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# Synthetic Principles for Bandgap Control in Linear π-Conjugated Systems

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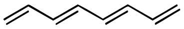
## *I. Introduction*

The electronic properties of linear π-conjugated systems (LCSs) have acquired a growing importance in many areas of modern chemistry and physics of condensed matter. At the molecular level, LCSs represent the simplest models of molecular wires,[1] which together with their complementary functions such as molecular switches, or logical gates, have contributed to the emergence of the concepts of molecular electronics and logic.[2,3] On a quite different dimensional scale, LCSs constitute the elemental bricks of molecular materials that have given rise to considerable research effort in basic and applied material science with the view to developing new materials for information and communication technologies. Until recently, conjugated polymers (CPs) represented the best known protopypes of LCSs.[4]

Jean Roncali was born in Paris in 1949. After several years of work as synthetic chemist in Industrial companies, he received his B.Sc. from the Conservatoire National des Arts et Métiers and his Ph.D. degree from the University of Paris XIII. In 1980 he joined the Laboratory of Solar Photochemistry of CNRS as research engineer. In 1984 he started to work on conducting polymers in the group of Francis Garnier at the Laboratory of Molecular Materials of CNRS in Thiais. Since 1991 he has been a member of the Laboratory of Organic Materials and Molecular Engineering at the University of Angers. Presently Directeur de Recherche at CNRS, his current interests lie in the development of organic polymers and molecular materials with specific electronic properties in view of technological applications in the fields of electronic and photonic devices and energy conversion.

Current interest in CPs started in the late 1970s with the discovery of metallic electrical conductivity in oxidatively doped polyacetylene $(CH)_x$ (**1**).[5,6]



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In the wake of this pioneering work, new classes of CPs based on aromatic precursors such as pyrrole,[7,8] benzene,[9] aniline,[10] or thiophene[11,12] have been developed. In addition to improved environmental stability, these polymers differ from $(CH)_x$ by (i) their nondegenerate ground state, which has important consequences regarding the nature of the charged species involved in the mechanisms of charge transport,[13] and (ii) by their electrochemical synthesis which leads in one step to a doped conducting polymer, thus contributing to extending their potential practical applications.

During the past 20 years these CPs have given rise to an enormous amount of experimental and theoretical work devoted to (i) the analysis of their structure and properties using a whole arsenal of physical techniques, (ii) the development of synthetic methods allowing a better control of their structure and electronic properties, (iii) the synthesis of functional polymers in which the electronic properties of the LCS are associated with specific properties afforded by covalently attached prosthetic groups,[12,14,15] and (iv) the analysis of their multiple technological applications extending from bulk utilizations such as antistatic coatings, EMI shieldings or energy storage, to highly sophisticated electronic, photonic, and bioelectronic devices.

However, whereas the number of envisioned applications soon mushroomed, attempts to develop industrial scale utilizations of CPs have remained limited. This situation essentially results from the fact that the present performance of CPs in terms of conductivity, charge storage capacity, and environmental stability are still insufficient to compete with existing technologies. Parallel to this sudden awareness concerning the initially envisioned applications of CPs, the past five years have been marked by an explosion of the number of works devoted to new advanced applications of LCSs in the fields of electronic and photonic devices. Electroluminescent diodes (LEDs) is probably the most demonstrative example.[16,17]

The conjunction of this new situation with the problems related to the industrial bulk applications of CPs probably explains the sudden emergence of problems related to bandgap control on the forefront of the synthetic chemistry of LCSs. As a matter of fact, a rapid survey of the various consequences of bandgap reduction shows that this approach probably represents the most appropriate response to many of the above discussed problems.

First of all, reduction of the bandgap ($E_g$) will enhance the thermal population of the conduction band and thus increase the number of intrinsic charge carriers. Apart from immediate implications for electronic and optoelectronic devices, in the long term, the decrease of $E_g$ can lead to true “organic metals” showing intrinsic electrical conductivity without resorting to oxidative or reductive doping. On the other hand, the lower oxidation potential (or less negative reduction potential) associated with narrow gaps will result in a stabilization of the corresponding doped state. Furthermore, the possibility of achieving stable reductive doping at moderate potential is of crucial importance for CP-based supercapacitors.[18]

The red shift of the absorption and emission spectra resulting from a decrease of $E_g$ will make available CPs transparent in the visible spectral range and potentially useful for the fabrication of LEDs operating in the IR.[19] Furthermore the increased electron affinity associated with a low-lying LUMO level allows the fabrication of LEDs with stable metals electrodes.[20]

Among other factors, a decrease of $E_g$ implies an optimization of the electron transmission properties of the LCS which has important implications for molecules or materials designed for quadratic or cubic nonlinear optics.

