Comparison of Bipolaron-like Charge State Generation in the Oxidative Doping of α,ω-Dithienyl and α,ω-Diphenyl Polyenes Stabilized by Methoxy and Methylthio Substituents

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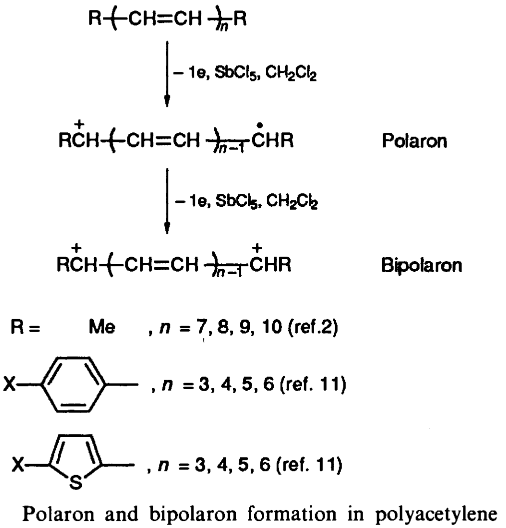
Several α,ω-dithienyl and diphenyl polyenes substituted with mesomerically interactive methylthio substituents have been synthesized by Wittig condensation. These polyenes can be oxidatively doped with $SbCl_5$ in solution to yield stable bipolaron-like charge states. The methylthio-substituted bipolaron spectra are considerably more red-shifted in the diphenyl polyene series than the methoxy-substituted counterparts, or the methylthiothienyl series. The potential of these states for enhanced non-linear optical response is presented.

It is now generally recognized that bipolaronic charge states dominate in most oxidatively doped π-electron conjugated polymers with non-degenerate ground states.[1] During the past five years, Spangler and co-workers have studied bipolaron formation and stabilization in a number of model systems representing the oligomeric series related to polyacetylene,[2] poly(*p*-phenylene vinylene) (PPV),[3] and poly(2,5-thienylene vinylene) (PTV).[4] In the case of polyacetylene oligomers, end-capped with either methyl or phenyl substituents, the formation of bipolaronic charge states indicates that charge delocalization involves stabilization by the end groups *via* either inductive or mesomeric interaction, and thus strictly speaking, these materials do not have degenerate states equivalent to polyacetylene itself, and more closely resemble PPV repeat units with an extended polyene segment. Thus, in the small molecule oligomers, we observe a complete bleaching of the original π–π* transition rather than simply a decrease in intensity with λ_{max} shifting to shorter wavelength as observed in the oxidative doping of polyacetylene. In the polyacetylene series, for example, oxidative doping in CH_2Cl_2 solution with $SbCl_5$ proceeds *via* successive one-electron transfers yielding first a transitory polaron-like radical cation (P), followed by a more stable bipolaron-like species (BP), as illustrated in Scheme 1.[5,6]

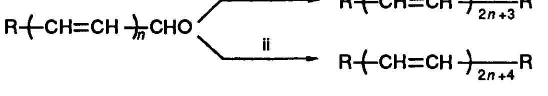


Scheme 1 Polaron and bipolaron formation in polyacetylene oligomers with alkyl, phenyl and thienyl end groups

In some cases careful control of the polyene–$SbCl_5$ ratio and rate of oxidation allows the formation of the polaron-like species, as we have previously reported for the α,ω-bis(4-methoxyphenyl) polyene series.[6] These P species have characteristic EPR and absorption spectra (three bands) normally observed in electroactive polymers. However, if the charge state formation is facilitated and stabilized by strong electron-donating substituents (*e.g.* Me_2N), it becomes quite difficult to observe the transitory P state either spectroscopically or by EPR, although a weak EPR signal is sometimes observed immediately upon mixing, which decays rapidly.[7,8] It should be emphasized that for the sake of simplicity in this discussion we have referred to oligomer oxidation states as polaronic (P) or bipolaronic (BP) while recognizing the fact that there are fundamental differences between these small model oligomers and the solid-state polymer.[9]

