Effect of Chain Extension on the Electrochemical and Electronic Properties of π-Conjugated Soluble Thienylenevinylene Oligomers

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Abstract: Thienylenevinylene oligomers (nTVs) containing up to 10 thiophene rings and bearing solubilizing hexyl groups at the α-position of the end thiophene rings or octyl or dibutyl chains at the 3-position or the 3- and 4-positions of the thiophene rings have been synthesized by a combination of formylation reaction, Wittig−Horner olefination, and McMurry dimerization. Owing to the good solubility imparted by alkyl chains, the electrochemical behavior of nTVs has been analyzed for the first time. Chain extension leads to a negative shift of the peak potentials corresponding to the formation of the cation radical and dication and to a decrease of their difference. For the octamers the dication is formed directly through a two-electron transfer while the system can be reversibly charged up to the tetracationic state. Electronic absorption spectra show the expected bathochromic shift of λ_{max} and decrease of the HOMO−LUMO gap with extension of the conjugation length. Thus, solution-cast films of octamers exhibit band-gap values comparable to or even smaller than that of the parent poly(thienylenevinylene) (PTV). Extrapolation of the electrochemical and optical data to infinite chain length suggests that the oxidation potential and intrinsic band gap of a defect-free PTV could be significantly smaller than the present experimental values.

Introduction

Conjugated oligomers with a well-defined chemical structure are aquiring a growing importance in the field of organic conductors. From a technological viewpoint, electronic properties of these compounds that approach and sometimes even surpass those of the corresponding polydisperse polymers[1−5] have been used in the fabrication of electronic and optoelectronic devices such as diodes,[2] field-effect transistors,[3] and light-emitting diodes (LEDs).[4]

At a more fundamental level, conjugated oligomers have attracted considerable interest as model compounds for the analysis of the electrochemical and electronic properties of the corresponding polymers. Thus, the evolution of the electronic and electrochemical properties of oligothiophenes (nTs) as a function of chain length has been analyzed by several groups, and the data obtained have been extrapolated to predict the oxidation potential, absorption maximum, and band gap of an infinite defect-free poly(thiophene) (PT) chain.[5]

More recently, the potentialities of π-conjugated oligomers as molecular wires[6] for future development in molecular electronics and logic[7] has received special attention. Such an application puts specific requirements on the structure and properties of the envisioned linear π-conjugated system which must simultaneously possess precisely controlled structure and dimensions, good stability, and optimal electron transmission properties. From this latter viewpoint, simple polyenic structures should in principle exhibit optimal π-electron delocalization as exemplified by the high performances of the derived push−pull chromophores in nonlinear optics (NLO).[8] However, due to the lack of thermal and photothermal stability of polyenes, the synthesis of models for molecular wires has been focused on the more stable *p*-phenylene,[9] phenylene−ethynylene and thiophene−ethynylene oligomers.[10] However, due to excessive

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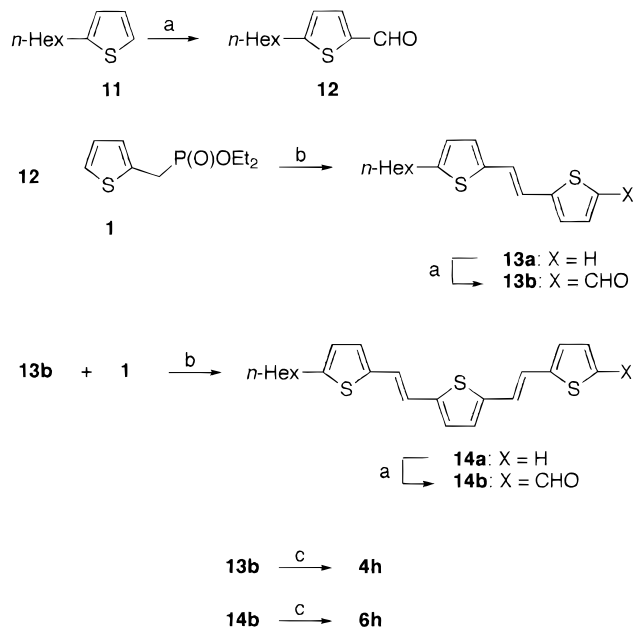
Chart 1

4h

6h
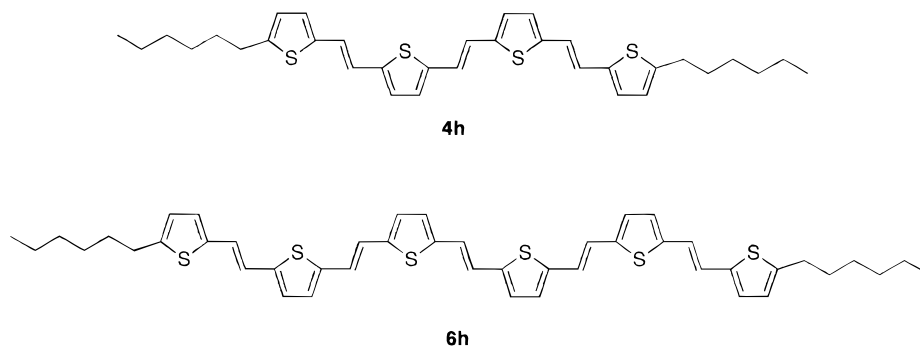
π-electron confinement, these systems exhibit a rapid saturation of effective conjugation with chain length.

Poly(thienylenevinylene) (PTV) is known to have a smaller band gap than PT.[11,12] In fact, the presence of double bonds of defined configuration leads to (i) a decrease of the overall aromatic character of the system and hence of π-electron localization and (ii) a limitation of the rotational disorder inherent to nTs,[13] which contributes to increasing the band gap.[14] Although the good π-electron delocalization of thienylenevinylene oligomers (nTVs) has been used in the design of NLO chromophores[15] and extended tetrathiafulvalene analogs,[16] the synthesis and the characterization of the electronic properties of nTVs have attracted much less attention than those of nTs. Kossmehl first reported the synthesis of nTVs up to the heptamer by means of a succession of formylation and Wittig reactions.[17] More recently, the same compounds have been synthesized by other groups,[18,19] while some cyclic versions of nTVs have been described by Cava et al.[20] As shown in these previous works, the rapid drop of solubility caused by chain extension has represented a major obstacle to the development of longer nTVs and to the detailed investigation of their electronic and electrochemical properties.[17,18]

We report here the synthesis and characterization of nTVs substituted by alkyl chains either at the α-position of the terminal thiophene rings (Chart 1) or at the β-position or the β,β′-positions of each thiophene (Charts 2 and 3).[21] The enhanced solubility imparted by substitution allowed extension of the chain

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Scheme 1[a]

a Reagents and conditions: (a) *n*-BuLi, DMF/THF, room temperature; (b) *t*-BuOK/THF, room temperature; (c) TiCl₄, Zn/THF, reflux; (d) NBS/CHCl₃−AcOH, 1:1, room temperature; (e) *n*-BuLi/Et₂O −100 °C, then DMF room temperature; (f) POCl₃, DMF/DCE, reflux; (g) *n*-BuLi, TMEDA/hexane, reflux, then −40 °C, DMF/THF room temperature.

length up to the octamer and decamer, which are the longest nTVs reported so far. Owing to this improved solubility, the electrochemical properties of nTVs have been investigated for the first time. Electrochemical and optical data are discussed with regard to their implications for the electronic properties of PTV as well as for future applications of linear π-conjugated systems.

Results and Discussion

Three series of nTVs were synthesized. In a first set of experiments the synthesis of nTVs bearing hexyl chains at the α-position of the end thiophene rings was carried out (Chart 1). However, due to the limited solubility of these oligomers, two other series of nTVs based on 3-octylthiophene (series **a**) or 3,4-dibutylthiophene (series **b**) were synthesized (Charts 2 and 3).

Commercially available 2-hexylthiophene (**11**) (Lancaster) was converted into the corresponding 5-carboxaldehyde **12** in 94% yield by lithiation followed by reaction with DMF (Scheme 1). Wittig olefination of **12** using diethyl (2-thienylmethyl)-

(21) Preliminary communication: Elandaloussi, E.; Frère, P.; Roncali, J. *Chem. Commun.* **1997**, 301.

Chart 2

2a

4a

6a

8a
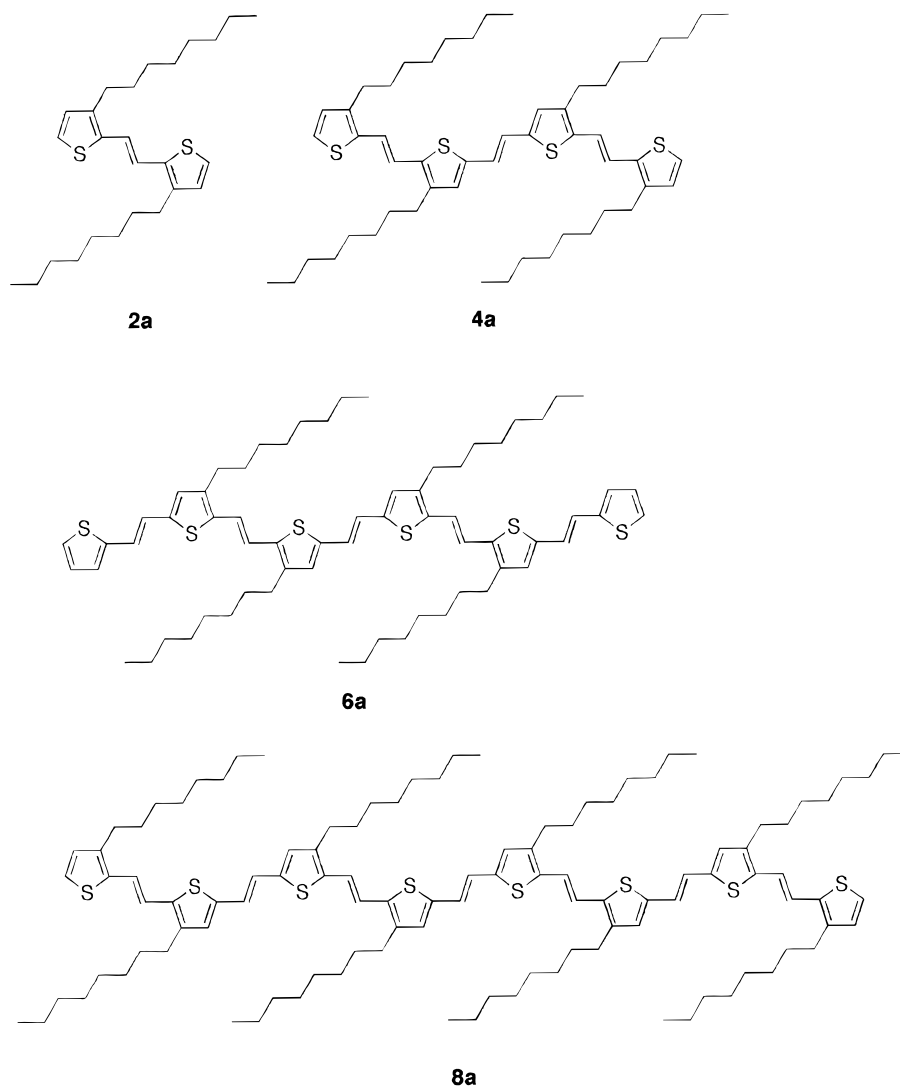
phosphonate (**1**)[22] afforded compound **13a** in 87% yield. Carboxaldehyde **13b** was then obtained in 82% yield using the same method as for **12**. Wittig olefination of **13b** with **1** afforded **14a** (88%), which was subsequently converted into aldehyde **14b** in 73% yield. The target compounds containing four and six thiophene rings **4h** and **6h** were then obtained in 41% and 21% yields, respectively, by McMurry coupling of aldehydes **13b** and **14b** using low-valent titanium.[23]

