

Oligothiénylenevinylenes as a New Class of Multinanometer Linear π -Conjugated Systems for Micro- and Nanoelectronics

JEAN RONCALI*

Ingénierie Moléculaire et Matériaux Organiques, CNRS UMR 6501, Université d'Angers, 2 Boulevard Lavoisier, F-49045 Angers, France

Received July 30, 1999

ABSTRACT

This Account deals with the synthesis and characterization of monodisperse soluble oligothiénylenevinylenes with chain lengths up to 100 Å. The chain length dependence of the electronic and electrochemical properties both in solution and in the solid state are analyzed and discussed in the context of the potential use of oligothiénylenevinylenes as molecular wires. Problems related to interchain interactions are illustrated by the analysis of the effects of structure on the reversible dimerization of cation radicals and by the synthesis of new series of end-substituted oligomers.

Introduction

Linear π -conjugated systems (LCSs), namely conjugated polymers and oligomers, are the focus of intense research effort motivated by the fundamental problems posed by their electronic properties and by their multiple potential applications as advanced materials for electronic and photonic applications.¹ Whereas during the 1980–90 period polydisperse conjugated polymers (CPs) have represented the most widely investigated class of LCSs, the beginning of the 1990s marked a turning point in the field, with a relative loss of interest in some initially envisioned bulk applications associated with the conducting properties of CPs and a parallel explosion of research on new applications based on the semiconducting properties of LCSs, such as electronic devices and light-emitting diodes.^{2–4} A major difference with the bulk applications of CPs was that, instead of large quantities of materials of relatively simple basic structure, these novel advanced applications require small amounts of material fulfilling stringent specific requirements in terms of structural definition, processability, and electronic and optical properties. The quest for novel conjugated structures capable of fulfilling these new prerequisites has also underlined the existence of lacunae in the basic knowledge of the electronic properties of CPs.

Jean Roncali was born in Paris in 1949. He received his education in chemistry at the Conservatoire National des Arts et Métiers and his Ph.D. at the University of Paris 13. After successive positions as engineer and Chargé de Recherche at CNRS, he is currently Directeur de Recherche at CNRS and co-manager of the Laboratory of Molecular Engineering and Organic Materials in Angers. His research interests encompass the synthesis and characterization of organic molecules and materials with tailored electronic properties in view of energy conversion and electrochemical, electronic, and photonic applications.

The conjunction of this need for a more detailed understanding of the structure/electronic properties relationships of LCSs and for molecularly defined materials with tailored electronic properties has strongly contributed to the considerable development of research on monodisperse π -conjugated oligomers (COs) since the beginning of the 1990s.^{5–7}

One of the main initial motivations to develop monodisperse structurally defined COs has been the ability to model the electronic properties of the parent CPs. In fact, the polydispersity of CPs and the marked sample dependence of many of their physicochemical properties make it quite difficult to establish clear structure–property relationships. Consequently, many of their electronic properties and, in particular, the mechanisms of charge transport in doped CPs remain not fully understood and are still a matter of debate. In contrast, the use of COs of perfectly controlled structure offers the possibility of establishing unequivocal structure–property relationships. Furthermore, the analysis of the chain length dependence of quantities such as oxidation potential or HOMO–LUMO gap allows us to define, by extrapolation, the properties of ideal defect-free polymers.^{5–7}

Concurrently, COs have also gained interest in their own right as a novel class of molecular materials widely investigated as organic semiconductors for the fabrication of electronic devices such as field-effect transistors (FETs).^{2,3} Compared to the previously used parent CPs, the use of COs as active material presents several distinct advantages in terms of purity and material organization. These properties, together with the processing of COs by vacuum sublimation, have allowed a considerable improvement of the FETs' performances.

The most recent interest in monodisperse COs arises from their possible use as molecular wires designed to interconnect molecular switches or logic gates in future ultradense and ultrafast devices based on nanoscopic molecular architectures.^{6–8} While during two decades this research area has given rise to much speculation, the widespread development of scanning tunneling microscopy together with recent advances in the synthesis and characterization of COs with dimensions comparable to the present limit of nanolithography (~100 Å) provides favorable conditions for significant progress in the near future.

Despite the numerous series of COs investigated in the past few years, a great need still exists for further effort in synthetic chemistry aiming at the development of novel conjugated structures with properties specifically designed for advanced applications both as molecular materials and as nanoscopic structures.

The aim of this Account is to provide an overview of recent work carried out in our laboratory on the synthesis and characterization of oligothiénylenevinylenes as a new class of COs with original and promising properties.

* E-mail jean.roncali@univ-angers.fr.

Background

Linear π -conjugated systems (LCSs) involve two main classes of compounds, namely polydisperse CPs and the parent monodisperse COs. The unique electronic properties of LCSs originate from the delocalization of π -electrons over a large number of recurrent monomer units. Polyenes $(\text{CH})_n$ which have alternating single and double carbon-carbon bonds are the archetype of this type of structure. Using a simple Hückel approximation, the HOMO-LUMO gap (ΔE) of an infinite $(\text{CH})_n$ chain should be ideally zero; i.e., the frontier orbitals are two degenerate nonbonding orbitals with two electrons as in the case of $[4n]$ annulenes.⁹ However, as predicted by theory,¹⁰ such low-dimensional systems are unstable, and the coupling of electrons and phonons with lattice distortions leads to a localization of single and double bonds with the opening of a gap generally larger than 1.50 eV. The degree of bond length alternation, i.e., the difference between single and double bond lengths, thus represents the major contribution to the existence of a finite gap in LCSs.¹¹ For systems involving aromatic units, ΔE additionally depends on two factors which contribute to a further localization of π -electrons within the rings, namely the resonance energy of the aromatic ring and the rotations around the single bonds connecting the monomer units.¹²

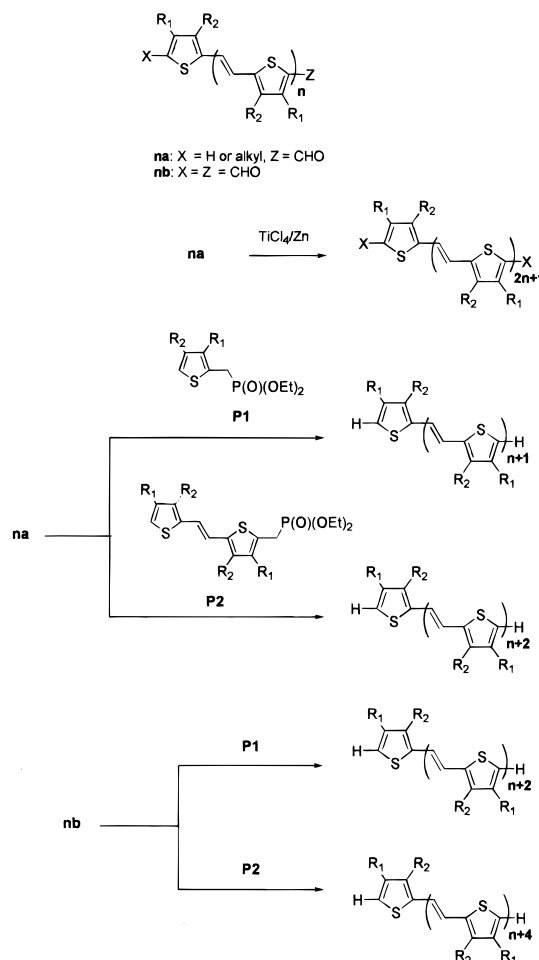
While these factors determine the lower limit of ΔE for an "infinite" LCS, short-chain COs of course show larger gaps which progressively decrease with chain extension until a chain length corresponding to the effective conjugation length of the system and hence to the lowest limit of ΔE is attained. The effective conjugation length, the corresponding ΔE value, and the rate at which this value is approached thus represent parameters of crucial importance for the design of COs both as elemental bricks of molecular materials and as molecular wires.¹³