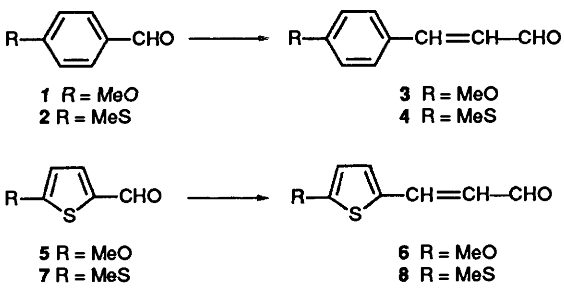
In all of the studies of oligomer charge state generation, both BP long-term stability and the large red shift of the BP spectrum from the original polyene π–π* transition has followed the electron-releasing ability of substituents in conjugation with the polyene chain (Me_2N > MeO > halogen > H).[5] In this paper we have extended these investigations to the more polarizable alkylthio substituent, and compared both BP stability and spectroscopic shift with the previously reported alkoxy substituent effects.

Synthesis of Bis-substituted Polyenes.—In several previous publications we have outlined a general approach to the synthesis of symmetrically substituted polyenes *via* Wittig or Horner–Emmons–Wadsworth methodology.[10,11] This approach is illustrated in Scheme 2.



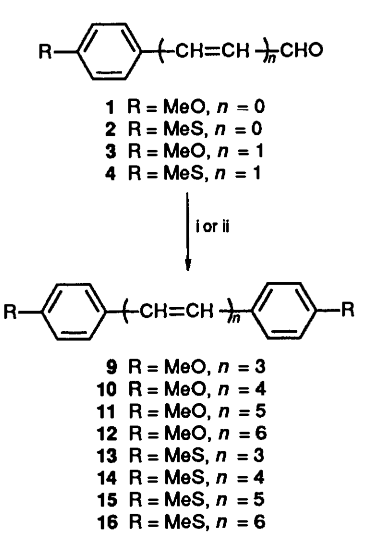
Scheme 2 *Reagents:* i, $Bu_3P^+CH_2CH{=}CHCH_2P^+Bu_3$, $2Cl^-$, NaOEt, EtOH or DMF; ii, $Bu_3P^+CH_2(CH{=}CH)_2CH_2P^+Bu_3$, $2Br^-$, NaOEt, EtOH or DMF

Bis-(4-methoxyphenyl), bis-(4-methylthiophenyl), bis(5-methoxy-2-thienyl) and bis(5-methylthio-2-thienyl) polyenes containing three and four double bonds were prepared in good yield from 4-methoxybenzaldehyde, 4-methylthiobenzaldehyde, 5-methoxythiophene-2-carbaldehyde and 5-methylthiothiophene-2-carbaldehyde respectively, while polyenes containing five or six double bonds were obtained from the corresponding 4-substituted cinnamaldehydes or thienylpropenals. The aldehydes were either available commercially or were prepared by Wittig aldehyde extension methodology developed in our laboratory based on the original suggestion by Cresp *et al.*,[12,13] illustrated in Scheme 3.

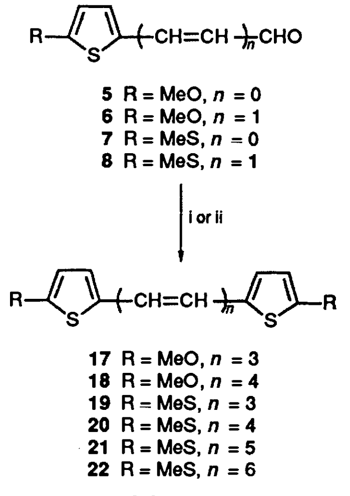


Scheme 3

All polyenes were synthesized by the Wittig methodology outlined in Scheme 2 and were obtained as shown in Schemes 4 and 5.