The synthesis of oligomers substituted at the 3-position or the 3- and 4-positions of the thiophene rings is depicted in Scheme 2. 3-Octylthiophene (**15a**) and 3,4-dibutylthiophene (**15b**) were synthesized from the corresponding bromothiophenes by nickel-catalyzed cross coupling with alkyl Grignard reagents.[24] Regioselective bromination of **15a** with NBS gave **15c** in 91% yield. Treatment of **15c** with *n*-butyllithium and reaction with DMF afforded aldehyde **16a** in 96% yield. Vilsmeier formylation of **15b** gave aldehyde **16b** in 96% yield while 3,4-dibutyl-2,5-thiophenedicarbaldehyde (**16c**) was synthesized in 58% yield by reaction of DMF on the dilithiated derivative of **15b** prepared in the presence of TMEDA.[25]

McMurry coupling of aldehydes **16a** and **16b** afforded dithienylethylenes **2a** and **2b** in 89% and 67% yields, respectively. Vilsmeier formylation of **2a** and **2b** gave aldehydes **17a** and **17b** in 70% and 92% yields. Vilsmeier formylation was found more selective for the preparation of the monoaldehydes than reaction of DMF on the lithio derivatives, which always gave a mixture of mono- and dicarboxaldehyde presumably because of the difficulty of selectively performing metallation at a single position. **3b** with a substituted median thiophene was prepared in 79% yield by a double Wittig reaction of the dialdehyde **16c** with **1**. Conversion of **3b** into the monoaldehyde **18b** was achieved in 69% yield by Vilsmeier formylation. McMurry coupling of aldehydes **17a** and **17b** afforded **4a** and **4b** in 71% and 78% yields, respectively. These compounds were then converted into the corresponding monoaldehydes **19a** and **19b** and dialdehyde **19c** by Vilsmeier formylation (yields 38%, 46%, and 83%, respectively). Oligomers containing six thiophenes (**6a,b**) were synthesized by two different routes. Wittig olefination of dialdehyde **19c** with **1** gave **6a** in 82% yield, while **6b** was obtained by McMurry dimerization of the monoaldehyde **18b** (yield 25%). The target compounds **8a** and **8b** were synthesized in 25% and 52% yields, respectively, by McMurry dimerization of aldehydes **19a** and **19b**. Vilsmeier formylation of **8b** gave the dialdehyde **20b** (81%), which was converted into the longest oligomer **10b** by a double Wittig olefination with **1**. All nTVs were satisfactorily characterized by NMR,
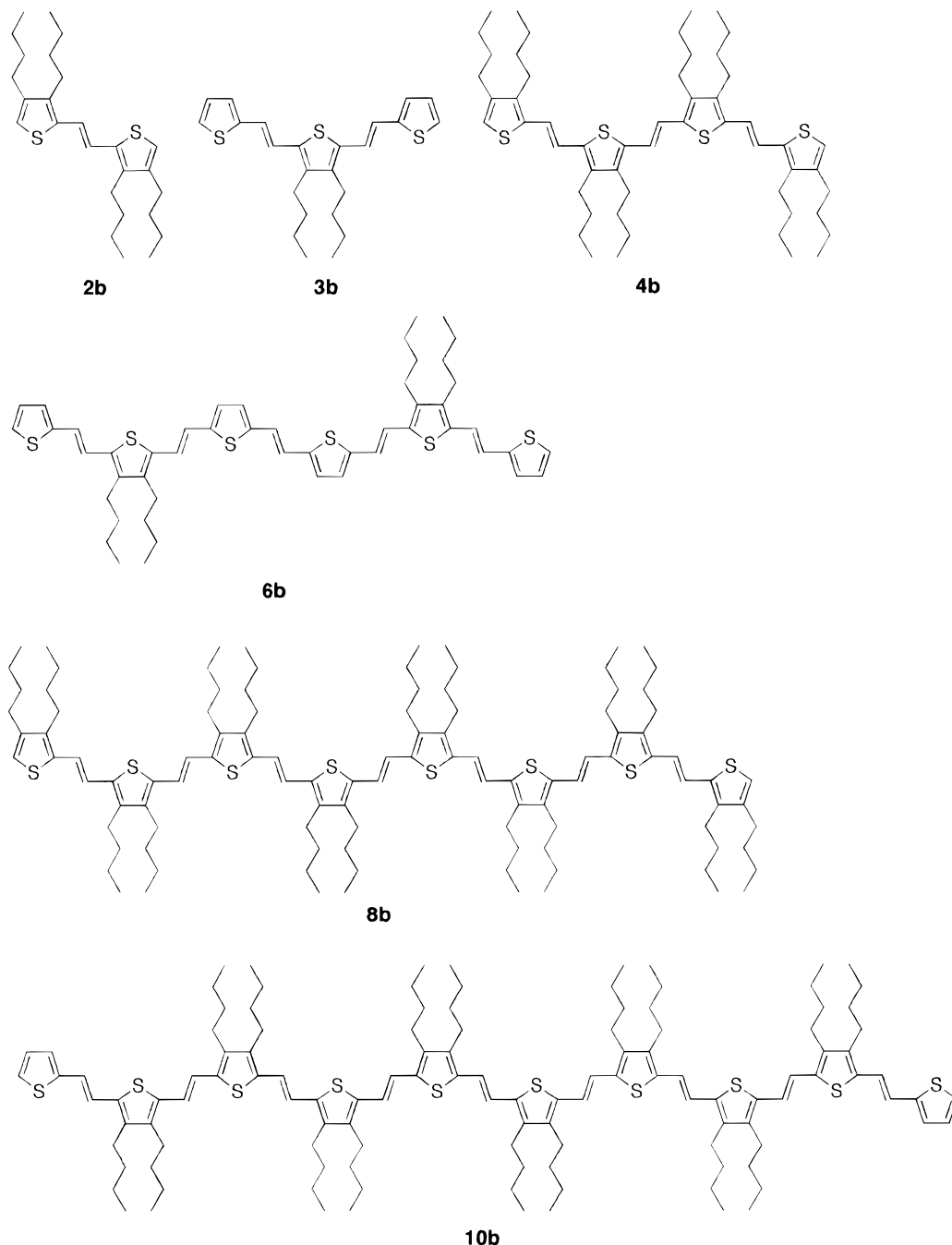
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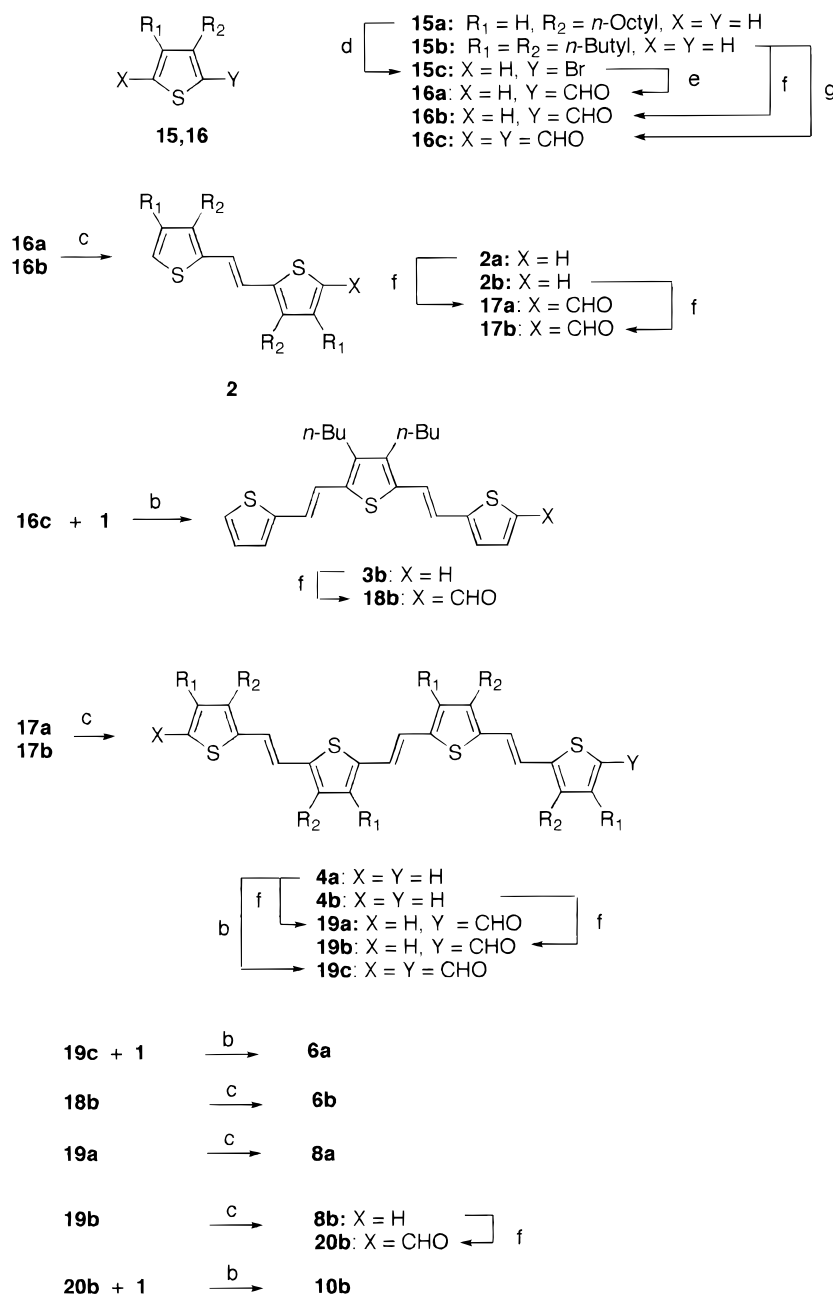
Chart 3

2b   **3b**   **4b**

6b

8b

10b

mass, and UV−vis spectroscopies. For **6b** and **8a**, ^{1}H NMR spectra recorded in C_6D_6 + $CDCl_3$ (2:1) allowed the separation of ethylenic and aromatic protons (Figure 1), thus confirming the *all-trans* configuration. However, due to their sensitivity toward oxygen, especially for the longest ones, correct combustion analyses were difficult to obtain in some cases. Therefore, electrochemical and spectroscopic experiments were performed on samples purified by column chromatography immediately before use.