Based on the consideration of the structural factors that determine ΔE , simple polyenes in principle represent the optimal structure. However, their lack of stability constitutes a major drawback for practical use as well as for the synthesis of highly extended systems. Oligophenylenes are representative examples of the other extreme situation in which the combined effect of the high resonance energy of the benzene ring and severe steric hindrance to planarity produce excessive π -electron confinement.¹²

Owing to their stability, moderate band gap, and structural versatility, polythiophenes and the parent oligomers (n Ts) rank among the most widely investigated LCSs from both fundamental and technological viewpoints.¹⁴ Because of this unique combination of properties, n Ts thus represent an interesting starting point for the design of LCSs with optimized electronic properties.

Oligothiénylenevinylenes (n TVs) can be viewed as a combination of the structures of n Ts and $(\text{CH})_n$. In this system, the presence of double bonds of defined configuration produces at the same time a decrease of the overall aromatic character of the LCSs and hence of π -electron localization and the suppression of the rotational disorder. These synergistic effects are illustrated by

Scheme 1. Synthesis of Soluble n TVs



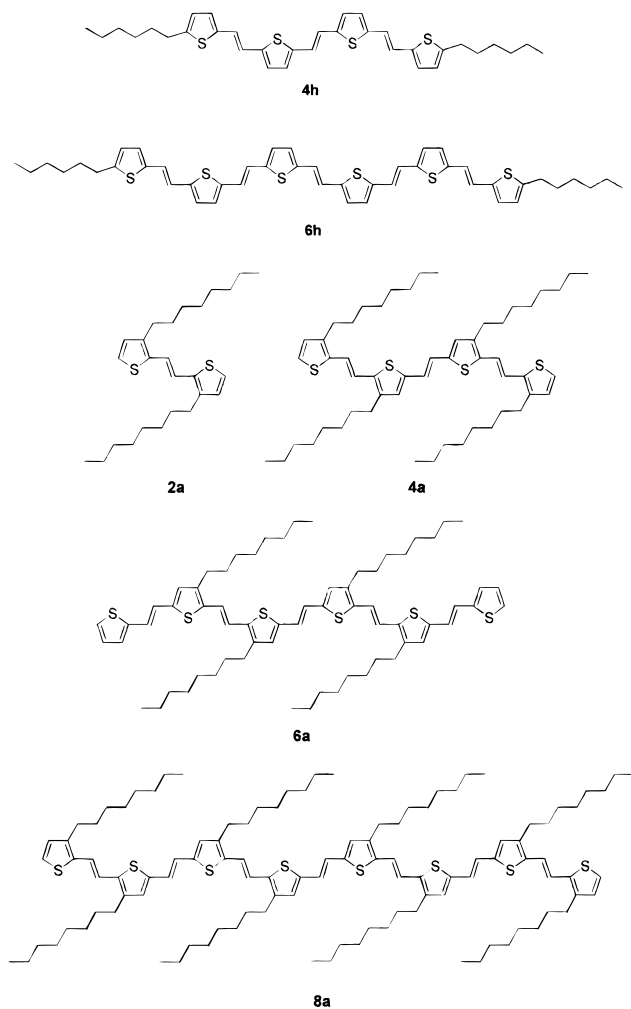
the fact that poly(thiénylenevinylene) (PTV) exhibits a band gap 0.20–0.30 eV smaller than that of PT.¹²

However, despite this a priori better π -electron delocalization, n TVs have scarcely been considered so far. Whereas n TVs up to the heptamer stage have been known for some time,^{15,16} further chain extension as well as the detailed characterization of the electronic properties of this class of COs has been hampered by their poor solubility.

Synthesis of n TVs

To achieve the solubilization of the n TV system, various approaches involving either substitution at the α -positions of both terminal thiophenes or the use of 3-alkyl- or 3,4-alkylthiophenes as building blocks have been considered. Construction of each series of n TVs basically involves three types of reactions. Each oligomer of degree n is first converted into the corresponding mono- or dialdehyde, and chain growth is then achieved either by McMurry coupling of monoaldehydes, which results in chain length doubling, or by stepwise chain extension by Wittig or Wittig-Horner olefination. In this latter case, the rate of chain growth depends on the number of TV units in the Wittig reagent (P1 or P2) and on the use of a single or double olefination of a mono- or a dialdehyde (Scheme 1). However, as chain length increases, selective mono-

Chart 1



formylation becomes increasingly difficult, and, for instance, formylation of the tetramer invariably produced a mixture of mono- and dialdehydes that was difficult to separate. To circumvent this problem, the synthesis of the longest n TVs was performed using double formylation followed by two-fold Wittig–Horner olefination of the resulting dialdehyde using P2. The presence of *cis*–*trans* isomerizable double bonds in the structure requires a careful ^1H NMR characterization of the configuration at each synthetic step in order to eventually eliminate the less conjugated *cis* isomer.

Application of the above methodology led to the synthesis of three series of n TVs (Charts 1 and 2). The chain length of the first series end-disubstituted by hexyl chains (**4h**, **6h**) was limited to the hexamer because of the insufficient increase of solubility produced by this type of substitution. Substitution of one β -position by an octyl chain (**2a**–**8a**) produces a larger increase of solubility but is still insufficient to surpass the octamer stage. The use of 3,4-dibutylthiophene as starting material allowed the decamer stage (**2b**–**10b**) to be reached, but further chain extension was again hampered by solubility problems.^{17,18} Finally, redoing the whole synthesis starting from 3,4-dihexylthiophene overcame these difficulties and allowed the synthesis of a fourth series of n TVs from the dimer to