Scheme 4



Scheme 5

The Potential Significance of Bipolaronic Enhancement of Non-linear Optical Response.—The formation of organic charge states in both electroactive polymers and their oligomers has recently been of interest owing to theoretical predictions of their enhanced third-order non-linear optical properties. In the past few years, the non-linear optical properties of several electroactive polymers have been studied in detail, such as polyacetylene,[14] polythiophene,[15] PPV[16] and PTV.[17] In general, these materials display resonance enhanced $\chi^{(3)}$ values of *ca.* 10^{-10} esu. The fact that this value is not large enough to use for commercial devices has recently prompted comprehensive structure–property relationship studies to elucidate how charges in organic structure might enhance the molecular hyperpolarizability γ and thus $\chi^{(3)}$.[18–20]

The molecular hyperpolarizability γ, or the bulk susceptibility $\chi^{(3)}$, is related to the extent of electron delocalization associated with the π-conjugation sequence. Flytzanis and co-workers initially suggested that γ might follow a power law dependence on π-electron delocalization as high as the sixth power.[21,22] More recent studies have shown that the power dependence of γ_{xxxx} with chain length is of a lower order, 4.6 ± 0.2.[23] Prasad has measured γ for a series of polythiophene oligomers by degenerate four-wave mixing (DFWM) in solution and found a power law dependence of γ of four.[24] $\chi^{(3)}$ measurements for poly(3-dodecylthiophene) showed the same effect, and Prasad concluded that effective conjugation does not extend much beyond ten repeat units. Similar measurements of poly(*p*-phenylene) showed that $\chi^{(3)}$ levels off at the terphenyl level ($N = 3$). Thus γ or $\chi^{(3)}$ appears to level off with increasing N, and simply increasing the length of the conjugation sequence may not produce an enhanced γ sufficient for proposed applications. Thus, if γ is limited by a molecule's effective conjugation length, as opposed to the total length, then other mechanisms for enhancement of third-order non-linearity need to be explored.

DeMelo and Silbey have recently postulated that enhancement of γ_{xxxx} or γ^{π} may be possible by incorporating delocalized charge states in the π-conjugation sequence.[25,26] These workers utilized a perturbative density matrix treatment to investigate first and second hyperpolarizabilities of linear conjugated chains C_nH_{n+2} described by a PPP Hamiltonian. They concluded that the different components of γ_{iiii} were highly dependent on the geometry and charge on the conjugated chain. In all cases γ_{xxxx} dominates the orientationally averaged γ^{π}. Their data indicates that saturation does not occur for γ_{xxxx} up to $N \sim 20$. Regardless of sign, all components increase in absolute value as a function of N. Their data fits a power series aN^b for neutral, polaron and bipolaron charge states, and γ_{xxxx} has the following calculated values: neutral ($a = 52.0, b = 4.25$); bipolaron ($a = 0.247, b = 6.04$). The power law dependence for the neutral polyenes is in accord with experiment.[24] What is the most intriguing aspect of this work is the much larger power dependence of the bipolaronic states compared with the neutral chains. Thus bipolaronic charge state formation may lead to significant enhancement of γ_{xxxx}. As we have previously shown, mesomeric stabilization of oligomeric bipolarons allows delocalization of the whole oligomer length, thus allowing for long effective conjugation lengths for bipolarons.

Birge and co-workers[27] have recently improved upon deMelo and Silbey's calculations, and while they have found a lower dependence of γ_{xxxx} on charge state, it is still larger than for the neutral species. Thus, for 1,8-bis(4′-methoxyphenyl)octa-1,3,5,7-tetraene, the calculated γ_{xxxx} for the neutral and bipolaronic states are: γ_{xxxx}* calc. 327, exp. 251; calc. 494, exp. na, respectively.

Experimental measurement of γ_{xxxx} (BP) has not yet been obtainable by DFWM owing to a variety of experimental difficulties particularly the lack of solubility of oligomers with highly polar end groups which precludes accurate measurement in solution by either DFWM or THG,[28] but the good agreement for the neutral calculated and experimental values lends support to the expectation that the BP state does indeed have larger γ_{xxxx} values than the neutral polyenes. In this regard, Cao *et al.*,[29] have recently reported that $\chi^{(3)}$ can be

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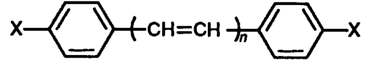
* 10^{-36} esu; na—experimental data not available.