Cyclic Voltammetry. Table 1 lists the values of the anodic peak potentials $E_{pa}(1)$ and $E_{pa}(2)$ corresponding to the successive generation of the cation radical and dication for the various series of nTVs. Comparison of the data for oligomers **4** and **6** which are available for three types of substitution shows that, for a given chain length, nTVs substituted at the β-positions of the thiophene ring (series **a** and **b**) exhibit less positive $E_{pa}(1)$ and $E_{pa}(2)$ values than their analogs substituted at the α-position of the end thiophene ring **4h** and **6h**. Furthermore, the larger

values of the difference $E_{pa}(2)-E_{pa}(1)$ indicate stronger Coulombic repulsion between positive charges in the dication for **4h** and **6h**. These differences can be related to the smaller number of alkyl substituents leading to a smaller overall +I effect. Similarly, nTVs of the **b** series exhibit less positive E_{pa} values than those of series **a** due to the cumulative electron-releasing effect of the twice larger number of alkyl substituents.

The effect of chain extension on the electrochemical behavior of nTVs is illustrated in Figures 2−5. The cyclic voltammogram (CV) of **2b** exhibits two successive oxidation waves with $E_{pa}(1)$ and $E_{pa}(2)$ at 0.97 and 1.32 V, respectively. While the CVs of **2a** and **2b** exhibit an irreversible first oxidation wave indicative of a followup chemical reaction, only **2a** gives rise to the formation of a polymeric film upon subsequent redox cycling. This polymer has already been investigated by Catellani et al.[26] and was not further characterized. The lack of electropolymerization of **2b** is probably related to the combined effects of the stabilization of the cation radical, as

Scheme 2[a]

15a: $R_1 = H$, $R_2 = n$-Octyl, $X = Y = H$
15b: $R_1 = R_2 = n$-Butyl, $X = Y = H$
15c: $X = H$, $Y = Br$
16a: $X = H$, $Y = CHO$
16b: $X = H$, $Y = CHO$
16c: $X = Y = CHO$

2a: $X = H$
2b: $X = H$
17a: $X = CHO$
17b: $X = CHO$

3b: $X = H$
18b: $X = CHO$

4a: $X = Y = H$
4b: $X = Y = H$
19a: $X = H$, $Y = CHO$
19b: $X = H$, $Y = CHO$
19c: $X = Y = CHO$

19c + 1 →b **6a**

18b →c **6b**

19a →c **8a**

19b →c **8b:** $X = H$
20b: $X = CHO$

20b + 1 →b **10b**

[a] Reagents and conditions: (a) *n*-BuLi, DMF/THF, room temperature; (b) *t*-BuOK/THF, room temperature; (c) TiCl$_4$, Zn/THF, reflux; (d) NBS/CHCl$_3$−AcOH, 1:1, room temperature; (e) *n*-BuLi/Et$_2$O −100 °C, then DMF room temperature; (f) POCl$_3$, DMF/DCE, reflux; (g) *n*-BuLi, TMEDA/hexane, reflux, then −40 °C, DMF/THF room temperature.

indicated by the *ca*. 0.10 V lower $E_{pa}(1)$ value, and of the steric hindrance to planarity during the coupling process caused by interactions bewteen the butyl groups.[12,27]

For both series of nTVs chain extension leads to an increase of the reversibility of the two oxidation waves, a negative shift of $E_{pa}(1)$ and $E_{pa}(2)$, and a decrease of the difference $E_{pa}(2) - E_{pa}(1)$ which reflects the reduction of the on-site Coulombic repulsion between positive charges in the dicationic state. For **8a** and **8b**, this evolution results in the coalescence of the two successive one-electron oxidation peaks into a single-step two-electron wave, as confirmed by the 30 mV difference between $E_{pa}(1)$ and the corresponding cathodic peak potential. Chain

extension leads also to an increase of the number of accessible oxidation states, and as appears in the CV of **8b** (Figure 5), the two-electron wave is followed by two successive one-electron waves at 0.78 and 0.93 V ($E_{pa}(3)$ and $E_{pa}(4)$) indicating that the system can be charged up to the tetracationic state. Further chain extension to **10b** causes a negative shift of $E_{pa}(3)$ to 0.63 V, but the rather poor definition of the CV due to the low solubility did not allow us to decide whether this wave involves one or two electrons.

Previous studies on different series of substituted thiophene oligomers from the monomer to the octamer have shown than nTs are oxidized to the dication state by means of two successive one-electron oxidation steps.[5d,e] Extrapolation of the CV data to an infinite chain length led to different views concerning the ultimate electrochemical properties of the polymer. The difference $E_{pa}(2) - E_{pa}(1)$ was predicted either to cancel[5d] or to

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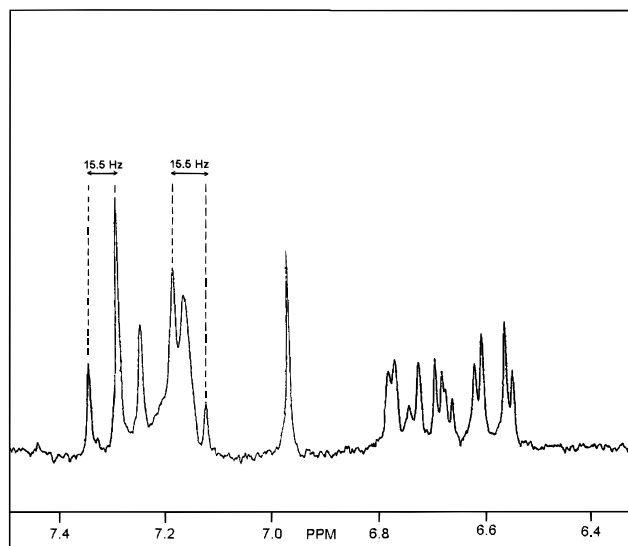
Figure 1. ^{1}H NMR spectrum of **6b** in C_6D_6 + $CDCl_3$ (2:1).

Table 1. Cyclic Voltammetric Data for nTVs, 10^{-4} M Substrate in 10^{-1} M TBAHP in CH_2Cl_2[a]

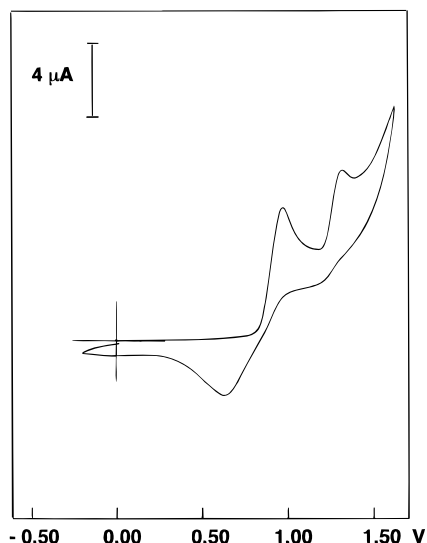| compd	$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pa}(2) - E_{pa}(1)$ (V)	$E_{pa}(3), E_{pa}(4)$ (V)
4h	0.68	0.92	0.24	
6h	0.66	0.84	0.18	
2a	1.06	1.39	0.33	
4a	0.70	0.88	0.18	
6a	0.60	0.70	0.10	
8a		0.56	0.00	
2b	0.97	1.32	0.35	
3b	0.84	1.20	0.36	
4b	0.60	0.78	0.18	
6b	0.57	0.69	0.12	
8b		0.45	0.00	0.78, 0.93
10b		0.43	0.00	0.63

[a] Pt electrodes, reference SCE, scan rate 100 mV s^{-1}.

Figure 2. Cyclic voltammogram of 10^{-4} M **2b** in 0.1 M Bu_4NPF_6/CH_2Cl_2: scan rate 100 mV s^{-1}, reference SCE.

converge to a limit of 0.18 V.[5e] In fact CV data for the longest known nTs (16-mer) seem to indicate the occurrence of two oxidation steps.[5f] As far as we know, the only evidence for formation of a dication by a single-step two-electron transfer in a conjugated heterocyclic oligomer has been reported by Parakka et al. for a heptamer containing four thiophene cycles and three pyrrole rings.[28] A second reversible one-electron wave
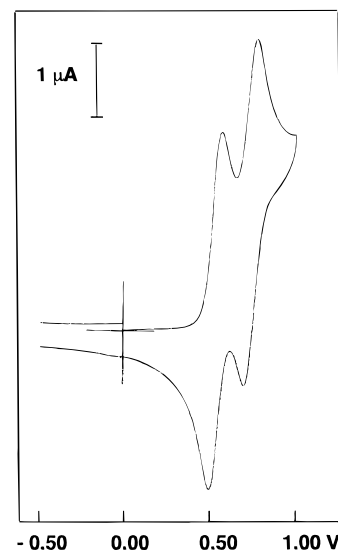

Figure 3. Cyclic voltammogram of 10^{-4} M **4b** in 0.1 M Bu_4NPF_6/CH_2Cl_2: scan rate 100 mV s^{-1}, reference SCE.

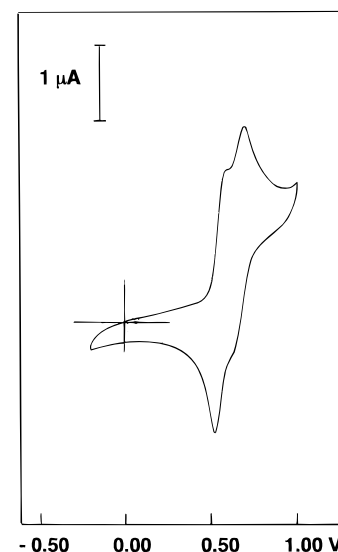**Figure 4.** Cyclic voltammogram of 10^{-4} M **6b** in 0.1 M Bu_4NPF_6/CH_2Cl_2: scan rate 100 mV s^{-1}, reference SCE.

corresponding to a third electron transfer was also observed, thus providing the first evidence for formation of a radical trication.

In this context, the above results appear particularly interesting as they provide the first unequivocal evidence for direct formation of a dication on a conjugated oligomer of homogeneous chemical structure. Furthermore the difference between $E_{pa}(1)$ and the peak corresponding to the formation of the radical trication ($E_{pa}(3)$) (0.35 V for **8b** and 0.20 V for **10b**) is much smaller than the 0.65 V observed for the pyrrole−thiophene heptamer.[28] This result indicates that the larger chain extension and the less overall aromatic character of nTVs leads to smaller Coulombic repulsion between positive charges, thus making multicationic higher oxidation states more easily accessible, as confirmed by the tetracationic state reached by **8b**.