Chart 2

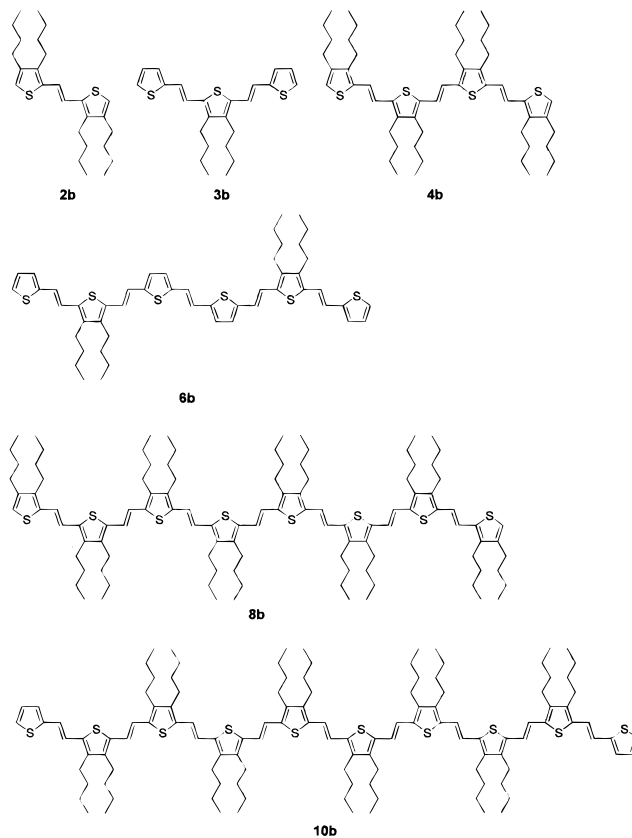
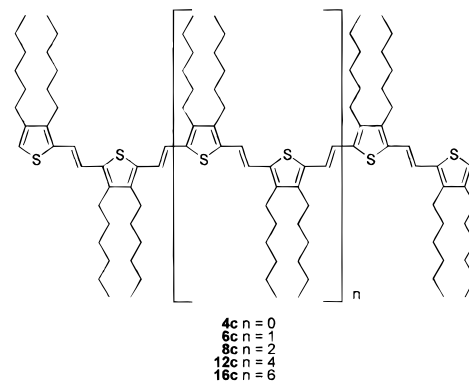


Chart 3



hexadecamer (**2c**–**16c**, Chart 3), which exhibit good solubility even at the maximum chain length.¹⁹

Optical Properties of n TVs

A major difference between most series of COs investigated to date and n TVs lies in their rigid and planar structure ensured by ethylene linkages. This planar geometry is clearly apparent in the X-ray structure of the tetramer dicarbonyl shown in Figure 1. The absence of rotational disorder is further demonstrated by the complete lack of thermochromic effect when solutions of n TVs derived from 3-alkyl- or 3,4-dialkylthiophenes are immersed in liquid nitrogen. This behavior contrasts strikingly with that of the parent oligothiophenes, which, under the same conditions, undergo a considerable red

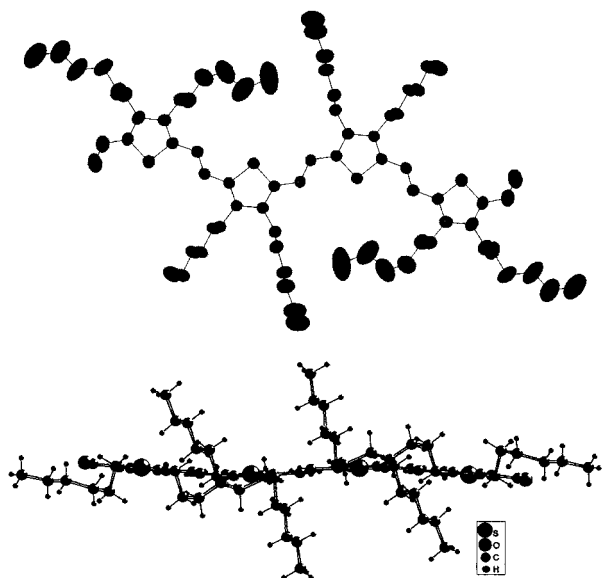


FIGURE 1. ORTEP view of the dicarbaldehyde of **4c**.

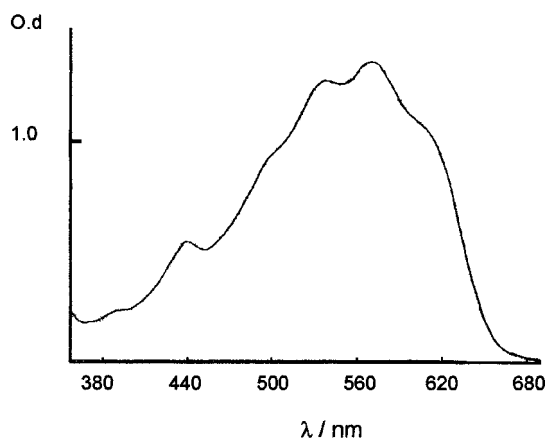


FIGURE 2. Electronic absorption spectrum of **8a** in CH_2Cl_2 .

shift of the absorption due to a planarization of the structure driven by alkyl substituent interactions.²⁰

Whereas introduction of alkyl chains at the α -position of the end thiophene rings has little effect on the absorption maximum, β -substitution of thiophene produces a bathochromic shift proportional to the number of alkyl substituents due to cumulative inductive effects. Apart from this difference, the various series of *n*TVs show rather similar spectra. In particular, they show a well-resolved vibronic fine structure which persists even at the hexadecamer stage. However, the resolution of the fine structure decreases with substitution of the thiophene ring and is minimal for *n*TVs derived from 3,4-dihexylthiophene. This effect can be related to an indirect enhancement of the vibrational disorder in the π -conjugated system caused by the alkyl substituents. This explanation is supported by the large thermal ellipsoids of the hexyl carbons in the X-ray structure in Figure 1. Figure 2 shows, as a representative example, the spectrum of the octamer **8a**. The lowest energy transition appears at 595 nm, with vibronic bands at 552, 517, 480, and 450 nm. The energy difference between two consecutive maxima (0.15–0.17 eV) is con-

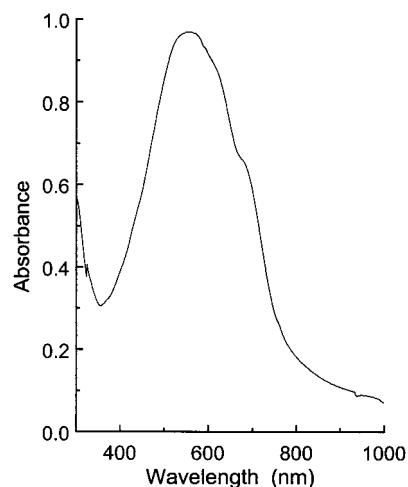


FIGURE 3. Electronic absorption spectrum for a film of **16a** on glass.

sistent with a C=C stretching mode strongly coupled to the electronic structure.