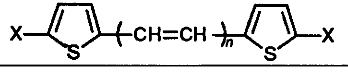
Table 1 Comparison between α,ω-bis(*p*-methylthiophenyl) and bis(*p*-methoxyphenyl) polyene bipolaron (BP) absorption spectra



Compound	π–π*[a]	X	*n*	BP A/nm[b]
9	348, **363**, 382	MeO	3	Unstable
10	370, **390**, 413	MeO	4	647, **700**
11	388, **410**, 435	MeO	5	664, **727**
12	402, **426**, 452	MeO	6	713, **776**
13	**385**, 403	MeS	3	670, 733, **815**
14	**400**, 422	MeS	4	705, 777, **869**
15	**417**, 443	MeS	5	740, 823, **920**
16	**433**, 461	MeS	6	785, 864, **966**

[a] 10^{-5} mol dm^{-3} CH_2Cl_2. [b] Excess of $SbCl_5$. Peak of maximum intensity in bold.

Table 2 Bipolaron absorption spectra for α,ω-bis(5-methylthiothienyl) and bis(5-methoxythienyl) polyenes



Compound	X	π–π*[a]	*n*	BP A/nm[b]
17	MeO	**398**, 420	3	**520**
18	MeO	**416**, 442	4	**577**
19	MeS	**404**	3	**580**sh, **610**, 643
20	MeS	**442**, 444	4	610sh, **663**, 702
21	MeS	**434**, 460	5	675sh, **717**, 775sh
22	MeS	**451**, 478	6	705sh, **773**, 830sh
23	Me[c]	**416**, 443	5	653, **713**
24	Me[c]	**432**, 461	6	713, **776**

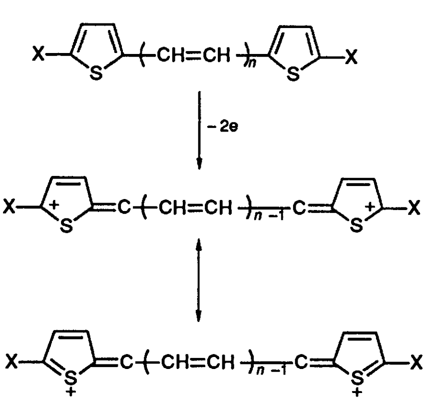
[a] 10^{-5} mol dm^{-3} CH_2Cl_2. [b] Excess of $SbCl_5$. [c] Ref. 11. Peak of maximum intensity in bold.

enhanced in ladder polymer models in solution by $SbCl_5$ oxidation to a bipolaronic state. The magnitude of enhancement is in accord with Birge and co-workers' predictions, albeit for a very different chemical structure.

Results and Discussion

If bipolaronic enhancement of γ_{xxxx} is indeed a general phenomenon then it becomes extremely important both to increase the stabilities of the BP states, and define their optical absorption characteristics to allow a match with available laser frequencies. In Tables 1 and 2, the absorption of the neutral and oxidized polyenes are shown. In comparing the absorption characteristics of MeO and MeS substituents in the α,ω-diphenyl polyene series, one sees a profound dependence of the absorption upon substituent identity, with an almost 200 nm further red-shift for the MeS series. However, in the α,ω-dithienyl series, the shift is considerably smaller (*ca.* 100 nm). In fact in this series, the MeS substituent is no more effective than Me groups in shifting the BP λ_{max}. This may argue for a much stronger influence of the ring S in stabilizing the BP state than the substituent (Scheme 6).

In the diphenyl polyene series; the large shift in λ_{max} may be explained on the basis of the greater polarizability of S *vs.* O, and the involvement of S d-orbitals in charge stabilization.



Scheme 6

These results indicate that a much greater degree of control over the absorption characteristics of the BP states is possible than was previously found for substituent groups based upon first-row elements (Me_2N, MeO, F, Me, *etc.*). Thus substituent group identity coupled with variable conjugation length may allow a BP state to be matched to specific laser fundamentals and harmonics to minimize two and three photon resonances.

Several problems remain to be solved before bipolaronic states may be useful for NLO applications. First, the solubility of these materials needs to be improved if DFWM or third-harmonic generation (THG) characterization is to be accomplished. Secondly, charge state stabilities need to be improved. Although the BP states reported in this study are stable in contact with moist air for several days to weeks, this is insufficient for NLO applications at the current time. Recent studies in our laboratory with bisanthracenyl polyenes, for which BP composites in polycarbonate show stabilities of the order of 3–4 months, are encouraging.[29] Substituent-group stabilization of these BP states has yet to be demonstrated, however, the effects we have observed for the diphenyl polyene series, coupled with the additional aromatic stabilization of the quinoidal states in these materials leads us to predict that these materials will have exceptional BP stability.