Finally it must be stressed that a better knowledge of the relationships between the structure and electronic properties of LCSs can contribute to improving our understanding of the structural variables that determine the possible synthesis of a superconducting organic polymer which remains a fascinating goal for chemists working on organic conductors.[21]

The design, synthesis, characterization, and theoretical evaluation of small bandgap LCSs involves many different scientific disciplines and the related literature is presently disseminated over a wide variety of specialty journals. In this context, it appears timely to try to consolidate this literature in a comprehensive format in order to identify and critically evaluate the various strategies allowing the control of the bandgap of LCSs.

## II. Background

For more than a century, synthetic chemists have demonstrated their ability to construct molecules and materials capable of fulfilling a huge variety of requirements in terms of mechanical, physical, and chemical properties. However, the synthesis of small bandgap LCSs or of a true organic metal poses specific problems that concern both the conception of the proper target compounds and the definition of the relevant synthetic strategies.

The unique properties of LCSs originate from their extended $\pi$-conjugated system delocalized over a large number of recurrent monomer units. $(CH)_x$ which consists of alternate single and double carbon−carbon bonds is the simplest model of this class of materials. By using a simple Hückel approximation, the bandgap of $(CH)_x$ should be ideally zero *i.e.* the frontier orbitals consist of two degenerate nonbonding orbitals with two electrons as in the case of [4*n*]-annulenes.[22]

However, as predicted by theory,[23] such a low dimensional structure is unstable and the coupling of electrons and phonons with lattice distortions leads to a localization of single and double bonds which lifts the degeneracy and results in a localization of $\pi$-electrons with the opening of a bandgap ($E_g$) generally larger than 1.50 eV. Since polyaromatic polymers have bandgaps significantly larger than this value, which corresponds to the bandgap of $(CH)_x$, polymers showing lower $E_g$ values can be considered as small bandgap conjugated polymers.

While the HOMO−LUMO energy gap of a LCS molecule ($\Delta E$) and the $E_g$ value of the resulting material are usually determined from the low-energy absorption edge of the electronic absorption spectrum, $\Delta E$ and $E_g$ can also be determined from solution oxidation ($E_{ox}$) and reduction ($E_{red}$) potentials. In the case of molecular materials, and provided that intermolecular interactions are not too high, it has been demonstrated[24−26] that $E_g$ can be estimated from $E_{ox}$ and $E_{red}$ using:

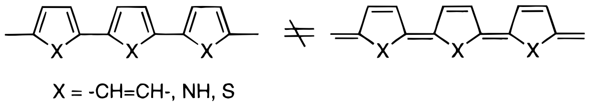
$$E_g \sim (E_{ox} - E_{red}) + (S^+ + S^-)[1 - [[1 - (1/\epsilon_2)]/[1 - (1/\epsilon_1)]]]$$

Where $S$ is the solvation energy of the ionized molecule minus the solvation energy of the neutral molecule and $\epsilon_1$ and $\epsilon_2$ are the dielectric constants of the solution and the solid, respectively.

In the case of CPs, the value of $E_g$ cannot be deduced from the optical or electrochemical characteristics of the precursor and must be determined from the material itself. While this is particularly easy for electrogenerated CPs directly deposited onto an electrode surface, such experiments have also been carried out with electrodes made from chemically prepared polymers. Measurements are generally performed using cyclic voltammetry (CV) although electrochemical voltage spectroscopy has also been employed for the determination of the threshold for electron and holes injection.[27−29]

As pointed out in many theoretical works, Peierls instability which depends on the degree of bond length alternation (BLA) in the conjugated path represents the major contribution to the existence of a finite $E_g$ value in LCSs.[30−34] This BLA contribution to $E_g$ ($E^{\delta r}$) is related to the difference between single and double bond lengths.

