.46 (d, 1 H$_c$, J_{bc} 15.5), 9.59 (d, 1 H$_a$, J_{ab} 7.7, CHO); δ_C 14.05, 22.61, 28.45, 29.03, 29.24, 29.43, 31.82, 37.85, 126.73, 131.21, 132.64, 140.24, 143.53, 143.64, 192.53 (Found: C, 65.6; H, 8.4. Calc. for $C_{17}H_{26}OS_2$: C, 65.80; H, 8.39).

5-(5-*Decylthio*-2-*thienyl*)*penta*-2,4-*dienal* **4**. A solution of sodium ethoxide (98 mmol, 1 mol dm^{-3}, 98 cm^3) in ethanol was added dropwise to a mixture of **3** (20 g, 65 mmol) and (1,3-dioxolan-2-ylmethyl)tributylphosphonium bromide (77 mmol, 1.2 mol dm^{-3}, 64 cm^3) in DMF (300 cm^3). The mixture was stirred at 90 °C under an N_2 atmosphere for 36 h then worked up in a manner similar to that described for **3**, yielding **4** after chromatography (13.4 g, 61%), m.p. 49–50 °C; δ_H 0.8–1.8 (m, 19 H), 2.87 (t, 2 H, *J* 7.3, Ar–S–CH$_2$–R), 6.23 (dd, 1 H$_b$, J_{ab} 8, *J* 15), 6.60–7.26 (m, 5 H), 9.58 (d, 1 H$_a$, J_{ba} 8, CHO); δ_C 14.05, 22.59, 28.40, 29.02, 29.22, 29.30, 29.41, 31.80, 38.19, 125.33, 129.89, 131.07, 132.06, 134.14, 142.80, 151.17, 193.11 (Found: C, 67.4; H, 8.7. Calc. for $C_{19}H_{28}OS_2$: C, 67.85; H, 8.33).

7-(5-*Decylthio*-2-*thienyl*)*hepta*-2,4,6-*trienal* (**5**). The title compound was prepared from **4** (6.0 g, 18 mmol), (1,3-dioxolan-2-ylmethyl)tributylphosphonium bromide (21 mmol, 1.2 mol dm^{-3}, 17.5 cm^3) and sodium ethoxide (27 mmol, 1 mol dm^{-3}, 27 cm^3) (EtOH) in DMF (200 cm^3). The reaction mixture was stirred at 60 °C under nitrogen for 36 h. The work-up and isolation was similar to that described for **3**, yielding **5** after purification by column chromatography over silica gel eluting with 10% ethyl acetate in hexane (6.2 g, 52%); δ_H 0.8–1.7 (m, 19 H), 2.85 (t, 2 H, *J* 7.3, ArSCH$_2$R), 6.28 (dd, 1 H$_b$, J_{ab} 8, *J* 15), 6.45–7.22 (m, 7 H), 9.59 (d, 1 H$_a$, J_{ba} 8, CHO); δ_C 14.09, 22.65, 28.46, 29.09, 29.27, 29.39, 29.47, 31.86, 38.46, 127.30, 128.40, 130.03, 130.42, 131.06, 132.70, 137.67, 141.98, 144.10, 151.45, 193.34 (Found: C, 69.65; H, 8.4. Calc. for $C_{21}H_{30}OS_2$: C, 69.61; H, 8.29).

9-(5-*Decylthio*-2-*thienyl*)*nona*-2,4,6,8-*tetraenal* (**6**). The title compound was prepared from **5** (2.55 g, 7 mmol), (1,3-dioxolan-2-ylmethyl)tributylphosphonium bromide (8.4 mmol, 1.2 mol dm^{-3}, 7.0 cm^3) and sodium ethoxide (10.5 mmol, 1 mol dm^{-3}, 10.5 cm^3) (EtOH) in DMF (150 cm^3). The resulting mixture was stirred at 20 °C for 72 h. The work-up, isolation and purification was similar to that described for **5**, yielding **6** (1.2 g, 44%), m.p. 58–60 °C; δ_H 0.7–1.8 (m, 19 H), 2.83 (t, 2 H, *J* 7, ArS*CH*$_2$R), 6.10–7.22 (m, 10 H), 9.57 (d, 1 H, *J* 8, CHO); δ_C 14.08, 22.65, 28.45, 29.09, 29.27, 29.40, 29.47, 31.86, 38.55, 127.58, 128.14, 128.27, 130.01, 131.00, 131.85, 132.95, 136.55, 138.19, 142.43, 144.83, 151.56, 193.34 (Found: C, 71.55; H, 8.65. Calc. for $C_{23}H_{32}OS_2$: C, 71.13; H, 8.25).