In a number of recent papers Miller et al. have reported evidence for the formation of cation radical π-dimers for nTs and discussed their possible role as alternatives for bipolarons in particular in the process of interchain charge transport in PT.[29] Such cation radical π-dimers have also been observed for the

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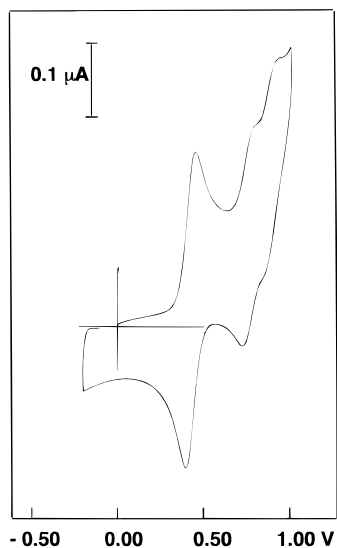
Figure 5. Cyclic voltammogram of 10^{-4} M **8b** in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$: scan rate 100 mV s^{-1}, reference SCE.

Table 2. UV−Visible Spectroscopic Data for nTVs in CH$_2$Cl$_2$

compd	$\lambda_{\max}$ (nm)	ΔE (eV)
4h	465	2.25
6h	511	2.06
2a	354	2.94
4a	473	2.09
6a	526	1.93
8a	552	1.84
8a[f]	556	1.70
2b	360	2.94
3b	423	2.52
4b	488	2.13
6b	522	1.99
8b	572	1.78
10b	580	1.72

longest nTs (16-mer).[5g] Although due to the direct access to the dication such a process seems less probable for long nTVs, the occurrence of additional one-electron oxidation waves (radical trication and tetracation) beyond the first two-electron wave seems difficult to reconcile with the bipolaron theory since, in this case, a (multi)dicationic state should represent the ultimate oxidation state. Although such a debate is clearly far beyond the scope of this paper, the above results pose intriguing questions regarding either the mechanisms of charge transport in conducting polymers or the limits of the use of oligomers as models for the corresponding conjugated polymers.

UV−Vis Spectroscopy. Table 2 lists the main electronic absorption data for the various nTVs. For each series, chain extension leads as expected to a bathochromic shift of the absorption maximum $\lambda_{\max}$ and to a narrowing of the HOMO−LUMO gap (ΔE) estimated from the low-energy absorption edge. Oligomers with *n*-hexyl chains at the α-position of the end thiophene rings absorb at shorter wavelengths and exhibit larger ΔE values than their β-substituted analogs. The $\lambda_{\max}$ values for **4h** and **6h** (465 and 511 nm) are very close to those reported for unsubstituted nTVs, namely, 460 and 510 nm.[17,18] This similarity suggests that introduction of alkyl chains at the α-position of the end thiophene rings has little influence on the electronic structure of the π-conjugated system. On the other hand, it is noteworthy that the additional weak shoulder in the
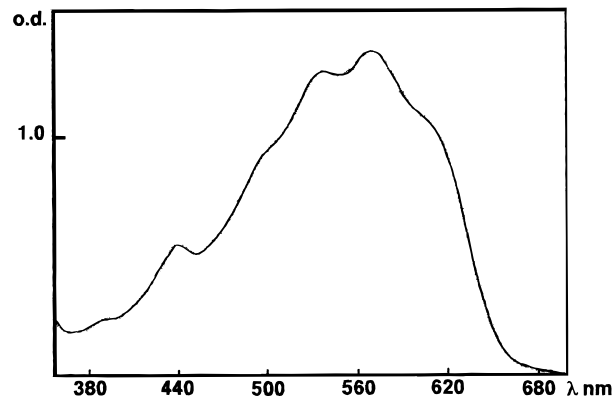

Figure 6. Electronic absorption spectrum of **8a** in CH$_2$Cl$_2$.

600−700 nm region in the spectra previously reported for unsubstituted hexamer and heptamer[18] was not observed here.

For a given chain length, nTVs of series **b** absorb at longer wavelengths and show smaller ΔE values than those of series **a**; these differences reflect the effect of the larger number of alkyl substituents on the electronic density of the π-conjugated system. Apart from these modest differences, the spectra of oligomers of the two series are very similar in shape and exhibit a well-resolved vibronic fine structure. This fine structure and the absence of a *cis* band in these spectra bring further support to a rigid and *all-trans* geometry.[30] The spectrum of **8a** (Figure 6) shows two maxima at 517 and 552 nm and several well-defined shoulders around 450, 480, and 595 nm. This spectrum is in agreement with a vibronic structure with a 0−0 transition at 595 nm and vibronic side bands at higher energy as already observed for other conjugated polymers and oligomers.[31] The energy difference between two consecutive maxima lies in the range 0.15−0.17 eV, which is consistent with a C=C stretching mode strongly coupled to the electronic structure.[32]

As shown in Table 2, the longest oligomers **8a**, **8b**, and **10b** show HOMO−LUMO gaps (ΔE) around 1.70−1.80 eV. These ΔE values are already smaller than the band gap of PT[12] and close to that of PTV.[11] In order to confirm this conclusion the preparation of thin films by solution casting has been attempted. Oligomers of series **b** were found less soluble than those of series **a**, and solubility decreased dramatically for **10b**. Furthermore, films cast from **8b** solutions were of limited optical quality due to their polycrystalline structure. In contrast, **8a** exhibits excellent film-forming properties. The optical spectrum of a solution-processed film is shown in Figure 7. The persistence of the vibronic fine structure is consistent with a well-ordered material while absorption onset indicates a band gap of ca. 1.70 eV. This value, similar to or even slightly smaller than that for PTV synthesized by the soluble precursor route (1.70−1.80 eV),[11] suggests that the mean effective conjugation length of PTV is limited to ca. eight TV units. Contrary to the spectrum of **8a**, that of PTV shows significant residual absorption in the 2.50−3.50 eV region, which corresponds to the absorption domain of the nonconjugated precursor. This difference suggests the presence of conjugation defects in PTV prepared by thermal elimination. In fact, several recent studies on the parent poly(*p*-phenylenevinylene) synthesized by

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π-Conjugated Soluble Oligomers

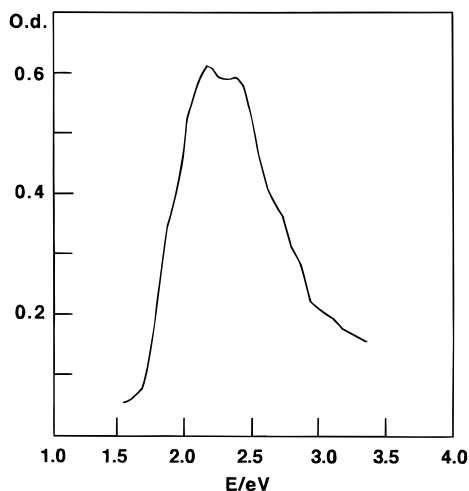*J. Am. Chem. Soc., Vol. 119, No. 44, 1997* 10781

Figure 7. Optical spectrum of a film of **8a** cast from a CH_2Cl_2 solution.
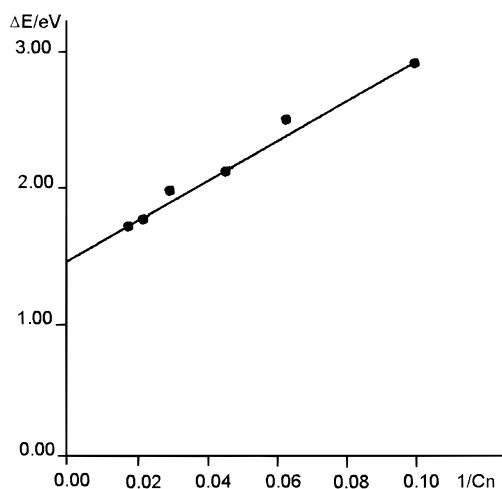

Figure 8. Variation of the HOMO–LUMO gap *vs* the reciprocal number of carbons in the conjugated chain for oligomers of series **b**.

the same route have clearly evidenced the strong effect of the conditions of thermal elimination (temperature and leaving group) on the effective conjugation as well as on the performances of LEDs based on these polymers.[33]

The data in Table 2 show that for both series chain extension produces a steady decrease of ΔE with no apparent saturation. The dependence of ΔE versus the reciprocal number of carbons in the conjugated chain (1/Cn) leads to a straight line with a slope of 15 (Figure 8). The location of the points corresponding to **3b** and **6b** above the line is due to the presence of unsubstituted thiophene rings. For nTs, a similar analysis done using literature data[5] gives a slope of 11.5 (not shown). The higher slope found for nTVs indicates that a similar increment in the number of carbons in the conjugated chain is more efficient in terms of increase of effective conjugation length and gap reduction for the nTVs than for the nTs series. Extrapolation to 1/Cn = 0 gives a ΔE of 1.45 eV for an infinite PTV chain. Comparison of this value with the band gap of PTV (1.70–1.80 eV)[11,14] and that of the **8a** film (1.70 eV) suggests that longer nTVs may exhibit even smaller band gaps.

As shown in Figure 9, $E_{pa}(1)$ scales linearly with 1/Cn except again for **3b** and **6b**. Intercept leads to an extrapolated $E_{pa}(1)$ value of 0.30 V for an infinite chain length. As for optical data, the slope of $E_{pa}(1)$ *vs* 1/Cn is higher for the nTV series
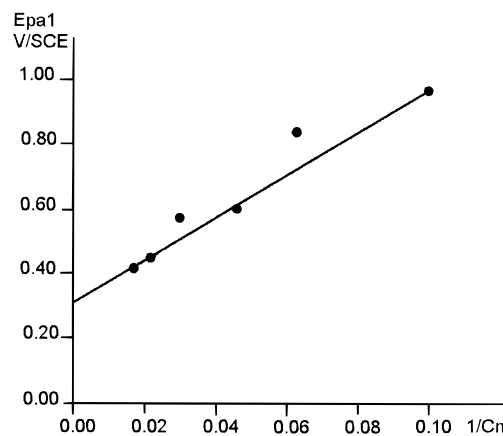

Figure 9. Variation of $E_{pa}(1)$ *vs* the reciprocal number of carbons in the conjugated chain for oligomers of series **b**.

(7.0) than for nTs (5.4, not shown). Interestingly, the slope in Figure 9 is about twice smaller than that of Figure 8. Since $E_{pa}(1)$ is related to the HOMO energy level,[34] this twice smaller slope indicates that the gap reduction resulting from chain extension involves symmetrical changes of the HOMO and LUMO energies with respect to mid-gap.