For all series of *n*TVs, chain extension produces the expected bathochromic shift of λ_{max} and decrease of ΔE reaching values of 580 nm and 1.72 eV for the decamer **10b**. Oligomers based on 3-octylthiophene (**a**) exhibit the best film-forming properties among *n*TVs of the first three series. The optical spectrum of a solution-processed film shows a persistent fine structure consistent with a well-ordered material, while the low-energy absorption onset indicates a band gap (E_g) of ca. 1.70 eV.¹⁸

A complete analysis of the optical properties from the dimer to the hexadecamer stage was carried out on a fourth series of *n*TVs based on 3,4-dihexylthiophene.^{19,21} Furthermore, the good film-forming properties of these oligomers allowed a parallel investigation of the chain length dependence of the electronic properties in solution and in the solid state. Chain extension to the dodecamer and hexadecamer stage leads to a further red shift of λ_{max} , with a decrease of ΔE and an increase of the molecular extinction coefficient (ϵ). For **16c**, λ_{max} and ϵ reach values of 601 nm and 319 000 $\text{mol L}^{-1} \text{cm}^{-1}$ respectively, which are by far the largest ever observed on a π -conjugated oligomer of homogeneous chemical structure. Again, the vibronic fine structure observed in the solution spectrum is still apparent in the spectrum of a film of **16c**, indicating a well-ordered material (Figure 3). The long-wavelength absorption edge leads to a band gap of 1.56 eV, a value close to that of polyacetylene. Comparison of the band gap values of films of *n*TVs with that of the parent PTV synthesized by the soluble precursor route (1.70–1.80 eV) suggests that the effective conjugation length of PTV is limited to ca. eight TV units. This rather limited conjugation length can be attributed to the occurrence of conjugation defects during the thermal elimination process. On the other hand, since the band gap of polyacetylene (~ 1.50 eV) can be considered as the lowest limit attainable by the *n*TV system, the band gap of 16TV films (1.56 eV) suggests that this chain length is close to the limit of convergence of the ECL.

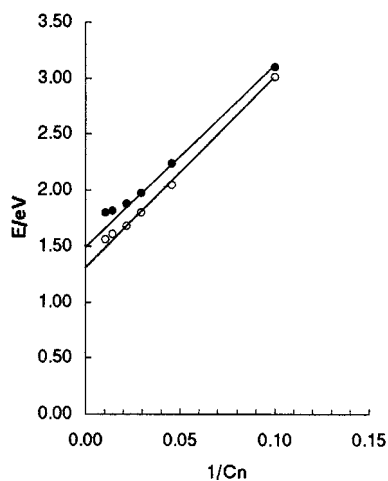


FIGURE 4. Plots of the HOMO–LUMO gap (●) and band gap (○) for **2a–16a** vs the reciprocal number of carbons in the conjugated chain.

Figure 4 shows plots of ΔE and E_g vs $1/C_n$ for **2c–16c**. Extrapolation of the linear part to $1/C_n = 0$ gives values of 1.60 and 1.30 eV for ΔE and E_g , respectively, for an infinite chain. However, for both series, a deviation from linearity occurs around the dodecamer stage, confirming the existence of a convergence limit.

Extrapolation of quantities such as oxidation potential, λ_{\max} , ΔE , and E_g , determined on short-chain oligomers, have been widely used in order to analyze the chain length dependence of the electronic properties of COs and to predict the properties of an infinite defect-free polymer chain.^{5–7,19–21,22} These extrapolations were based on the linear plot ($1/C_n$) of a hyperbolic function $f(n)$. However, as recently discussed by Meier et al., the existence of a finite effective conjugation length in LCSs implies the convergence of the above parameters toward a limiting value for a certain value of n .¹³ In fact, such a saturation limit has been observed for all series of COs investigated so far.¹³ As suggested by Meier et al., the maximum effective conjugation length can be considered reached when an incremental chain extension induces a red shift of λ_{\max} or λ_{0-0} smaller than 1 nm. On the basis of this definition, the 6-nm red shift of λ_{\max} and the related decrease of ΔE between **12c** and **16c** shows that, although close, the saturation limit is not yet reached and that the effective conjugation length of dihexyl *n*TVs is at least equal to 94 sp² carbons (16-mer).²¹

Comparison of these results with the optical data for other classes of extended π -conjugated oligomers based on thiophene,^{22,23} 1,4-dialkoxyphenylenevinylenes,²⁴ 1,4-phenyleneethynyls,⁶ triacetylenes,²⁵ and 2,5-thiopheneethynyls⁶ clearly shows that *n*TVs exhibit the longest effective conjugation length among known systems and the smallest ΔE value for both the 50- and 100-Å chain lengths (Figure 5). These outstanding properties suggest that, as far as the gap is concerned,^{8,26} *n*TVs rank among the best candidates as molecular wires in nanoscopic systems.

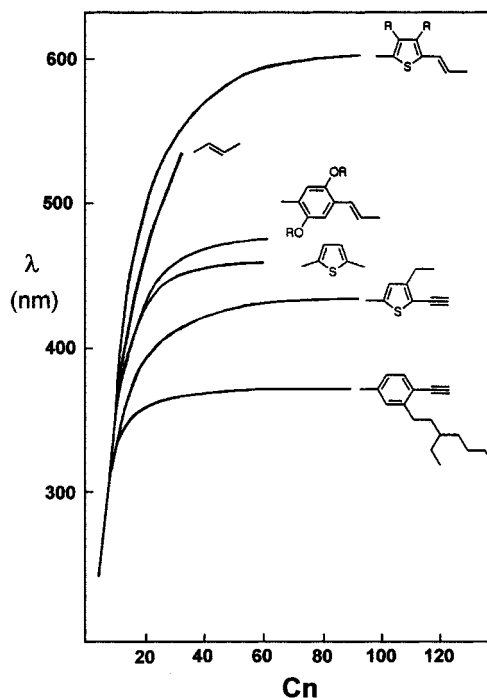


FIGURE 5. Chain length dependence of the absorption maximum for various classes of extended conjugated oligomers. Graphs for oligomers of thiophene,²² 1,4-dialkoxyphenylenevinyls,²⁴ 1,4-phenyleneethynyls,⁶ triacetylenes,²⁵ and 2,5-thiopheneethynyls⁶ are drawn from data taken in the cited references.

Electrochemical Properties of *n*TVs

The electrochemical properties of the various *n*TV series have been analyzed by cyclic voltammetry (CV). For a given chain length, the increase of the number of alkyl substituents produces a slight negative shift of the first anodic peak potential (E_{pa1}) associated with formation of the cation radical due to inductive effects. As expected, chain extension produces a negative shift of E_{pa1} and an increase of the number of oxidation stages. The CV of the dimers shows an irreversible first oxidation process due to follow-up polymerization.²⁷ At the tetramer stage, the two oxidation processes become reversible and their potential difference decreases due to a reduced Coulombic repulsion between positive charges in the dication. For hexamers, the two oxidation peaks almost merge into a single wave followed by a third reversible wave corresponding to the formation of the trication radical.

The case of the octamer is particularly interesting, with the full coalescence of the first two waves into a single step two-electron transfer followed by two one-electron waves corresponding to the formation of the trication radical and tetracation (Figure 6). This direct access to the dication is rather unique among COs.^{18,21} For example, recent work has demonstrated the occurrence of two polarons instead of a bipolaron in dodecathiophene.²⁸ This specific behavior of *n*TVs can be again related to their planar structure which prevents the charge localization associated with the rotational disorder in *n*Ts.