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 for CH_2Cl_2 solutions. ^1H NMR spectra were determined for solutions in $CDCl_3$ unless otherwise noted (Me_4Si internal reference, *J* values given in Hz) on an IBM WP-200 spectrometer. 4-Methylthiobenzaldehyde was obtained from Aldrich Chemical Co. Solutions of pure polyenes in CH_2Cl_2 (10^{-5} mol dm^{-3}) were doped by adding $SbCl_5$ solutions in CH_2Cl_2 (10^{-3} mol dm^{-3}) 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 VIS–NIR spectrometer model 200-25 *via* a fibre-optic cable link to the 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 20 mm repeat intervals were carried out for several hours. In all cases very rapid bleaching of the original π–π* transition was observed, simultaneous with the appearance of the BP band.

5-*Methoxythiophene-2-carbaldehyde* (**5**).—A solution of butyllithium (0.14 mol, 1.6 mol dm^{-3} solution in hexane, 86 cm^3) was added dropwise to a solution of 2-methoxythiophene[30] (13.0 g, 0.11 mol) and TMEDA (14.0 g, 0.12 mol) in anhydrous diethyl ether (200 cm^3) at 0 °C. The resulting solution was stirred at 0 °C for 40 min. Dimethylformamide (44.0 g, 0.6 mol) was added dropwise, and the solution stirred for 60 min at 0 °C, and then acidified by the addition of aq. HCl (3 mol dm^{-3}; 50

cm^3). The aq. layer was separated from the organic layer and extracted with ether (3 × 100 cm^3). The combined organic product solution was washed with brine (100 cm^3) and dried ($MgSO_4$). After solvent removal the crude product was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane yielding **5** (12.5 g, 77%), m.p. 25–26 °C (lit.,[30] 24–26 °C) δ_H 4.00 (s, 3 H, OMe), 6.35 (d, 1 H_a, J_{ab} 4, aromatic), 7.52 (d, 1 H_b, J_{AB} 4, aromatic), 9.67 (s, 1 H, CHO).

5-*Methylthiothiophene*-2-*carbaldehyde* (**7**).—A solution of butyllithium (0.24 mol, 1.6 mol dm^{-3} solution in hexane, 149 cm^3) was added dropwise to a solution of 2-methylthiothiophene[31] and TMEDA (23.2 g, 0.2 mol) in anhydrous ether (400 cm^3) at 0 °C. The resulting solution was stirred for 40 min at 0 °C, and dimethylformamide (39.4 g, 0.54 mol) was then added. The work-up and isolation of **6** was identical with that described above for **5**, yielding 26.2 g (90%), δ_H 2.62 (s, 3 H, $-SCH_3$), 7.02 (d, 1 H_a, J_{AB} 4.0, aromatic), 7.67 (d, 1 H_b, J_{AB} 4, aromatic), 9.87 (s, 1 H, CHO).

3-(5-*Methylthio*-2-*thioenyl*)*prop*-2-*enal* (**8**).—A solution of sodium ethoxide (60 mmol, 1 mol dm^{-3}, 60 cm^3) in ethanol was added dropwise to a solution of **6** (5.2 g, 33 mol) and tributyl-(1,3-dioxan-2-ylmethyl)phosphonium bromide (49 mmol, 1.2 mol dm^{-3}, 41 cm^3) in ethanol (200 cm^3) at 90 °C. The resulting mixture was stirred for 20 h under a N_2 atmosphere at 90 °C. The mixture was then poured into ice–water (300 cm^3), and extracted with ether (3 × 200 cm^3). The organic product was washed with brine, dried ($MgSO_4$) and concentrated. The crude liquid product was dissolved in THF (200 cm^3) and acidified with aq. HCl (3 mol dm^{-3}; 100 cm^3). The product was poured into ice–water (500 cm^3) and extracted with ether (3 × 200 cm^3). The ether solution was washed with brine, dried and concentrated. The crude product was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane to give **8** (2.5 g, 41%), δ_H 2.59 (s, 3 H, SCH_3), 6.38 (dd, 1 H_b, J_{AB} 7.7, J_{bc} 15.5), 6.93 (d, 1 H_d, J_{de} 4), 7.20 (d, 1 H_e, J_{de} 4), 7.47 (d, 1 H_c, J_{bc} 15.5), 9.58 (d, 1 H_a, J_{AB} 7.7, CHO); δ_C: δ 20.12, 126.51, 128.62, 132.91, 139.22, 143.70, 145.65, 192.61 (Found: C, 52.3; H, 4.5. Calc. for $C_8H_8OS_2$: C, 52.17; H, 4.35%).