As already discussed, one of the most interesting opportunities offered by linear π-conjugated systems is their use as molecular wires or as conjugating spacers in NLO chromophores. In this context, it is interesting to compare the above results with the performances of other known systems. Thus for nTs saturation occurs for 8–12 thiophene rings (Cn = 32–48) with a λ_{max} around 460–465 nm.[5] For dialkoxy-substituted oligo(phenylene–ethylene)s the limit occurs around 9–10 phenyl rings (Cn = 52–58, λ_{max} = 475–480 nm).[35] For oligo(1,4-phenylene–ethynylene)s and -(2,5-thiophene–ethynylene)s saturation occurs around the tetramer (Cn = 22, λ_{max} = 370 nm) and octamer (Cn = 46, λ_{max} = 440 nm), respectively.[10]

The effective conjugation and hence HOMO–LUMO gap of linear π-conjugated systems are related to the average delocalization (or confinement) length of π-electrons.[36] Whereas, for polyenes, this parameter depends essentially on the degree of bond length alternation, in polyaromatic systems, other factors such as planarity and aromatic resonance energy plays also a determining role.[14] Thus, for nTs statistical rotational disorder is one of the main limiting factors.[13,14,37] The larger HOMO–LUMO gap of oligo(phenyleneethylene)s compared to nTVs reflects the higher resonance energy of benzene, while excessive π-electron confinement within aromatic rings and acetylenic linkages can account for the very limited effective conjugation of oligo(1,4-phenylene–ethynylene)s and -(2,5-thiophene–ethynylene)s.[10]

In this context the optical data of nTVs indicate that they are at present the heterocycle-based oligomeric system with the highest ratio of effective conjugation/topological conjugation and hence may be well-suited as molecular wires in nanoscopic systems.

Conclusion

Soluble thienylenevinylene oligomers have been synthesized. Whereas substitution at the α-positions of the end thiophene

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rings has little influence on the solubility and electronic properties, mono- or disubstitution at the β-positions of the thiophene ring leads to a strong enhancement of solubility, thus allowing the synthesis of the longest oligomers reported so far.

In addition to a steady decrease in oxidation potential, chain extension leads to an increase of the number of oxidation states and to a reduction of the difference between the potential of formation of the cation radical and dication. For the octamers, a first conclusive evidence for direct generation of the dication through a two-electron transfer has been obtained while the tetracationic state is reached below 1.0 V/SCE. Chain extension leads to a steady decrease of the HOMO−LUMO gap without apparent saturation. Consequently some solution-processed films exhibit a band gap similar to or even smaller than that of PTV. Extrapolation of the HOMO−LUMO gap *vs* chain length leads to a predicted gap value ca. 0.30 eV smaller than the present experimental value for PTV, suggesting that the synthesis of longer nTVs may allow further band-gap reduction. Comparison of these results with data for other conjugated oligomers indicates that nTVs represent the system with the highest ratio of effective conjugation *vs* number of carbons in the chain. These results, which can already have important implications for further analyses of the mechanisms of charge transport in π-conjugated polymers or for further design of molecular wires or NLO chromophores, provide a strong incitement to develop longer nTVs. Work in this direction is now in progress in our laboratory and will be reported in the near future.

Experimental Section

Electrochemical experiments were carried out with a PAR 273 potentiostat−galvanostat in a three-electrode single-compartment cell equipped with platinum microelectrodes of 7.85×10^{-3} cm^2 area, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Cyclic voltammetry was performed in methylene chloride solutions (HPLC grade) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAHP) (Fluka puriss). Solutions were deaerated by nitrogen bubbling prior to each experiment which was run under a nitrogen atmosphere. UV−visible absorption spectra were recorded on a Lambda 2 Perkin-Elmer spectrophotometer.

3-Octylthiophene (**15a**),[24] 3,4-dibutylthiophene (**15b**),[24] 2-bromo-3-octylthiophene (**15c**), and diethyl (2-thienylmethyl)phosphonate[22] (**1**) were prepared according to know procedures.

5-Hexyl-2-thiophenecarboxaldehyde (12). To a stirred THF solution (40 mL) containing 2-hexylthiophene (**11**) (Lancaster) (3.36 g, 20 mmol) was slowly added 15.6 mL of *n*-BuLi (1.6 M in hexanes, 25 mmol) at 0 °C under a N$_2$ atmosphere, and the solution was stirred for 15 min. DMF (2.3 mL, 30 mmol) was added, and the mixture was allowed to warm to room temperature. The mixture was poured into an aqueous solution of ammonium chloride (1 N) and extracted with CH$_2$Cl$_2$. The organic layer was washed with water, dried over MgSO$_4$, and evaporated. The residue was purified by column chromatography (silica gel, petroleum ether (PE)/CH$_2$Cl$_2$, 4:1) to give 3.71 g (94%) of a yellow oil. ^{1}H NMR (CDCl$_3$): δ 9.82 (s, 1H); 7.55 (d, 1H, $^3J = 4$ Hz); 6.83 (d, 1H, $^3J = 4$ Hz); 2.85 (t, 2H, $^3J = 7.5$ Hz); 1.40−1.28 (m, 8H); 0.87 (t, 3H, $^3J = 6.5$ Hz).

(E)-1-(5-Hexyl-2-thienyl)-2-(2′-thienyl)ethylene (13a). To a stirred solution of **12** (3.53 g, 18 mmol) and **1** (5.05 g, 21.6 mmol) in dry THF (80 mL) was added *t*-BuOK (3 g, 27 mmol) portionwise under N$_2$ at room temperature. After 30 min of stirring, the reaction mixture was poured into water and extracted with CH$_2$Cl$_2$. The organic phase was washed, dried over MgSO$_4$, and evaporated under reduced pressure to leave an oil, which after chromatography on silica gel with PE/CH$_2$-Cl$_2$ (2:1) gave 4.33 g (87%) of the title compound as an orange viscous oil which crystallizes at + 4 °C. ^{1}H NMR (DMSO-d_6): δ 7.40 (d, 1H, $^3J = 5.2$ Hz); 7.16 (d, 1H, $^3J = 3.3$ Hz); 7.05 (d, 1H, $^3J = 16$ Hz); 7.03 (d, 1H, $^3J = 3.5$ Hz); 6.97 (d, 1H, $^3J = 3.5$ Hz); 6.96 (d, 1H, $^3J = 16$ Hz); 6.72 (d, 1H, $^3J = 3.3$ Hz); 2.73 (t, 2H, $^3J = 7.5$ Hz); 1.58−1.54 (m, 2H); 1.30 (broad signal, 6H); 0.84 (t, 3H, $^3J = 6.5$ Hz). ^{13}C

NMR (DMSO-d_6) 144.7, 141.9, 139.4, 127.9, 126.8, 126.3, 125.2, 124.8, 121.5, 119.9; 30.95, 30.9, 29.6, 28.1, 22.1, 13.9 ppm.

(E)-1-(5-Formyl-2-thienyl)-2-(5′-hexyl-2′-thienyl)ethylene (13b). This compound was prepared using the procedure described for **12** from **13a** (2.76 g, 10 mmol), *n*-BuLi (7.5 mL, 12 mmol), and DMF (1.2 mL, 15.5 mmol) in 25 mL of dry THF. The crude product was purified by silica gel column chromatography (PE/CH$_2$Cl$_2$ (1:1) to leave a yellow solid, which after recrystallization from hexane gave 2.5 g (82%) of **13b**. Mp: 49.5−50 °C. MS (EI): M$^+$ 304 (100). ^{1}H NMR (DMSO-d_6): δ 9.84 (s, 1H); 7.91 (d, 1H, $^3J = 3.29$ Hz); 7.39 (d, 1H, $^3J = 16$ Hz); 7.35 (d, 1H, $^3J = 3.52$ Hz); 7.12 (d, 1H, $^3J = 3.52$ Hz); 7.04 (d, 1H, $^3J = 16$ Hz); 6.78 (d, 1H, $^3J = 3.29$ Hz); 2.75 (t, 2H, $^3J = 7.5$ Hz); 1.61−1.56 (m, 2H); 1.26 (broad signal, 6H); 0.84 (t, 3H, $^3J = 6.5$ Hz). ^{13}C NMR (DMSO-d_6): 183.5, 151.4, 147.0, 140.7, 139.0, 138.6, 129.0, 127.1, 126.1, 125.6, 118.9 , 30.95, 30.9, 29.6, 28.1, 22.0, 13.9 ppm.

(E,E)-2-(5′-Hexyl-2′-thienylvinyl)-5-(2″-thienylvinyl)thiophene (14a)-. This compound was obtained using the procedure described for **13a** from 1.52 g (5 mmol) of **13b**, 1.4 g (6 mmol) of **1**, and 0.78 g (7 mmol) of *t*-BuOK. The crude product was purified by column chromatography (silica gel PE/CH$_2$Cl$_2$, 4:1) and recrystallized from PE to yield 1.7 g (88%) of a yellow solid. Mp: 74 °C. MS (EI): M$^+$ 384 (100). ^{1}H NMR (DMSO-d_6): δ 7.46 (d, 1H, $^3J = 5.17$ Hz); 7.21 (d, 1H, $^3J = 3.52$ Hz); 7.11 (d, 1H, $^3J = 3.76$ Hz); 7.09 (s, 2H); 7.06 (d, 1H, $^3J = 3.76$ Hz); 7.04 (d, 1H, $^3J = 16$ Hz); 7.02 (d, 1H, $^3J = 3.76$ Hz); 7.01 (d, 1H, $^3J = 3.76$ Hz); 6.94 (d, 1H, $^3J = 16$ Hz); 6.75 (d, 1H, $^3J = 3.52$ Hz); 2.76 (t, 2H, $^3J = 7.5$ Hz); 1.63−1.55 (m, 2H); 1.28 (broad signal, 6H); 0.85 (t, 3H, $^3J = 6.5$ Hz, CH$_3$). ^{13}C NMR (DMSO-d_6): 145.2, 141.7, 141.0, 140.5, 139.4, 128.1, 128.0, 127.6, 127.1, 126.9, 125.4, 125.0, 121.9, 121.1, 120.0, 119.9, 30.9, 29.6, 28.1, 22.0, 13.9 ppm. Anal. (calcd): C, 68.26 (68.70); H, 6.26 (6.29).