With further chain extension to **12c**, the two upper one-electron waves almost coalesce into a second two-electron transfer, while a new one-electron wave assigned to the

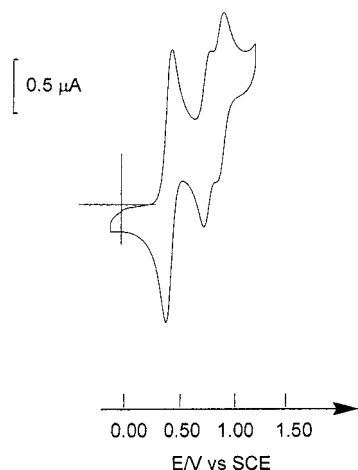


FIGURE 6. CV of **8c** in 0.10 M Bu₄NPF₆/CH₂Cl₂, $\nu = 100 \text{ mV s}^{-1}$.

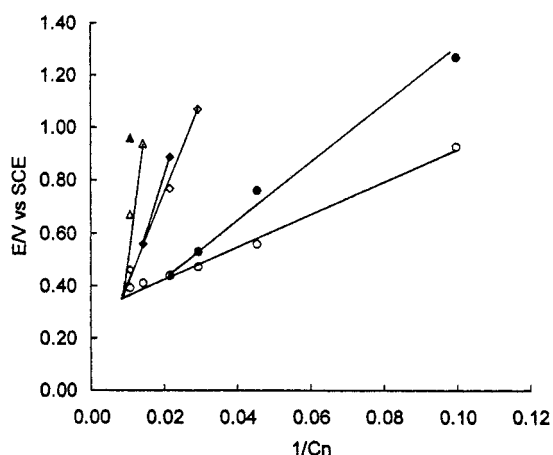


FIGURE 7. Variation of the anodic peak potential of the various oxidation steps of *n*TVs vs the reciprocal number of carbons in the conjugated chain. ○, Cation radical; ●, dication; ◇, trication radical; ◆, tetracation; △, pentacation radical; ▲, hexacation.

pentacation radical occurs. Finally, the CV of **16c** shows two close bielectronic transfers followed by two successive one-electron waves, allowing the system to be charged up to the hexacationic stage.^{19,21}

Figure 7 summarizes these results in the form of plots of the variation of the various redox potentials versus $1/C_n$. The two convergence points correspond to the two bielectronic transfers at the 8TV and 16TV stages. The slight deviation from linearity around $1/C_n = 0.015\text{--}0.020$ ($C_n = 50\text{--}60$) shows that the system begins to converge toward the saturation limit. A remarkable feature of this figure is that extrapolation of the lines corresponding to the various oxidation steps converges toward a common potential limit for a chain length of 120–130 carbons, (20–22-mer) which should correspond to the single-step multielectronic oxidation of the whole π -conjugated system.

In fact, full coalescence of the various redox states is observed in the CV of **16c** recorded in the solid state. The CV of films of **8c** and **16c** cast onto a platinum electrode (Figure 8) show that the passage from the solution to the solid state results in a dramatic narrowing of the potential window including the successive oxidation steps, which

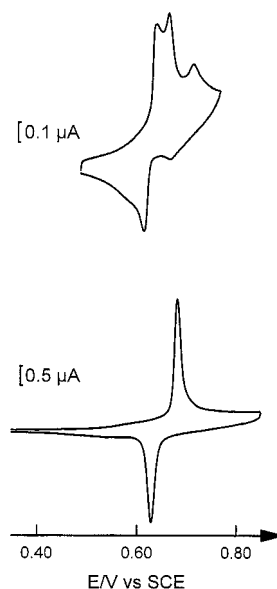


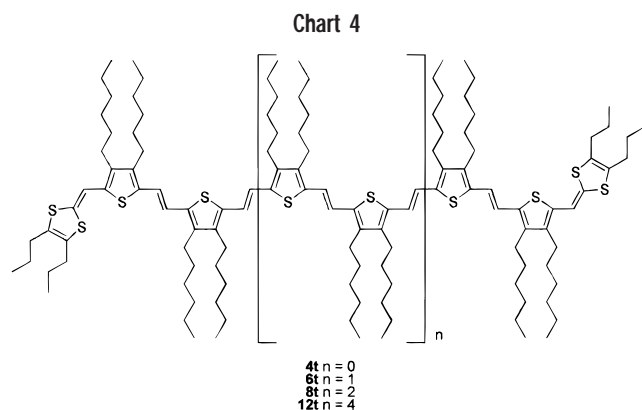
FIGURE 8. Solid-state CVs of films cast on Pt from CH₂Cl₂ solutions: **8a** (top) and **16a** (bottom). Electrolytic medium, 0.10 M Bu₄NPF₆/CH₃CN; $\nu = 50 \text{ mV s}^{-1}$.

decreases from 460 to 80 mV for **8c**, while for **16c** the various oxidation steps merge into a single wave corresponding to a six-electron oxidation.²¹

To interpret this result, two extreme cases corresponding to the formation of inter- or intrachain bipolarons have been considered. In the first case, coalescence would result from attractive interchain interactions related to the dimerization of single or multiple cation radical states. In recent years, this process has been widely investigated on various series of conjugated oligomers as a possible alternative to intrachain bipolarons in doped conjugated polymers.²⁹ On the other hand, an intramolecular mechanism would imply that the passage from solution to the solid state produces an enhancement of the effective conjugation length sufficient to reach the convergence point predicted in Figure 7.

To clarify this question, a systematic analysis of structural effects on the reversible dimerization of cation radicals of diversely substituted 4TVs has been carried out. Chain length was deliberately limited to the tetramer because of the direct formation of the dication in longer systems. Starting from the unsubstituted 4TV, alkyl chains were progressively introduced at the various positions of the conjugated system. In the course of this study it became rapidly evident that these various 4TVs undergo two types of behavior. The cation radicals of unsubstituted and end-substituted 4TVs readily dimerize, whereas those of 4TVs involving 3-substituted thiophene do not. Therefore, in the following, the discussion will be restricted to the case of **4h** and **4c** taken as representative examples.

When the concentration of substrate (C_0) is increased from 5×10^{-5} to 10^{-3} M, the first apparent redox potential (E_{app1}) of compound **4h** decreases linearly with a slope of $-29 \text{ mV}/\log C_0$ unit, as expected for a mechanism involving the reversible dimerization of two radical cations.³⁰ In contrast, for compound **4c**, E_{app1} is unaffected by the increase of C_0 . Similarly, E_{app1} exhibits a marked temper-



ature dependence for **4h** with a slope of 0.99 mV K^{-1} , but it is quite independent of temperature for **4c**.

These different behaviors are confirmed by the evolution of the optical spectrum upon chemical generation of the cation radical by trifluoroacetic acid. Oxidation of **4c** produces a decrease of the absorption bands of the neutral state at 489 and 542 nm with concomitant development of two bands at 880 and 1500 nm, corresponding to the subgap transitions of the polaron state. Under the same conditions, the spectrum of **4h** shows two additional bands at 1120 and 750 nm, characteristic of the cation radical π -dimer.²⁹

Finally, ESR data show that, whereas the ESR signal of the **4h** cation radical vanishes at low temperature due to spin pairing, for **4c** the signal of the monomeric cation persists even in the frozen state (150 K).³¹ These results, which provide the first conclusive evidence for a structural control of the reversible dimerization of oligomeric cation radicals, demonstrate that β -substitution of thiophene by an alkyl chain inhibits the dimerization process in the n TV system. On this basis, it can be inferred that the coalescence of the redox states observed in the CV of 16TV films involves an important intramolecular contribution. This could be related to an enhancement of the effective conjugation length resulting from a limitation of vibrational disorder in the solid state.