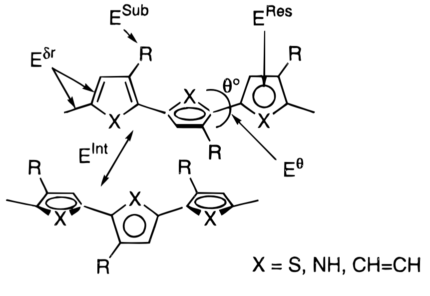
Polyaromatic polymers such as poly(*p*-phenylene) (X = −(CH=CH)−) poly(pyrrole) (X = NH) and poly(thiophene) (X = S) differ from $(CH)_x$ by their nondegenerate ground state *i.e.* the two limiting mesomeric forms aromatic vs quinoid are not energetically equivalent.[34] In most cases the quinoid form has a smaller $E_g$.[33]



Although the bandgap of these polymers depends mainly on $E^{\delta r}$, several other specific parameters also play a determining role (Scheme 1). Thus, the existence of what are essentially single bonds between the aromatic cycles allows the occurrence of interannular rotations. Because orbital overlap varies approximately with the cosine of the twist angle ($\theta$),[35,36] any departure from coplanarity will result in an increase in $E_g$. This problem has been widely investigated for poly(thiophene) (PT) and its oligomers (*n*Ts). Theory and experiment have shown that *n*Ts and the derived cation radicals are not planar but subject to a strong rotational disorder.[37−44] This statistical distortion, which can account for the observed saturation of effective conjugation with chain length in *n*Ts,[45−47] contributes to an increase in $E_g$ by a quantity $E^{\theta}$.

An important difference between $(CH)_x$ and poly(aromatic) LCSs lies in the resonance energy of the monomer unit. This aromaticity results in a competition between $\pi$-electron confinement within the rings and delocalization along the chain.[48] The contribution of the heteroatom[49,50] or more generally of the bridging group[51] to the bandgap has been considered in several theoretical works while the question of delocalization length or confinement length in aromatic LCSs was recently discussed.[48] Whereas this problem is still largely unsolved,[48,52] it is evident that the aromatic resonance energy of the cycle ($E^{Res}$) plays a major role in this process and in the final value of $E_g$.

**Scheme 1**



The most usual way to modifiy the HOMO and LUMO levels of a $\pi$-electron system involves the grafting of electron-releasing or -withdrawing substituents that will respectively increase the HOMO level or lower the LUMO one. Although such substituent effects represent a classical tool of synthetic chemistry, their eventual contribution to the bandgap ($E^{Sub}$) has been seldom considered in theoretical works.[32,53]

The above four factors determine the magnitude of the HOMO−LUMO gap of a single chain LCS. However, the interactions between individual molecules that are responsible for their organization into a condensed phase can represent an important contribution to the bandgap ($E^{Int}$). In fact it has been envisioned that such interchain coupling could contribute to considerably minimizing the Peierls instability.[54]

To summarize, the bandgap of polyaromatic LCSs is determined by five contributions *i.e.* the energy related to BLA, $E^{\delta r}$, the mean deviation from planarity $E^{\theta}$, the aromatic resonance energy of the cycle $E^{Res}$, the inductive or mesomeric electronic effects of eventual substitution $E^{Sub}$, and the intermolecular or interchain coupling in the solid state $E^{int}$.

$$E_g = E^{\delta r} + E^{\theta} + E^{Res} + E^{Sub} + E^{int}$$

Probably the most important feature of this equation is that it makes clear the various structural variables that have to be mastered in order to control the gap of LCSs. Consequently, the main synthetic strategies adopted for the design of small bandgap LCSs will be focused on the reduction of the energetic contribution of one or more of these parameters.

## *III. Structural Definition and Control of the Poly(thiophene) Bandgap*

### A. Electrochemical Synthesis

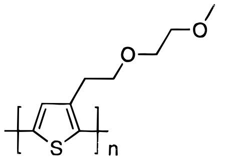
Among the various LCSs developed during the past two decades, poly(thiophene) derivatives (PTs) have become the focus of considerable interest due to a unique combination of original electronic properties, environmental stability, and structural versatility.[11,12,55−57] This interest has been confirmed in recent years with a sustained increase in the overall research efforts devoted to PTs and their relative share within the CPs field.[2,58] In such a context, it is not very surprising that PT has rapidly become the most widely investigated model system for the design of small bandgap LCSs.