(E,E)-2-(5′-Formyl-2′-thienylvinyl)-5-(5″-hexyl-2″-thienylvinyl)-thiophene (14b). This compound was prepared similarly to **13b** from **14a** (1.3 g, 3.4 mmol), *n*-BuLi (2.65 mL, 4.24 mmol), and DMF (0.5 mL). The crude product was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$, 2:1) and recrystallized from PE/CH$_2$Cl$_2$ (4:1) to give 1.03 g (73%) of red-orange crystals. Mp: 116−117 °C. MS (EI): M$^+$ 412 (100). ^{1}H NMR (DMSO-d_6): δ 9.85 (s, 1H), 7.94 (d, 1H, $^3J = 3.76$ Hz); 7.45 (d, 1H, $^3J = 16$ Hz); 7.40 (d, 1H, $^3J = 3.76$ Hz); 7.25 (d, 1H, $^3J = 3.76$ Hz); 7.15 (d, 1H, $^3J = 3.76$ Hz); 7.14 (d, 1H, $^3J = 16$ Hz); 7.05 (d, 1H, $^3J = 3.76$ Hz); 7.02 (d, 1H, $^3J = 16$ Hz); 7.00 (d, 1H, $^3J = 16$ Hz); 7.08 (d, 1H, $^3J = 3.76$ Hz); 2.76 (t, 2H, $^3J = 7.5$ Hz); 1.64−1.56 (m, 2H); 1.28 (broad signal, 6H); 0.85 (t, 3H, $^3J = 6.5$ Hz). Anal. (calcd): C, 66.92 (66.95); H, 5.99 (5.86).

(E,E,E)-1,2-Bis[5-(5′-hexyl-2′-thienylvinyl)-2-thienyl]ethylene (4h). To a suspension of low-valent Ti prepared from TiCl$_4$ (0.66 mL, 6 mmol)) and Zn (0.78 g, 12 mmol) in 30 mL of dry THF under N$_2$ at 0 °C was added a dry solution of **13b** (1.52 g, 5 mmol) in 10 mL of THF. After 2 h of refluxing, the mixture was cooled to room temperature, poured into water, and then extracted with CH$_2$Cl$_2$. The organic phase was washed with water and dried over MgSO$_4$. After solvent removal, the crude solid was recrystallized from CHCl$_3$/hexane to give 0.6 g (41%) of a red solid. Mp: 146 °C. MS (EI): 576 (100). ^{1}H NMR (CDCl$_3$): δ 6.95 (d, 2H, $^3J = 15.7$ Hz); 6.92 (s, 2H); 6.89 (d, 2H, $^3J = 4$ Hz); 6.87 (d, 2H); 6.86 (d, 2H, $^3J = 15.7$ Hz); 6.84 (d, 2H, $^3J = 3.76$ Hz); 6.65 (d, 2H, $^3J = 3.76$ Hz); 2.78 (t, 4H, $^3J = 7.3$ Hz); 1.70−1.65 (m, 4H); 1.33 (br, 12H); 0.90 (t, 6H, $^3J = 6.4$ Hz). ^{13}C NMR (DMSO-d_6): 145.8, 141.8, 141.0, 140.0, 127.2, 126.7, 126.4, 127.7, 122.2, 121.4, 120.2, 31.5, 31.4, 30.4, 28.7, 22.5, 14.0 ppm. Anal. (calcd): C, 69.95 (70.81); H, 6.94 (7.00); S, 21.81 (22.20).

(E,E,E,E)-1,2-Bis{5-[5′-(5″-hexyl-2″-thienylvinyl)-2′-thienylvinyl]-2-thienyl}ethylene (6h). This compound was prepared using the procedure described for **4h** from **14b** (0.74 g, 1.8 mmol), TiCl$_4$ (0.24 mL, 2.19 mmol), and Zn (0.29 g, 4.40 mmol) in THF. The usual workup and recrystallization from CH$_2$Cl$_2$ gave 0.15 g (21%) of a dark red solid. Mp: 248 °C dec. MS (EI): M$^+$ 792 (100). Solubility was too low to perform spectroscopic analyses.

3-Octyl-2-thiophenecarboxaldehyde (16a). A solution of *n*-BuLi (2.5 M in hexanes, 16.8 mL, 42 mmol) was added dropwise at −100 °C under N$_2$ to a stirred solution of **15c** (11g, 40 mmol in 60 mL of ether). During the whole addition, the reaction temperature was kept at −100 °C and then was allowed to gradually rise to −60 °C. At this

π-Conjugated Soluble Oligomers

J. Am. Chem. Soc., Vol. 119, No. 44, 1997 10783

temperature, DMF (4.65 mL, 60 mmol) was slowly added and the mixture allowed to warm to room temperature. The mixture was poured into a 1 M aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was passed through a short column (silica gel, CH_2Cl_2) to give 8.6 g (96%) of yellow oil. ^1H NMR (CDCl₃): δ 9.99 (s, 1H); 7.59 (d, 1H, ^3J = 5 Hz); 6.97 (d, 1H, ^3J = 5 Hz); 2.91 (t, 2H, $3J$ = 7.5 Hz); 1.62−1.59 (m, 2H); 1.27−1.23 (br, 10H); 0.83 (t, 3H, ^3J = 6.5 Hz). ^{13}C NMR (CDCl₃): 182.0, 152.7, 137.4, 134.2, 130.5, 31.6, 31.2, 29.1, 29.0, 28.9, 28.2, 22.4, 13.9 ppm.

3,4-Dibutyl-2-thiophenecarboxaldehyde (16b). POCl₃ (6.1 mL, 65.3 mmol) was added at 0 °C to a stirred solution of **15b** (8 g, 40.8 mmol) and dry DMF (5.7 mL, 73.7 mmol) in 40 mL of 1,2-dichloroethane under N₂. After 2 h of refluxing, the mixture was cooled to room temperature and neutralized with a sodium acetate solution (1 M). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined extracts were washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The oily residue was purified by column chromatography (silica gel, PE/CH₂Cl₂, 3:2) to give 8.48 g (92%) of a yellow oil. ^1H NMR (CDCl₃): δ 9.93 (s, 1H); 7.26 (s, 1H); 2.88 (t, 2H, ^3J = 8 Hz); 2.53 (t, 2H, ^3J = 8 Hz); 1.60−1.45 (m, 8H); 0.87 (t, 6H, ^3J = 7 Hz).

3,4-Dibutyl-2,5-thiophenedicarbaldehyde (16c). *n*-BuLi (20.6 mL, 32.9 mmol) was added dropwise to a solution of **15b** (2.69 g, 13.7 mmol) and TMEDA (5 mL, 32.9 mmol) in 10 of mL hexane. The resulting mixture was refluxed for 30 min, then THF (50 mL) was added, and the mixture was cooled to −40 °C and treated with an excess of DMF (3.2 mL, 41.1 mmol). The reaction mixture was allowed to warm to room temperature and then poured into 300 mL of HCl solution (0.5 M). Saturated NaHCO₃ solution was added until neutrality of the aqueous layer. The organic phase was separated and the aqueous layer extracted with 2 × 60 mL of CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to leave a dark orange oil. Chromatography (silica gel, CH₂Cl₂/PE, 1:1) afforded a yellow solid, which after recrystallization from PE gave 2.03 g (58%) of white crystals. Mp: 65 °C. MS (EI): M⁺ 252 (96); 223 (100, −CHO). ^1H NMR (CDCl₃): δ 10.12 (s, 2H); 2.92 (t, 4H, ^3J = 8 Hz); 1.61−1.43 (m, 8H); 0.97 (t, 6H, ^3J = 7.3 Hz). ^{13}C NMR (CDCl₃): 183.2, 151.6, 143.2 , 34.2, 26.3, 22.7, 13.7 ppm.

(E)-1,2-Bis(3-octylthienyl)ethylene (2a). This compound was prepared from **16a** (8.52 g, 38 mmol), TiCl₄ (5 mL, 45.6 mmol), and Zn (6 g, 91.2 mmol) using the procedure described for **4h** and purified by column chromatography (silica gel, PE/CHCl₃, 6:1) to give 7.05 g (89%) of an orange solid. Mp: 35 °C. MS (EI): M⁺ 416 (100). ^1H NMR (CDCl₃): δ 7.08 (d, 2H, ^3J = 5.17 Hz); 7.01 (s, 2H); 6.86 (d, 2H, ^3J = 5.17 Hz); 2.67 (t, 4H, ^3J = 7.5 Hz); 1.63−1.57 (m, 4H); 1.35−1.25 (m, 20H); 0.88 (t, 6H, ^3J = 6.5 Hz). ^{13}C NMR (CDCl₃): 140.7, 136.3, 129.7, 122.5, 119.5, 31.9, 30.6, 31.0, 29.5, 29.2, 28.4, 22.7, 14.1 ppm.

(E)-1,2-Bis[2-(3,4-dibutylthienyl)]ethylene (2b). This compound was prepared using the procedure described for **4h** from TiCl₄ (4.7 mL, 42.85 mmol) and Zn (5.6 g, 85.7 mmol). After the usual workup, the residue was purified by column chromatography (silica gel, PE) and recrystallized from pentane to yield 5 g (67%) of the title product as light yellow crystals. Mp: 88 °C. MS (EI): M⁺ 416 (100). ^1H NMR (CDCl₃): δ 7.01 (s, 2H); 6.76 (s, 2H); 2.62 (t, 4H, ^3J = 8 Hz); 2.51 (t, 4H, ^3J = 8 Hz); 1.66−1.40 (m, 16H); 0.97 (t, 12H, ^3J = 7.3 Hz). ^{13}C NMR (CDCl₃): 143.3, 139.7, 136.9, 119.6, 117.6, 33.2, 31.8, 28.7, 26.6, 22.7, 22.6, 14.0, 13.9 ppm.

(E)-1-(5-Formyl-3-octyl-2-thienyl)-2-(3′-octyl-2′-thienyl)ethylene (17a). This compound was prepared from **2a** (20 g, 48 mmol), DMF (5.6 mL, 72 mmol), and POCl₃ (5.65 mL, 60.5 mmol) in 1,2-dichloroethane (200 mL) using the procedure described for **16b**. The crude product was purified by column chromatography (silica gel, PE/CH₂Cl₂, 3:2) to give 15 g (70%) of the title compound as a dark orange viscous oil. $C_{27}H_{40}OS_2$ MS (EI): M⁺ 444 (100). ^1H NMR (CDCl₃): δ 9.80 (s, 1H); 7.51 (s, 1H); 7.26 (d, 1H, ^3J = 15.5 Hz); 7.17 (d, 1H, ^3J = 5.17 Hz); 6.96 (d, 1H, ^3J = 15.5 Hz); 6.88 (d, 1H, ^3J = 5.17 Hz); 2.67 (t, 4H, ^3J = 7.5 Hz); 1.65−1.57 (m, 4H); 1.32−1.22 (m, 20H); 0.87 (m, 6H). ^{13}C NMR (CDCl₃): 182.4, 146.9, 143.2, 141.5, 139.1, 138.9, 135.3, 130.1, 124.4, 123.7, 117.8, 31.8, 31.0, 30.5, 29.3, 29.2, 28.4, 22.6, 14.0 ppm.