Control of Interchain Interactions

These various investigations have underlined the major role played by substitution of the n TV system in the control of interchain interactions. Beyond its fundamental aspect, this question is of crucial importance for future applications of n TVs both as elemental units of organic semiconducting materials and as individual molecular wires. In the first case, strong intermolecular interactions are needed to enhance the compactness of the material and hence charge carrier mobility. In contrast, the manipulation of a single n TV chain requires weak interchain interactions. These contrasting prerequisites imply the definition of synthetic strategies in order to either reinforce or weaken interchain interactions.

A first step in this direction has involved the synthesis of n TVs end-capped with 1,4-dithiafulvenyl groups (DTFs). We had previously shown that introduction of cyano groups at the ethylene linkage of the n TV system signifi-

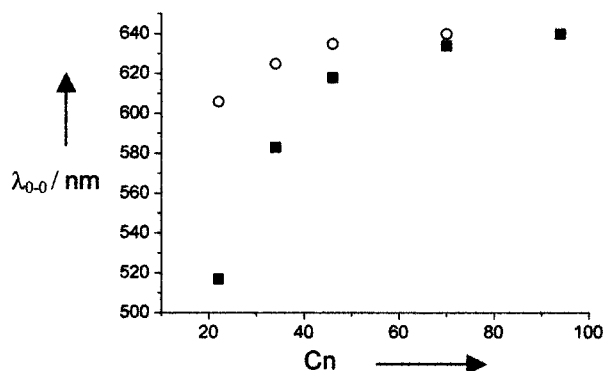


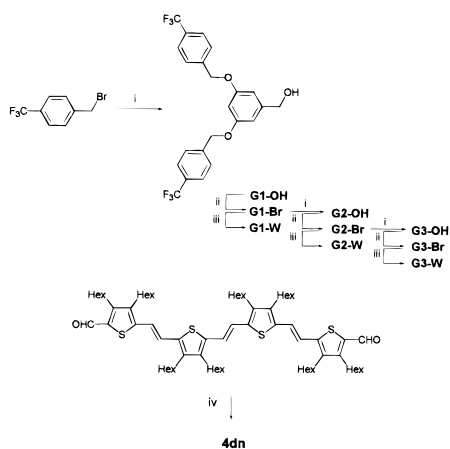
FIGURE 9. Absorption maximum of the 0–0 band versus the number of carbons in the n TV chain. \circ , Compounds **4t**–**12t**; \blacksquare , n TVs **4c**–**16c**.

cantly increases its electron affinity.³² In contrast, end-substitution by the strong π -donor DTF groups can raise the HOMO level and possibly push back the effective conjugation length limit. Furthermore, the propensity of DTF groups to self-assemble into π -stacks can enhance intermolecular interactions.

Compounds **4t**–**12t** (Chart 4) have been prepared by two-fold Wittig–Horner olefination of the appropriate dicarbaldhyde.³³ Similarly to their shorter analogues containing 2TV or 3TV,^{34,35} compounds **4t**–**12t** are directly oxidized into their dication through a two-electron transfer around 0.30 V vs SCE. For **4t**, this bielectronic transfer is followed by two one-electron waves at 0.73 and 1.00 V, corresponding to the generation of the trication radical and tetracation. These two one-electron waves shift negatively for **6t**, while for **8t** formation of the pentacation radical and the hexacation occurs at 0.96 and 1.07 V. Finally, the CV of **12t** exhibits two almost coalesced two-electron waves and four one-electron steps, allowing the system to reach the octacationic state. Except for compound **4t**, which is reduced to the dianion via two one-electron steps, all longer compounds are directly reduced to the dianion via a bielectronic transfer. The number of reduction steps increases with chain length, and **12t** is reduced to the hexaanion by three bielectronic transfers.³³

A striking difference between compounds **4t**–**12t** and the corresponding n TVs lies in the complete chain length independence of the first oxidation potential.^{33–35} This implies that the HOMO level is essentially determined by end DTF groups, in agreement with previous results, while the positive shift of the first reduction potential indicates that the LUMO level depends on chain length.³⁶

The UV–vis spectra of **4t**–**12t** are similar to those of extended n TVs, with the typical well-resolved vibronic fine structure. Strong 1,5-intramolecular interactions between the sulfur atoms of the thiophene and DTF moieties contribute to rigidify the end parts of the molecule.³⁶ Although chain extension produces the expected red shift of λ_{max} , comparison with the data for the corresponding n TVs shows that the red shift of λ_{max} caused by the DTF groups is quite large at the tetramer stage (517–606 nm) but practically negligible for the longest system ($\lambda_{\text{max}} = 634$ and 640 nm for **12c** and **12t**, respectively). Thus, as shown in Figure 9, whereas introduction of DTF groups

Scheme 2. Synthesis of Dendritic nTVs^a

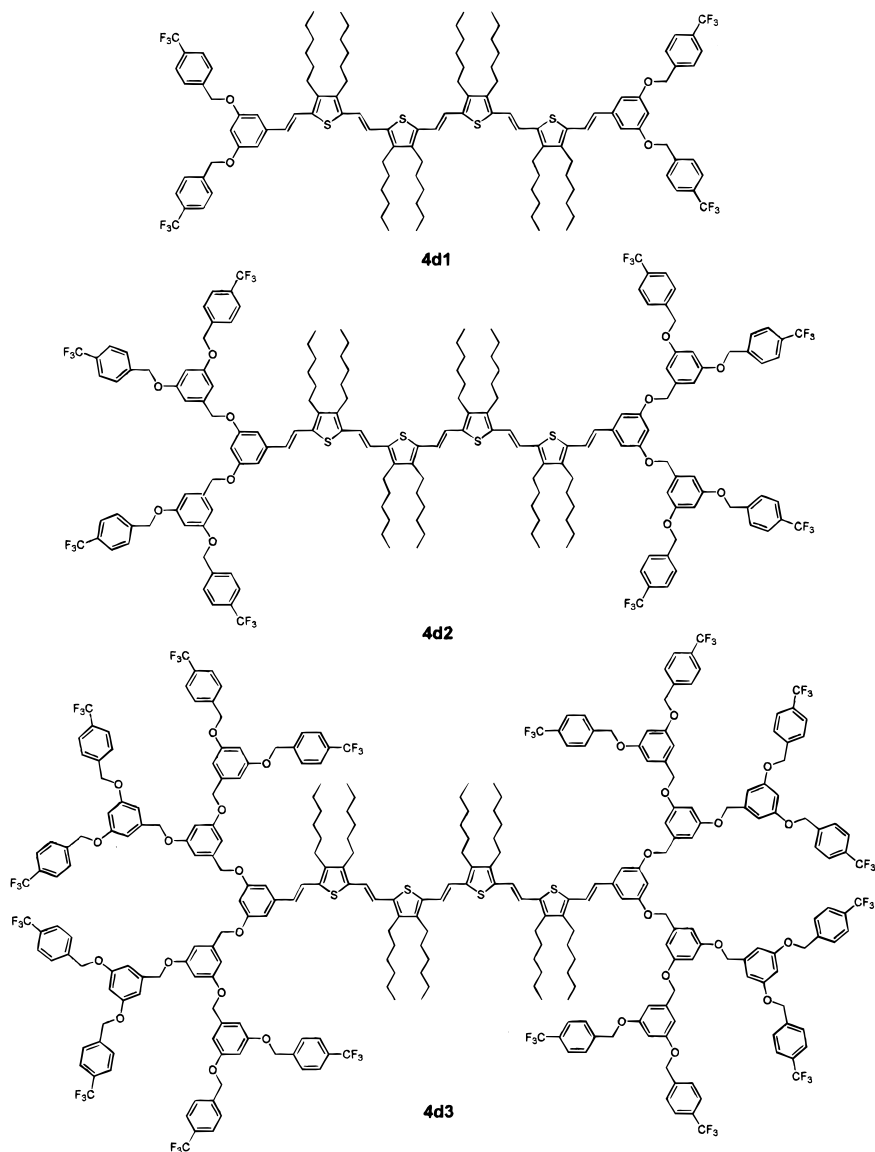
^a Reagents and conditions: (i) 3,5-dihydroxybenzyl alcohol, K_2CO_3 , 18-C-6, acetone; (ii) PBr_3 , toluene; (iii) G1-W, G2-W $HPO(OEt)_2$, NaH, THF, G3-W $P(OEt)_3$, heat; (iv) Gn-W, *t*-BuOK, THF.