The extent of the effective conjugation in the PT backbone was identified early as a crucial parameter to achieving high electrical conductivity.[59−62] Consequently, the control of the structural regularity of the polymer chain has rapidly become a major problem. During the period 1985 to 1990 this objective was essentially pursued through the optimization of the electrochemical synthesis.[63−67] These works focused mainly on 3-substituted monomers that produce more conductive polymers containing fewer α−β′ linkage defects.[68]

Systematic analyses of the mechanisms of electropolymerization and polymer growth and correlations established between electrosynthesis conditions and polymer structure led to the definition of electropolymerization conditions leading to PT films with enhanced effective conjugation and conductivities reaching 2000 S $cm^{-1}$.[66] In parallel, analyses of the evolution of the electrochemical and optical properties of the polymer have revealed that the increase in conductivity was correlated to a decrease of the bandgap from 2.20 to 1.90 eV.[67,69]

Similar strong effects of electrosynthesis conditions were observed for 3-alkylthiophenes and other 3-substituted monomers and it was concluded that interactions among side substituents could indirectly contribute to controling the long-range order in the polymer.[70−76]

Indirect substituent effects leading to an improved structural regularity were also reported for PTs derivatized by polyether chains or by substituted phenyl groups.[71,72] In particular with poly[3-(3,6-dioxaheptylthiophene)][71] (**2**) no irregular head-to-head (HH) or tail-to-tail (TT) linkages were detected in the soluble fraction of the electrochemically synthesized polymer. This is in striking contrast to the results obtained for the chemically prepared one.[76]



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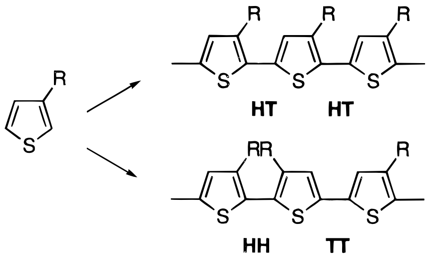
This low amount of linkage errors was attributed to a preferential orientation of the monomers with a nonzero dipole moment under the high electric field present at the electrode solution interface (typically in the range of $10^7$ V $m^{-1}$). While these various works have allowed the bandgap of PTs to be reduced from 2.20 to *ca.* 1.85−1.90 eV,[67,70,72,75] they have also underlined the problems related to the chemical polymerization of thiophene derivatives.

## B. Chemical Synthesis

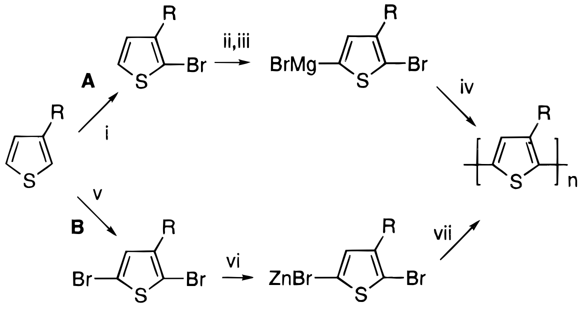
Since their first synthesis in 1986,[77−79] poly(3-alkylthiophenes) (PATs) have attracted increasing interest owing to the significant improvement in solubility resulting from the grafting of flexible hydrocarbon chains onto the PT backbone. This processability and the prospect of industrial applications have triggered a strong renewal of interest in chemical synthesis. Thus, polymerization of 3-alkylthiophenes using $FeCl_3$ as oxidant acquired a growing importance.[80]

However, it became rapidly evident that the polymers produced by this method contained a significant amount of regiochemical defects. As a matter of fact, whereas 3-substitution by long alkyl or polyether chains can exert positive effects on the long-range order of electrogenerated polymers,[70−75] the counterpart is that any defect in the ideal head-to-tail (HT) relative placement of consecutive monomer units induces a severe steric repulsion between substituents and thus a distortion of the conjugated chain with a loss of effective conjugation (Scheme 2).

**Scheme 2**



**Scheme 3**



*Reagents and conditions:* i), $Br_2/AcOH$; ii), LDA/THF; iii), $MgBr_2.OEt_2$; iv), Ni(dppp)$Cl_2$; v), $Br_2/CHCl_3$; vi), Zn/THF; vii), Ni(dppe)$Cl_2$

While this problem can be minimized by the use of optimized electrosynthesis conditions,[67,70,76] this it not the case for oxidative polymerization with $FeCl_3$ which leads to polymers containing about 25% of regiochemical defects.[81] In order to circumvent this obstacle, new regiospecific chemical syntheses have been proposed. These methods are based on the selective formation of an organometallic group at a selected α-position of the thiophene ring. Thus, McCullough et al. have developed a synthesis based on the lithiation of 2-bromo-3-alkylthiophenes at the 5-position followed by metal exchange to obtain the Grignard compound which is then polymerized by cross coupling using Ni(dppp)$Cl_2$[82] as catalyst (Scheme 3, route A).[83] Another approach reported by Rieke et al. involves the regiospecific formation of an organozinc compound by the reaction of dibromo-3-alkylthiophenes with highly reactive Zn, and subsequent nickel-catalyzed polymerization (Scheme 3, route B).[84]