(E)-1-(5-Formyl-3,4-dibutyl-2-thienyl)-2-(3′,4′-dibutyl-2′-thienyl)-ethylene (17b). Compound **17b** was prepared similarly to **17a** from **2b** (3.85 g, 9.25 mmol), DMF (0.93 mL, 12.03 mmol), and POCl₃ (1.03 mL, 11.1 mmol) in 1,2-dichloroethane (30 mL). The crude product was purified by column chromatography (silica gel, PE/CH₂Cl₂, 1:1) to give 3.78 g (92%) of the title compound as an orange viscous oil which crystallized at +4 °C. $C_{27}H_{40}OS_2$ MS (EI): M•⁺ 444 (100). ^1H NMR (CDCl₃): δ 9.97 (s, 1H); 7.27 (d, 1H, ^3J = 15.5 Hz); 6.96 (d, 1H, ^3J = 15.5 Hz); 6.84 (s, 1H); 2.85 (t, 2H, ^3J = 7.5 Hz); 2.63−2.47 (m, 6H); 1.63−1.36 (m, 16H); 1.00−0.90 (m, 12H). ^{13}C NMR (CDCl₃): 181.82, 152.9, 147.1, 143.6, 142.2, 140.2, 135.9, 134.5, 124.2, 119.7, 117.8, 34.3, 33.3, 31.8, 31.7, 28.5, 26.8, 26.7, 26.0, 22.8, 22.7, 22.6, 22.5, 14.0, 13.9, 13.8, 13.7 ppm.

(E,E)-2,5-Bis(2′-thienylvinyl)-3,4-dibutylthiophene (3b). This compound was prepared by Wittig−Horner bis-olefination using the procedure described for **13a** from **16c** (1 g, 4 mmol), **1** (2.8 g, 12 mmol), and *t*-BuOK (1.57 g, 14 mmol). The crude product was purified by column chromatography (silica gel, PE/CH₂Cl₂, 4:1) and recrystallized from PE to give 1.3 g (79%) of orange crystals. Mp: 68 °C. MS (EI): M⁺ 412 (100). ^1H NMR (CDCl₃): δ 7.17 (d, 2H, ^3J = 5 Hz); 7.06 (d, 2H, ^3J = 15.5 Hz); 7.02 (br 2H); 6.99 (dd, 2H, ^3J = 4 Hz); 6.98 (d, 2H, ^3J = 15.5 Hz); 2.59 (t, 4H, ^3J = 7.6 Hz); 1.46−1.24 (m, 8H); 0.98 (t, 6H, ^3J = 7 Hz). ^{13}C NMR (CDCl₃): 142.4, 141.1, 134.0, 127.2, 125.2, 123.5, 120.2, 119.5, 32.9, 28.7, 22.1, 13.4 ppm. Anal. (calcd): C, 70.37 (69.88); H, 6.79 (6.85); S, 23.35 (23.27).

(E,E)-2-(5′-Formyl-2′-thienylvinyl)-5-(2″-thienylvinyl)-3,4-dibutylthiophene (18b). This compound was prepared by Vilsmeier formylation of **3b** (1 g, 2.42 mmol), using POCl₃ (0.36 mL, 3.88 mmol) and DMF (0.34 mL, 4.36 mmol) as already described for **16b**. After the usual workup, the crude product was purified by column chromatography (silica gel, eluting first with PE/CH₂Cl₂ (4:1) to separate the unreacted starting material (0.22 g), then with PE/CH₂Cl₂ (1:1) to afford 0.74 g (69%) of the title compound as a red solid). Recrystallized from ethanol: mp 72−73 °C. MS (EI): M⁺ 440 (100). ^1H NMR (DMSO-d_6): δ 9.85 (s, 1H); 7.95 (d, 1H, ^3J = 3.78 Hz); 7.47 (d, 1H, ^3J = 14.8 Hz); 7.46 (d, 1H, ^3J = 3.78 Hz); 7.45 (d, 1H, ^3J = 14.8 Hz); 7.37 (d, 1H, ^3J = 3.5 Hz); 7.28 (d, 1H, ^3J = 3.5 Hz); 7.10−6.98 (m, 3H); 2.63 (t, 4H, ^3J = 7.6 Hz); 1.47−1.38 (m, 8H); 0.93 (t, 6H, ^3J = 7 Hz). Anal. (calcd): C, 68.12 (68.16); H, 6.39 (6.41); S, 21.59 (21.79).

(E,E,E)-1,2-Bis[5-(3′-octyl-2′-thienylvinyl)-4-octyl-2-thienyl]ethylene (4a). This compound was prepared from **17a** (14 g, 31.5 mmol), TiCl₄ (4.15 mL, 37.8 mmol), and Zn (5 g, 75.6 mmol) as already described for **4h**. The crude product was purified by column chromatography (silica gel, PE/CH₂Cl₂, 1:1) and recrystallized from hexane to yield 9.56 g (71%) of a red solid. Mp: 120 °C. MS (FAB): M⁺ 856. ^1H NMR (CDCl₃): 7.09 (d, 2H, ^3J = 5.17 Hz); 6.97 (s, 4H); 6.91 (s, 2H); 6.86 (d, 2H, ^3J = 5.17 Hz); 6.77 (s, 2H); 2.67 (t, 4H, ^3J = 7.5 Hz); 2.61 (t, 4H, ^3J = 7.5 Hz); 1.65−1.56 (m, 8H); 1.35−1.25 (m, 40H); 0.89 (m, 12H). ^{13}C NMR (CDCl₃): 142.2, 141.4, 139.9, 136.8, 136.2, 130.4, 129.9, 123.2, 121.8, 119.9, 119.5, 32.4, 32.3, 31.4, 31.2, 30.0, 29.9, 29.8, 29.7, 28.9, 28.8, 23.1, 14.6 ppm. Anal. (calcd): C, 75.85 (75.66); H, 9.91 (9.41); S, 14.95 (14.93).

(E,E,E)-1,2-Bis[5-(3′,4′-dibutyl-2′-thienylvinyl)-3,4-dibutyl-2-thienyl]ethylene (4b). This compound was obtained using the same procedure from **17b** (3.6 g, 8.1 mmol), TiCl₄ (1.07 mL, 9.72 mmol), and Zn (1.27 g, 19.45 mmol). The crude product was chomatographed (silica gel, CH₂Cl₂) and recrystallized from hexane to yield 2.7 g (78%) of red crystals. Mp: 162 °C. MS (EI): M⁺ 856 (100). ^1H NMR (CDCl₃): δ 6.99 (s, 4H); 6.97 (s, 2H); 6.76 (s,2H); 2.7−2.56 (m, 16H); 1.65−1.40 (m, 32H); 0.98−0.93 (m, 24H). ^{13}C NMR (CDCl₃): 143.8, 141.9, 141.8, 140.5, 137.5, 135.5, 135.4, 120.4, 119.8, 119.6, 118.4, 33.9, 33.7, 32.3, 31.4, 29.1, 27.2, 27.1, 23.2, 23.1, 14.5, 14.4 ppm. Anal. (calcd): C, 75.27 (75.66); H, 9.50 (9.41); S, 15.07 (14.93).

(E,E,E)-1-[5-(5′-Formyl-3′-octyl-2′-thienylvinyl)-4-octyl-2-thienyl]-2-[5″-(3‴-octyl-2‴-thienylvinyl)-4″-octyl-2″-thienyl]ethylene (19a). This compound was prepared similarly to **16b** from **4a** (1.46 g, 1.7 mmol), DMF (0.16 mL, 2.07 mmol), and POCl₃ (0.16 mL, 1.7 mmol). After the usual workup, the crude product was purified by column chromatography (silica gel, eluting first with PE/CH₂Cl₂, 7:3, to recover the unreacted starting material (0.72 g), then with PE/CH₂Cl₂, 1:1) to afford 0.57 g (38%) of a dark red solid Recrystallized from hexane:

mp 114 °C. MS (FAB): M$^+$ 884. ^{1}H NMR (CDCl$_3$): δ 9.80 (s, 1H); 7.51 (s, 1H); 7.22 (d, 1H, ^3J = 15.5 Hz); 7.09 (d, 1H, ^3J = 5.17 Hz); 7.00 (d, 1H, ^3J = 15.5 Hz); 6.96 (d, 1H, ^3J = 15.5 Hz); 6.95 (d, 1H, ^3J = 15.5 Hz); 6.93 (d, 1H, ^3J = 15.5 Hz); 6.92 (d, 1H, ^3J = 15.5 Hz); 6.86 (d, 1H, ^3J = 5.17 Hz); 6.79 (s, 2H); 2.67−2.59 (m, 8H); 1.60 (br, 8H); 1.29 (br, 40H); 0.86 (m, 12H). ^{13}C NMR (CDCl$_3$): 182.4, 147.0, 144.4, 141.7, 141.6, 141.5, 141.2, 141.0, 139.2 (C-3′), 139.1 138.9, 136.3, 134.6, 129.9 129.4, 129.3, 123.4, 122.9, 122.4, 120.9, 119.7, 118.9, 117.7, 31.9, 31.8, 30.9, 30.8, 30.7, 30.6, 29.5, 29.4, 29.3, 29.2, 28.4, 28.2, 22.6, 14.1, 14.0 ppm. Anal. (calcd): C, 74.40 (74.62); H, 9.25 (9.12); S, 14.32 (14.46); O, 1.83 (1.81).

(E,E,E)-1-[5-(5′-Formyl-3′,4′-dibutyl-2′-thienylvinyl)-3,4-dibutyl-2-thienyl]-2-[5″-(3‴,4‴-dibutyl-2‴-thienylvinyl)-3″,4″-dibutyl-2″-thienyl]ethylene (19b). This compound was prepared from **4b** (1.53g, 1.78 mmol), DMF (0.16 mL, 2.07 mmol), and POCl$_3$ (0.17 mL, 1.78 mmol) using the procedure described for **16b**. After the usual workup, the crude product was purified by chromatography (silica gel), eluting first with PE/CH$_2$Cl$_2$, 7:3, to recover the unreacted starting material (0.5 g) and then with PE/CH$_2$Cl$_2$, 1:1, to afford 0.74 g (46%) of the title product as a dark solid (purple in solution). Recrystallized from hexane: mp 153 °C. MS (EI): M$^+$ 884 (100). ^{1}H NMR (CDCl$_3$): δ 9.98 (s, 1H), 7.27 (d, 1H, ^3J = 15.5 Hz); 7.04 (d, 1H, ^3J = 15.5 Hz); 7.03 (d, 1H, ^3J = 15.5 Hz); 6.97 (d, 2H, ^3J = 15.5 Hz); 6.95 (d, 1H, ^3J = 15.5 Hz); 6.77 (s, 1H); 2.85 (t, 2H, ^3J = 7.5 Hz); 2.62−2.50 (m, 14H); 1.62−1.38 (m, 32H); 1.02−0.94 (m, 24H). ^{13}C NMR (CDCl$_3$): 182.3, 153.5, 147.8, 144.5, 143.5, 142.5, 142.1, 141.8, 140.6, 137.6, 137.4, 136.0, 135.1, 135.0, 134.4, 124.2, 120.9, 120.7, 119.5, 118.5, 118.4, 34.86, 34.08, 33.94, 33.888, 33.85, 33.76, 33.67, 33.62, 32.26, 29.14, 27.33, 27.28, 27.20, 27.16, 27.11, 26.55, 23.25, 23.20, 23.08, 23.02, 22.91, 14.43, 14.40, 14.32 ppm.