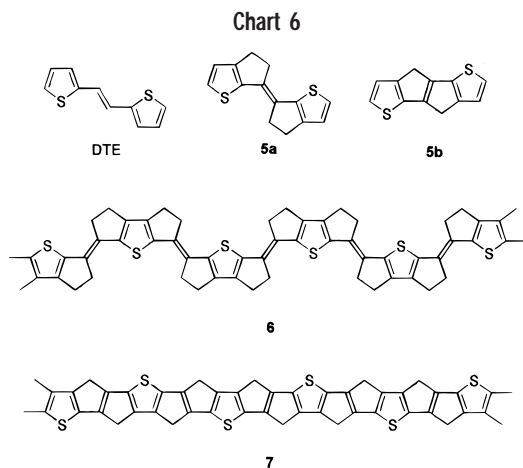
allows a faster approach of the convergence limit of ΔE , it does not allow surpassing it. This suggests that, in the

most extended systems such as **12t**, ΔE reaches the limit imposed by the topology of the carbon backbone (Peierls distortion) and cannot be surpassed by means of simple electronic substituent effects. However, comparison of the optical spectra of films of compounds **6t–12t** with those of films of **6c–16c** shows that even if the passage from the solution to the solid state produces in both cases a red shift of λ_{0-0} , the magnitude of this shift is significantly larger for compounds **6t–12t**. Thus, whereas compounds **12t** and **16c** show the same λ_{0-0} in solution (640 nm), the corresponding films show λ_{0-0} values of 694 and 682 nm, respectively. This small decrease of ΔE suggests that the DTF end groups enhance interchain interactions, thus allowing the limit of the effective conjugation length observed in solution to be pushed back in the solid state.

The search for the reverse effect led us to synthesize *n*TVs end-capped with dendritic chains. It was hoped that steric shielding of the *n*TVs system might hinder aggregation, thus making easier the manipulation of individual molecular wires. To this end, Fréchet-type dendrons³⁷ of

Chart 5





generations 1, 2, and 3 were attached at both ends of a 4TV system. The originality of our synthetic strategy lies in the conversion of each generation of dendron into the corresponding phosphonate (**Gn-W**), with final assembly of the target system via a two-fold Wittig–Horner olefination of the 4TV dialdehyde (Scheme 2).³⁸

Compounds **4d1–4d3** (Chart 5) exhibit identical optical spectra with λ_{max} at 542 nm and a persistent vibronic fine structure, indicating that the planarity and rigidity of the π -conjugated backbone are independent of **Gn**. Similarly, the compounds show identical CVs, with two reversible one-electron oxidation waves corresponding to the formation of the cation radical and dication at redox potentials of 0.53 and 0.65 V. The linear dependence of the intensity of the first anodic peak of compound **4d3** vs the square root of scan rate between 25 and 5000 mV s^{-1} shows that the charge-transfer process between the electrode and the core electrophore is not subject to kinetic limitation. Furthermore, the absence of a substrate concentration effect on the first redox potential confirms the expected absence of dimerization of the cation radical.

Conclusion and Outlook

Oligothiénylenevinylenes belong to the emerging second generation of COs, in which monodispersity and structural definition are associated with chain dimensions reaching the 10-nm range. Due to the combined effects of their planar structure and reduced overall aromatic character, n TVs exhibit the largest effective conjugation and hence the lowest HOMO–LUMO gap among COs of comparable dimensions.

These original properties offer large potentialities in the fields of material science and molecular electronics. However, the contradictory requirements regarding intermolecular interactions imposed by these two applications imply the definition of synthetic strategies aiming at the control of interchain interactions and more generally of the supramolecular organization through noncovalent interactions.

At a more basic level, several pieces of evidence suggest that the convergence limit of the HOMO–LUMO gap predicted around the 20-mer stage is probably determined

by the limit imposed by the Peierls distortion. In the frame of this hypothesis, further progress in gap reduction should attack the problem at its roots by minimizing longitudinal distortions of the LCS. Theoretical and experimental work on dithienylethylene (DTE), i.e., the simplest model of n TVs, has shown that the covalent bridging of the DTE system (**5a**, Chart 6) leads to a significant reduction of ΔE and of the band gap of the resulting polymers.^{39,40} On the other hand, theoretical calculations have suggested that the “internal” bridging of DTE (**5b**) should produce an appreciable further decrease of ΔE .⁴¹ On this basis, bridged n TV structures such as **6** and especially **7** (Chart 6) appear as particularly attractive targets. While such objectives will undoubtedly require a considerable effort in synthetic chemistry, the significant improvement in terms of gap reduction and stability expected from such structural modifications provides a strong incitement to undertake this challenging task.

I would like to thank all my co-workers, post-doc fellows, and Ph.D. students named in the cited references for their invaluable participation in the work summarized in this review.