The resulting polymers show conductivity levels considerably higher than those of PATs obtained by oxidative polymerization with $FeCl_3$,[83−87] and of the same order of magnitude for values obtained under optimized electrosynthesis conditions.[66,67,69] The improvement of the regioregularity of the polymer induces important changes in the optical spectrum with a bathochromic shift of absorption bands and the emergence of a well-defined vibronic fine structure with maxima at 525, 560, and 610 nm.[85−87] Such optical features previously observed for electrogenerated PT films are typical of highly ordered polymers (Figure 1).[70,72,75]

This brief summary shows that recent advances in the synthesis and control of the regularity of PT

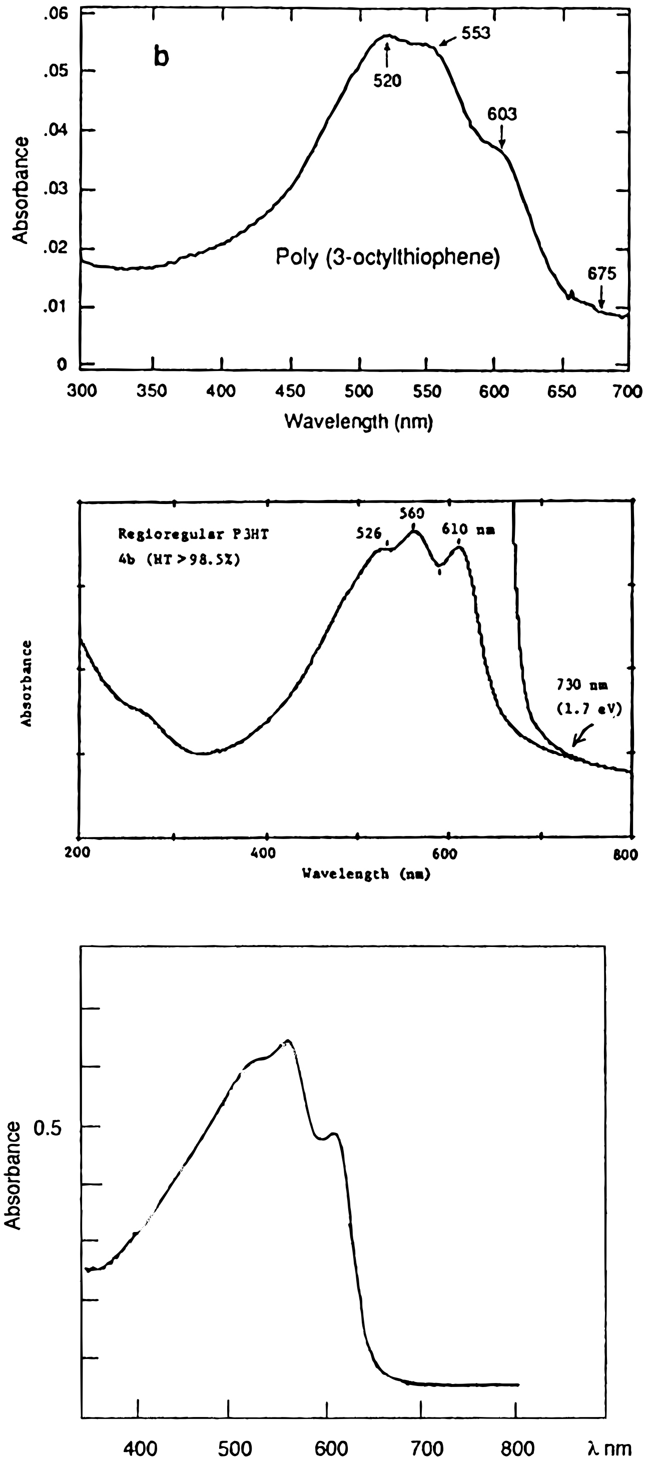


**Figure 1.** Solid-state UV–vis absorption spectra of substituted poly(thiophenes): (top) poly(3-octylthiophene), (from ref 85); (middle) poly(3-hexylthiophene) (from ref 87); (bottom) PDHT (from ref 74). (Reprinted from the references cited. Copyright 1991, 1993, and 1995 by the American Chemical Society.)

chains have led to considerable progress in terms of structural definition, conjugation length, and conductivity. These changes can be correlated to a reduction of the bandgap which decreases from 2.20 eV[24] to values in the range of 1.70–1.80 eV.[67,72,85,86] These values, close to those calculated by the VEH technique,[88] represent the current experimental limit for classical PTs and are thus the reference point for the evaluation of new strategies for gap reduction.