3-(4-*Methylthiophenyl*)*prop*-2-*enal* (**4**).—A solution of sodium ethoxide (150 mmol, 1 mol dm^{-3}, 150 cm^3) in ethanol was added dropwise to a solution of 4-methylthiobenzaldehyde (15.2 g, 100 mmol) and 1,3-dioxan-2-ylmethyltributylphosphonium bromide (77 mmol, 1.2 mol dm^{-3} solution in DMF, 64 cm^3) in DMF (150 cm^3). The work-up and isolation was identical with that described for **8**. The crude product was recrystallized from ethanol to yield **4** (11.5 g, 64%), m.p. 58–60 °C, δ_H 2.52 (s, 3 H, SCH_3), 6.68 (dd, 1 H_b, J_{AB} 7.7, J_{bc} 15), 7.26 (d, 1 H_d, J_{de} 8, aromatic), 7.42 (d, 1 H_c, J_{bc} 15), 7.48 (d, 1 H_e, J_{de} 8, aromatic), 9.68 (d, 1 H_a, J_{ab} 7.7, CHO); δ_C 14.69, 125.61, 127.28, 128.61, 130.17, 143.35, 151.96, 193.34 (Found: C, 67.5; H, 5.6. Calc. for $C_{10}H_{10}OS$: C, 67.42; H, 5.62%).

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 (**25**) (0.05 mol) in either ethanol or DMF (250 cm^3). The reaction mixture was stirred for 20 h at 90 °C, then poured into ice–water (500 cm^3). The crude product was isolated by vacuum filtration and purified by recrystallization. For polyenes with an even number of double bonds, (*E,E*)-hexa-2,4-diene-1,6-diylbis(tributylphosphonium) dibromide (**26**) was utilized in place of **25**.

1,6-Bis(4-methoxyphenyl)hexa-1,3,5-triene (**9**) 1,8-bis(4-methoxyphenyl)octa-1,3,5,7-tetraene (**10**), 1,10-bis(4-methoxyphenyl)deca-1,3,5,7,9-pentaene (**11**), and 1,12-bis(4-methoxyphenyl)dodeca-1,3,5,7,9,11-hexaene (**12**) were all prepared essentially by the method of Spangler *et al.*[10]

1,6-*Bis*(4′-*methylthiophenyl*)-*hexa*-1,3,5-*triene* (**13**). Reaction of **25** (10 mmol), **6** (3.04 g, 2 mmol) and sodium ethoxide (30 mmol) in ethanol (200 cm^3) gave crude **13**. Recrystallization from ethanol gave **13** (1.6 g, 47%), m.p. 231–233 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 403sh, 385 (5.6) (Found: C, 73.9; H, 6.2. Calc. for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21%).

1,8-*Bis*(4-*methylthiophenyl*)*octa*-1,3,5,7-*tetraene* (**14**). Reaction of **26** (10 mmol), **6** (3.04 g, 2 mmol) and sodium ethoxide (30 mmol) in ethanol (200 cm^3) gave crude **14**. Recrystallization from ethanol–toluene yielded **14** (1.7 g, 50%), m.p. 251–253 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 422sh and 400 (8.8) (Found: C, 75.4; H, 6.3. Calc. for $C_{22}H_{22}S_2$: C, 75.43; H, 6.29%).

1,10-*Bis*(4-*methylthiophenyl*)*deca*-1,3,5,7,9-*pentaene* (**15**). Reaction of **25** (11 mmol), **8** (3.9 g, 22 mmol) in DMF (200 cm^3) gave crude **15**. Recrystallization from DMF gave **15** (2.2 g, 55%), m.p. 262–263 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 443sh and 417 (13) (Found: C, 76.3; H, 6.2. Calc. for $C_{24}H_{24}S_2$: C, 76.60; H, 6.38%).