General Procedure for Polyene Synthesis via *Wittig Condensation.*—For polyenes with an odd number of double bonds, a solution of sodium ethoxide (0.15 mol) in ethanol (1 mol dm^{-3}) was added dropwise to a solution of the aldehyde (0.11 mol) and (*E*)-but-2-ene-1,4-diylbis(tributylphosphonium) dichloride (**18**) (0.05 mol) in either ethanol or DMF (250 cm^3). The reaction mixture was stirred for 20 h at 90 °C and then poured into ice water (500 cm^3). The crude product was isolated by vacuum filtration and recrystallized. For polyenes with an even number of double bonds, (*E*,*E*)-hexa-2,4-diene-1,6-diylbis(tributylphosphonium)dibromide (**19**) was used in place of **18**.

1,6-*Bis*(5-*decylthio*-2-*thienyl*)*hexa*-1,3,5-*triene* (**7**). Reaction of **18** (2 mmol), **2** (1.0 g, 4 mmol) and sodium ethoxide (4.5 mmol) in ethanol gave crude **7**. Recrystallization from ethanol gave **7** (0.4 g, 32%), m.p. 93–94 °C, λ_{max}/nm(ε_{max}) 402 (64 000); δ_C 14.12, 22.69, 28.48, 29.13, 29.30, 29.47, 29.51, 31.91, 38.73, 125.36, 126.36, 129.09, 133.05, 133.38, 134.76, 145.83 (Found: C, 69.55; H, 9.1. Calc. for $C_{34}H_{52}S_4$: C, 69.39; H, 8.84).

1,8-*Bis*(5-*decylthio*-2-*thienyl*)*octa*-1,3,5,7-*tetraene* (**8**). Reaction of **19** (2 mmol), **2** (1.0 g, 4 mmol) and sodium ethoxide (4.5 mol) in ethanol gave crude **8**. Recrystallization from ethanol–toluene gave **8** (0.52 g, 43%), m.p 110.5–112 °C; λ_{max}/nm(ε_{max}) 418 (81 000); δ_C 14.11, 22.69, 28.48, 29.14, 29.31, 29.46, 29.51, 31.89, 38.73, 125.29, 126.30, 129.24, 132.99, 133.36, 133.60, 134.76, 145.89 (Found: C, 70.25; H, 8.8. Calc. for $C_{36}H_{54}S_4$: C, 70.36; H, 8.79).

1,10-*Bis*(5-*decylthio*-2-*thienyl*)-*deca*-1,3,5,7,9-*pentaene* (**9**). Reaction of **18** (3.2 mmol), **3** (2.0 g, 6.4 mmol) and sodium ethoxide (9.6 mmol) in ethanol gave crude **9**. Recrystallization from ethanol–toluene gave **9** (1.1 g, 53%), m.p. 142–143.5 °C; λ_{max}/nm(ε_{max}) 435 (130 000) (Found: C, 71.2; H, 8.75. Calc. for $C_{38}H_{56}S_4$: C, 71.19; H, 8.80).

1,12-*Bis*(5-*decylthio*-2-*thienyl*)*dodeca*-1,3,5,7,9,11-*hexaene* (**10**). Reaction of **19** (1.6 mmol), **3** (1.0 g, 3.2 mmol) and sodium ethoxide (4.8 mmol) in ethanol gave crude **10**. Recrystallization from ethanol–toluene gave **10** (0.52 g, 49%), m.p. 192–194 °C; λ_{max}/nm(ε_{max}) 452 (180 000) (Found: C, 72.2; H, 8.65. Calc. for $C_{40}H_{58}S_4$: C, 72.07; H, 8.71).