References

- (1) *Handbook of Conductive Polymers*; Elsenbaumer, R. L., Skotheim, T., Reynolds, J. R., Eds; Dekker: New York, 1998.
- (2) Katz, H. E. Organic Molecular solids as thin film transistor semiconductors. *J. Mater. Chem.* **1997**, *7*, 369–376.
- (3) Garnier, F. Organic-based electronics à la carte. *Acc. Chem. Res.* **1999**, *32*, 209–215.
- (4) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 403–428.
- (5) *Electronic Materials: The oligomer approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1997.
- (6) Tour, J. M. Conjugated macromolecules of precise length and constitution. Organic synthesis for the construction of nanoarchitectures. *Chem. Rev.* **1996**, *96*, 537–553.
- (7) Kraft, A.; Diederich, F. Linear monodisperse π -conjugated oligomers: model compounds and more. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377.
- (8) Magoga, M.; Joachim, C. Conductance and transparency of long molecular wires. *Phys. Rev. B* **1997**, *56*, 4722–4729.
- (9) Choi, C. H.; Kertesz, M. Do localized structures of [14] and [18] annulenes exist? *J. Am. Chem. Soc.* **1997**, *119*, 11994.
- (10) Peierls, R. E. *Quantum Theory of Solids*; Oxford University Press: London, 1956.
- (11) Brédas, J. L. Relationships between band gap and bond length alternation in organic conjugated polymers. *J. Chem. Phys.* **1985**, *82*, 3808–3811.
- (12) Roncali, J. Synthetic principles for bandgap control in linear π -conjugated systems. *Chem. Rev.* **1997**, *97*, 173–205.
- (13) Meier, H.; Stalmach, U.; Kolshorn, H. Effective conjugation length and UV/vis spectra of oligomers. *Acta Polym.* **1997**, *48*, 379–384.
- (14) Roncali, J. Conjugated polythiophenes: Synthesis, functionalization and applications. *Chem. Rev.* **1992**, *92*, 711–738.
- (15) Kossmehl, G. Semiconductive Conjugated Polymers. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 417–426.
- (16) Nakayama J.; Fujimori, T. Preparation of a series of oligo-(thiophene-2,5-diyl)vinylenes. *Heterocycles* **1991**, *32*, 991.
- (17) Elandaloussi, E.; Frère, P.; Roncali, J. Extensively π -conjugated soluble oligothiénylenevinylenes. *Chem. Commun.* **1997**, 301–302.
- (18) Elandaloussi, E.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. Effect of chain extension on the electrochemical and optical properties of π -conjugated soluble thiénylenevinylene oligomers. *J. Am. Chem. Soc.* **1997**, *119*, 10774–10784.
- (19) Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. Extended thiénylenevinylene oligomers as highly efficient molecular wires. *Angew. Chem., Int. Ed.* **1998**, *37*, 942–945.
- (20) Faid, K.; Leclerc, M. Thermochromic Properties of Polythio-

- phenes: Oligomers vs. Polymers. *J. Chem. Soc., Chem. Commun.* **1993**, 962–963.
- (21) Jestin, I.; P.; Frère, P.; Mercier, N.; Levillain, E.; Stiévenard, D.; Roncali, J. Synthesis and characterization of the electronic and electrochemical properties of thienylenevinylene oligomers with multianometer dimensions. *J. Am. Chem. Soc.* **1998**, *120*, 8150–8158.
- (22) Bauerle, P.; Fisher, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. Oligothiophenes—yet longer? Synthesis, characterization and scanning tunneling microscopy images of homologous, isomerically pure oligo(alkylthiophene)s. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303–307.
- (23) Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. Synthesis and properties of the longest oligothiophenes: the icosamer and heptacosamer. *J. Org. Chem.* **1998**, *63*, 8632–8633.
- (24) Stalmach, U.; Kolshorn, H.; Brehm, I.; Meier, H. Monodisperse dialkoxy-substituted oligo(phenyleneethynylene)s. *Liebigs Ann.* **1996**, 1449–1456.
- (25) Martin, R. E.; Gubler, U.; Boudon, C.; Gramlich, V.; Bosshard, C.; Gisselbrecht, J.-P.; Günter, P.; Gross, M.; Diederich, F. Poly-(triacetylene) oligomers: synthesis, characterization and estimation of the effective conjugation length by electrochemical, UV/vis and nonlinear optical methods. *Chem. Eur. J.* **1997**, *3*, 1505–1512.
- (26) Krzeminski, C.; Delerue, C.; Allan, G.; Haguet, V.; Stievenard, D.; Frère, P.; Levillain, E.; Roncali, J. Theoretical study of the electronic properties of extended thienylenevinylene oligomers. *J. Chem. Phys.* **1999**, *111*, 6643–6649.
- (27) Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E.; Frère, P. Control of the Bandgap of Conducting Polymers by Rigidification of the π -Conjugated System. *J. Chem. Soc. Chem. Commun.* **1994**, 2249–2250.
- (28) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Brédas, J.-L. Redox states of long oligothiophenes: two polarons on a single chain. *Chem. Eur. J.* **1998**, *4*, 1509–1522.
- (29) Miller, L. L.; Mann, K. R. π -Dimers and π -stacks in solution and in conducting polymers. *Acc. Chem. Res.* **1996**, *29*, 417–423.
- (30) Savéant, J. M.; Vianello, E. Potential-sweep voltammetry: theoretical analysis of monomerization and dimerization mechanisms. *Electrochim. Acta* **1967**, *12*, 1545–1561.
- (31) Levillain, E.; Roncali, J. Structural control of the reversible dimerization of conjugated oligomeric cation radicals. *J. Am. Chem. Soc.* **1999**, *121*, 8760–8765.
- (32) Ho, H. A.; Brisset, H.; Elandaloussi, E.; Frère, P.; Roncali, J. Thiophene-Based Conjugated Oligomers and Polymers with High Electron Affinity. *Adv. Mater.* **1996**, *8*, 990–995.
- (33) Jestin, I.; Frère, P.; Levillain, E.; Roncali, J. Extended oligothiénylenevinylene end-capped with 1–4-dithiafulvenyl π -donor groups: towards a supramolecular control of the bandgap convergence. *Adv. Mater.* **1999**, *11*, 134–138.
- (34) Elandaloussi, E.; Frère, P.; Roncali, J.; Richomme, P.; Jubault, M.; Gorgues, A. Extended Hybrid Tetrathiafulvalene π -Donors with Oligothiénylenevinylene Conjugated Spacer Groups. *Adv. Mater.* **1995**, *7*, 390–394.
- (35) Elandaloussi, E.; Frère, P.; Roncali, J. Soluble Thienylenevinylene Oligomers End-capped with 1,3-dithiole-2-ylidene Moieties. *Tetrahedron Lett.* **1996**, *37*, 6121–6124.
- (36) Roncali, J. Linearly extended π -donors: when tetrathiafulvalene meets conjugated oligomers and polymers. *J. Mater. Chem.* **1997**, *7*, 2307–2321.
- (37) Hawker, C. J.; Fréchet, J. M. Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.
- (38) Jestin, I.; Levillain, E.; Roncali, J. Electroactive dendritic oligothiénylenevinylenes. *Chem. Commun.* **1998**, 2655–2656.
- (39) Brisset, H.; Blanchard, P.; Illien, B.; Riou, A.; Roncali, J. Bandgap control through reduction of bond length alternation in bridged poly(dithienylethylenes). *Chem. Commun.* **1997**, 569–570.
- (40) Blanchard, P.; Brisset, H.; Riou, A.; Roncali, J. Bridged dithienylethylenes as precursors of small bandgap electrogenerated conjugated polymers. *J. Org. Chem.* **1997**, *62*, 2401–2408.
- (41) Mena-Ortiz, E.; Roncali, J., unpublished results.

AR990023M