1,12-*Bis*(4-*methylthiophenyl*)*dodeca*-1,3,5,7,9,11-*hexaene* (**16**). Reaction of **26** (20 mmol), **8** (7.5 g, 43 mmol) in DMF gave crude **16**. Recrystallization from DMF gave **16** (4.0 g, 50%) m.p. 265–266 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 461sh, 433 (9.7) (Found: C, 77.6; H, 6.6. Calc. for $C_{26}H_{26}S_2$: C, 77.56; H, 6.51%).

1,6-*Bis*(5-*methoxy*-2-*thienyl*)*hexa*-1,3,5-*triene* (**17**). Reaction of **25** (7 mmol), **5** (2.0 g, 14 mmol) in ethanol (200 cm^3) gave crude **17**. Recrystallization from ethanol–toluene gave **17** (1.2 g, 56%), m.p. 167–169 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 420sh and 398 (6) (Found: C, 63.4; H, 5.7. Calc. for $C_{16}H_{16}O_2S_2$: C, 63.15; H, 5.26%).

1,8-*Bis*(5-*methoxy*-2-*thienyl*)*octa*-1,3,5,7-*tetraene* (**18**). Reaction of **26** (7 mmol), **5** (2.0 g, 14 mmol) in ethanol (200 cm^3) gave crude **18**. Recrystallization from ethanol–toluene gave **18** (1.2 g, 52%), m.p. 187.5–189 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 442sh and 416 (9.1) (Found: C, 66.0; H, 5.7. Calc. for $C_{18}H_{18}O_2S_2$: C, 65.45; H, 5.45%).

1,6-*Bis*(5-*methylthio*-2-*thienyl*)*hexa*-1,3,5-triene (**19**). Reaction of **25** (8 mmol), **7** (2.5 g, 16 mmol) in ethanol (200 cm^3) gave crude **19**. Recrystallization from ethanol–toluene gave **19** (1.3 g, 49%), m.p. 155–157 °C, λ_{max}/nm (a_{max}10^4 m^{-1}) 404 (6.5); δ_C 21.64, 125.27, 126.33, 128.92, 131.01, 132.97, 136.86, 144.95 (Found: C, 56.9; H, 5.0. Calc. for $C_{16}H_{16}O_2S_2$: C, 57.14; H, 4.76%).

1,8-*Bis*(5-*methylthio*-2-*thienyl*)*octa*-1,3,5,7-*tetraene* (**20**). Reaction of **26** (4.7 mmol), **7** (1.5 g, 9.5 mmol) in ethanol (200 cm^3) gave crude **20**. Recrystallization from ethanol–toluene gave **20** (1.1 g, 65%), m.p. 172–173.5 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 444sh and 422 (7.9) (Found: C, 59.8; H, 5.1. Calc. for $C_{18}H_{18}S_4$: C, 59.69; H, 4.97%).

1,10-*Bis*(5-*methylthio*-2-*thienyl*)*deca*-1,3,5,7,9-*pentaene* (**21**). Reaction of **25** (1.7 mmol), **8** (0.7 g, 3.7 mmol) in DMF (200 cm^3) gave crude **21**. Recrystallization from toluene gave **21** (0.9 g, 63%), m.p. 204–205.5 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 460sh and 434 (9) (Found: C, 61.8; H, 5.2. Calc. for $C_{20}H_{20}S_4$: C, 61.86; H, 5.15%).

1,12-*Bis*(5-*methylthio*-2-*thienyl*)*dodeca*-1,3,5,7,9,11-*hexaene* **22**. Reaction of **26** (2.7 mmol), **8** (1.0 g, 5.4 mmol) in DMF (200 cm^3) gave crude **22**. Recrystallization from toluene gave **22** (0.6 g, 53%), m.p. 220–224 °C, λ_{max}/nm (a_{max}/10^4 m^{-1}) 478sh and 451 (12) (Found: C, 63.9; H, 5.4. Calc. for $C_{22}H_{22}S_4$: C, 63.77; H, 5.25%).

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