1,14-*Bis*(5-*decylthio*-2-*thienyl*)*tetradeca*-1,3,5,7,9,11,13-*heptaene* (**11**). Reaction of **18** (1.5 mmol), **4** (1.0 g, 3 mmol) and sodium ethoxide (4.5 mmol) in ethanol gave crude **11**. Recrystallization from toluene gave **11** (0.35 g, 34%), m.p. 206–208 °C; λ_{max}/nm(ε_{max}) 462 (76 000) (Found: C, 72.6; H, 8.8. Calc. for $C_{42}H_{60}S_4$: C, 72.78; H, 8.72).

1,16-*Bis*(5-*decylthio*-2-*thienyl*)*hexadeca*-1,3,5,7,9,11,13,15-*octaene* (**12**). Reaction of **19** (1.5 mmol), **4** (1.0 g, 3 mmol) and sodium ethoxide (4.5 mmol) in ethanol gave crude **12**. Recrystallization from toluene gave **12** (0.41 g, 38%), m.p. 230 °C (decomp.); λ_{max}/nm(ε_{max}) 475 (160 000) (Found: C, 73.5; H, 8.65. Calc. for $C_{44}H_{62}S_4$: C, 73.48; H, 8.69).

1,18-*Bis*(5-*decylthio*-2-*thienyl*)*octadeca*-1,3,5,7,9,11,13,15,17-*nonaene* (**13**) and 1,20-*bis*(5-*decylthio*-2-*thienyl*)*eicosa*-1,3,5,7,9,11,13,15,17,19-*decaene* (**14**). Both of the title compounds were obtained in extremely small quantities (< 10 mg) *via* low yield reactions (< 5%) from **5** as described above. These impure materials had the characteristic absorptions expected for the nonaene and decaene (see Table 1) but were not purified further.

1,8-*Bis*{5-[8-(5-*decylthio*-2-*thienyl*)*octa*-1,3,5,7-*tetraen*-1-*yl*]-2-*thienyl*}-1,8-*dithiaoctane* (**15**). Reaction of 1,8-bis[5-(tributylphosphiniomethyl)-2-thienyl]-1,8-dithiaoctane dibromide (1 mmol), 7-(5-decylthio-2-thienyl)hepta-2,4,6-trienal, (0.7 g, 2 mmol) and sodium ethoxide (3 mmol) in ethanol gave crude **15**. Recrystallization from toluene yielded **15** (0.4 g, 38%), m.p. 160 °C (d), λ_{max}/nm(ε_{max}) 420 (35 000) (Found: C, 66.1; H, 7.45. Calc. for $C_{58}H_{78}S_8$: C, 67.57; H, 7.57).

1,8-*Bis*{5-[10-(5-*decylthio*-2-*thienyl*)*deca*-1,3,5,7,9-*pentaen*-1-*yl*]-2-*thienyl*}-1,8-*dithiaoctane* (**16**). Reaction of 1,8-bis[5-(tributylphosponiomethyl)-2-thienyl]-1,8-dithiaoctane dibromide (0.5 mmol), 9-(5-decylthio-2-thienyl)nona-2,4,6,8-tetraenal (0.39 g, 1 mmol) and sodium ethoxide (1.5 mmol) in ethanol gave crude **16**. Recrystallization from toluene gave **16** (0.14 g, 26%), m.p. 230 °C (decomp); λ_{max}/nm(ε_{max}) 435 (140 000) (Found: C, 68.65; H, 7.5. Calc. for $C_{62}H_{82}S_8$: C, 68.76; H, 7.58).

1,12-*Bis*{5-[8-(5-*decylthio*-2-*thienyl*)*octa*-1,3,5,7-*tetraen*-1-*yl*]-2-*thienyl*}-1,12-*dithiadodecane* (**17**). Reaction of 1,12-bis-[5-(tributylphosphoniomethyl)-2-thienyl]-1,12-dithiadodecane dibromide (1 mmol), 7-(5′-decylthio-2′-thienyl)hepta-2,4,6-trienal (0.7 g, 2 mmol) and sodium ethoxide (3 mmol) in ethanol gave crude **17**. Recrystallization from toluene gave **17** (0.4 g, 38%), m.p. 155 °C (d), λ_{max}/nm(ε_{max}) 420 (50 000) (Found: C, 67.05; H, 8.3. Calc. for $C_{62}H_{86}S_8$: C, 68.51; H, 7.92).

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