(E,E,E)-1,2-Bis-[5-(5′-formyl-3′-octyl-2′-thienylvinyl)-4-octyl-2-thienyl]ethylene (19c). This compound was prepared from **4a** (0.428 g, 0.5 mmol), POCl$_3$ (0.2 mL, 2 mmol), and DMF (0.25 mL, 3 mmol) in 1,2-dichloroethane (15 mL) using the procedure already described for **16b**. The crude product was purified by column chromatography (silica gel, CH$_2$Cl$_2$) and then recrystallized from CHCl$_3$/hexane to give 0.38 g (83%) of mauve crystals. Mp: 98 °C dec. MS (FAB): M$^+$ 912 (100). ^{1}H NMR (CDCl$_3$): δ 9.79 (s, 2H); 7.50 (s, 2H); 7.21 (d, 2H, ^3J = 15.5 Hz); 6.93 (s, 2H); 6.91 (d, 2H, ^3J = 15.5 Hz); 6.81 (s, 2H); 2.67 (t, 4H, ^3J = 7.5 Hz); 2.59 (t, 4H, ^3J = 7.5 Hz); 1.63−1.57 (m, 8H); 1.29 (br, 40H); 0.90−0.86 (m, 12H). ^{13}C NMR (CDCl$_3$): 182.8, 147.3, 144.8, 142.2, 141.5, 139.7, 139.3, 135.5, 130.3, 123.6, 122.4, 118.5, 32.3, 31.2, 31.0, 29.9, 29.8, 29.7, 29.6, 28.8, 28.7, 23.1, 14.5 ppm. Anal. (calcd): C, 73.66 (73.64); H, 8.93 (8.84); S, 13.87 (14.02); O, 3.36 (3.51).

(E,E,E,E,E)-1,2-Bis{5-[5′-(2″-thienylvinyl)-(3′-octyl-2′-thienylvinyl]-4-octyl-2-thienyl}ethylene (6a). This compound was prepared by using the procedure described for **3b** from **19c** (91.2 mg, 0.1 mmol), **1** (120 mg, 0.5 mmol), and t-BuOK (80 mg, 0.7 mmol) in 20 mL of dry THF. After 2 h of stirring at room temperature, the solvent was evaporated under reduced pressure and the solid residue was purified by column chromatography (silica gel, CH$_2$Cl$_2$) to yield 88 mg (82%) of a dark mauve solid. Mp: 123 °C. MS (FAB): M$^+$ 1072 (69). ^{1}H NMR (CDCl$_3$): δ 7.19 (d, 2H, ^3J = 5 Hz); 7.10−6.90 (m, 14 H); 6.81−6.79 (2s, 2H); 2.67 (t, 4H, ^3J = 7.5 Hz); 2.61 (t, 4H, ^3J = 7.5 Hz); 1.65−1.56 (m, 8H); 1.35−1.25 (m, 40H); 0.89, (m 12H). Anal. (calcd): C, 74.28 (73.84); H, 8.45 (8.27).

(E,E,E,E)-1,2-Bis{5-[5′-(2″-thienylvinyl)-3′,4′-dibutyl-2′-thienylvinyl]-2-thienyl}ethylene (6b). This compound was obtained as described for **4h** from **18b** (0.52 g, 1.18 mmol), TiCl$_4$ (0.26 mL, 2.36 mmol), and Zn (0.31 g, 4.72 mmol). After the usual workup, the crude product was recrystallized from CHCl$_3$ to yield 125 mg (25%) of a dark mauve solid. Mp: 235 °C dec. MS (FAB): M$^+$ 848 (100). ^{1}H NMR (CDCl$_3$): δ 7.18 (d, 2H, ^3J = 5 Hz) 7.09−6.89 (m, 18H); 2.60 (t, 8H, ^3J = 7.5 Hz); 1.56−1.42 (m, 16H); 1.02−0.96 (m, 12H). ^{1}H

NMR (C$_6$D$_6$ + CDCl$_3$ (2:1)): δ 7.30 (d, 4H, ^3J = 16 Hz, 4H ethyl); 7.15 (d, 4H, ^3J = 16 Hz, 4H ethyl); 6.95 (s, 2H, 2H ethyl, centr); 6.77 (d, 2H, ^3J = 3.4 Hz, 2H′ thioph); 6.73 (d, 2H, ^3J = 4.5 Hz, 2H‴ thioph); 6.66 (dd, 2H, ^3J = 4.5 Hz and ^3J = 3.4 Hz, 2H‴ thioph); 6.62 (d 2H, ^3J = 4.3 Hz, 2H thioph, centr); 6.55 (d, 2H ^3J = 4.3 Hz, 2H thioph).

(E,E,E,E,E,E,E)-1,2-Bis{5-[5′-[5″-(3‴-octyl-2‴-thienylvinyl)-4″-octyl-2″-thienylvinyl]-(3′-octyl-2′-thienylvinyl)-4-octyl-2-thienyl}ethylene (8a). This compound was prepared using the procedure described for **4h** from **19a** (1.6 g, 1.8 mmol), TiCl$_4$ (0.4 mL, 3.6 mmol), and Zn (0.47 g, 7.2 mmol). After the usual workup, the crude product was recrystallized from CHCl$_3$ to give 0.4 g (25%) of a dark blue solid. Mp: 180 °C dec. MS (FAB): M + 1 1737. ^{1}H NMR (CDCl$_3$): δ 7.08 (d, 2H, ^3J = 5.17 Hz); 6.97 (s, 4H); 6.93 (s, 4H); 6.91 (s, 6H); 6.85 (d, 2H, ^3J = 5.17 Hz); 6.78 (s, 6H); 2.62−2.57 (m, 16H); 1.61 (br 16H); 1.30−1.26 (br 80H); 0.95−0.88 (m, 24H). ^{1}H NMR (C$_6$D$_6$ + CDCl$_3$ (2:1)): δ 7.30 (d, 4H, ^3J = 15.5 Hz); 7.15 (d, 4H, ^3J = 15.5 Hz); 6.95 (s, 2H); 6.78 (d, 2H, ^3J = 3.1 Hz); 6.73 (d, 2H, ^3J = 4.5 Hz); 6.67 (dd, 2H, ^3J = 4.5 Hz, ^3J = 3.1 Hz); 6.61 (d, 2H, ^3J = 3.7 Hz); 6.55 (d, 2H, ^3J = 3.7 Hz); 2.60 (t, 8H, ^3J = 7.5 Hz); 1.56−1.47 (m, 16H), 1.07−0.96 (m, 12 H).

(E,E,E,E,E,E,E)-1,2-Bis{5-[5′-[5″-(3‴,4‴-dibutyl-2‴-thienylvinyl)-3″,4″-dibutyl-2″-thienylvinyl]-3′,4′-dibutyl-2′-thienylvinyl]-3,4-dibutyl-2-thienyl}ethylene (8b). This compound was prepared similarly to **4h** from **19b** (0.884 g, 1 mmol), TiCl$_4$ (0.22 mL, 2 mmol), and Zn (0.26 g, 4 mmol). After 12 h of refluxing, the mixture was cooled to room temperature and poured into a 10% K$_2$CO$_3$ solution. The resulting mixture was vigorously stirred for 30 min to deposit a solid material, which was filtered, washed with acetone in a Soxhlet extractor for 6 h, and then extracted with CH$_2$Cl$_2$ for 20 h. The extract was evaporated under reduced pressure to leave a dark blue solid material, which was washed again with hot acetone, filtered, and recrystallized from CHCl$_3$/hexane to afford 0.45 g (52%) of the pure title compound as a dark blue solid. Mp: 180 °C dec. MS (FAB): (M + 1)$^+$ 1737. ^{1}H NMR (CDCl$_3$): δ 6.99 (s, 14H); 6.76 (s, 2H); 2.62−2.50 (m, 32H); 1.62−1.43 (m, 64H); 1.03−0.94 (m, 48H). Anal. (calcd): C, 75.59 (75.99); H, 9.24 (9.28); S, 14.64 (14.72).

(E,E,E,E,E,E,E)-1,2-Bis{5-[5′-[5″-(5‴-formyl-3‴,4‴-dibutyl-2‴-thienylvinyl)-3″,4″-dibutyl-2″-thienylvinyl]-3′,4′-dibutyl-2′-thienylvinyl]-3,4-dibutyl-2-thienyl}ethylene (20b). This compound was prepared as described for **16b** by Vilsmeier formylation of **8b** (0.15 g, 8.6×10^{-2} mmol), DMF (excess, 1 mL), and POCl$_3$ (60 mL, 8 equiv) in 1,2-dichloroethane (30 mL). After the usual workup, the crude product was recrystallized from CHCl$_3$ to afford 0.125 g (81%) of the title compound as a dark blue solid, which was directly used for the next step.

(E,E,E,E,E,E,E,E)-1,2-Bis{5-[5′-[5″-[5‴-(2‴′-thienylvinyl)-3‴,4‴-dibutyl-2‴-thienylvinyl]-3″,4″-dibutyl-2″-thienylvinyl]-3′,4′-dibutyl-2′-thienylvinyl]-3,4-dibutyl-2-thienyl}ethylene (10b). This compound was prepared using the procedure described for **3b**, from **20b** (0.1 g, 5.6×10^{-2} mmol), **1** (70 mg, 0.56 mmol), and t-BuOK (94 mg, 0.84 mmol) in 15 mL of dry THF. After 2 h of stirring at room temperature, the solvent was evaporated under reduced pressure and the solid residue was taken up with methanol, filtered, and washed several times with methanol and then with ether. Recrystallization from CH$_2$Cl$_2$ afforded 95 mg (87%) of **10b** as a dark blue solid. Mp: >260 °C, MS (FAB): (M + 2)$^+$ 1954 (100), (M + 1)$^+$ 1953 (66). ^{1}H NMR (CDCl$_3$): δ 7.06−7.01 (m, 6H); 6.99 (s, 16 H); 6.97 (s, 2H); 2.62−2.59 (m, 32H); 1.60 (br, 64 H); 1.01−0.89 (m, 48 H).

Supporting Information Available: ^{1}H NMR spectra for compounds **4h, 4a, 4b, 8a,** and **8b** (9 pages). See any current masthead page for ordering and Internet access instructions.