## *IV. Fused Ring Systems as Precursors*

### A. Isothianaphthene

Since its first synthesis more than 10 years ago, poly(isothianaphthene) (PITN) has become the prototype for small bandgap polymers and the subject of much theoretical work. While isothianaphthene (ITN) had been known for some time[89] it was only in 1984 that Wudl et al. considered its possible use as a precursor for a new type of PT.[90] This approach was based on the idea that the relative weight of the limiting resonance forms **c** and **d** (Scheme 4) could be expected to be important and hence could contribute to stabilizing the quinoid form of the polymer.[90]

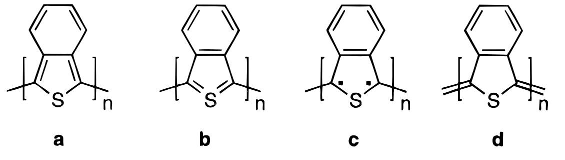
This conclusion can be reached intuitively by considering that after fusion of the thiophene and benzene cycles only one of them can accomodate an aromatic sextet (Scheme 5). Then, on the basis of the comparison of the aromatic resonance energy of benzene (1.56 eV) and thiophene (1.26 eV)[91] it is likely that the benzene ring will have a greater tendency to remain aromatic to the detriment of the thiophene cycle.

Optical and electrochemical determination of the bandgap of PITN gave consistent results with values of 1.0–1.2 eV *i.e.* about 1.0 eV lower than PT.[92,93]

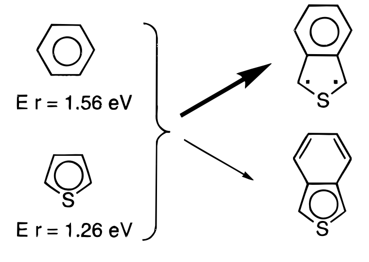
As the first example of a small bandgap CP, PITN rapidly became the focus of considerable theoretical interest[34,94–96] and the origin of the small gap, a matter of debate.[94–105] First Brédas et al. concluded that the ground electronic state of PITN should have an aromatic structure for which a gap value of 0.54 eV was proposed.[94] Later, Lee et al. carried out quantum chemical calculations which suggested a quinoid structure with a bandgap of 1.16 eV,[34,96] which was in good agreement with experiment.[92,93] However, shortly after it was pointed out that such a quinoid structure implies terminal doubly bonded sp$^2$ carbon at each end of the polymer chain, and a mixed structure with a middle part essentially quinoid and aromatic regions at both ends of the conjugated chain was proposed.[98]

From a comparative experimental and theoretical study of short-chain model compounds of aromatic and quinoid geometry based on $^{13}$C NMR data, it was concluded that the quinoid form was slightly more stable than its aromatic counterpart.[100,102] This

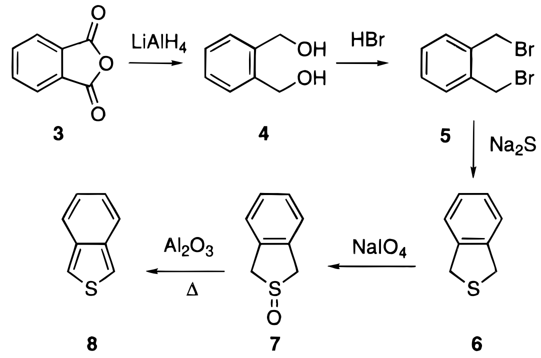
**Scheme 4**



**Scheme 5**



**Scheme 6**



conclusion was confirmed by a comparative analysis of the vibrational spectra of these model compounds, although it was pointed out that the aromatic and quinoid forms are almost isoenergetic and could actually coexist.[104] Extrapolation of the HOMO–LUMO transition of ITN oligomers (monomer to the tetramer) led to an estimated bandgap of 0.63 eV for a fully planar PITN while extrapolation of the X-ray structure of the dimer (*syn* conformation with a dihedral angle of 50°), led to a predicted bandgap value of 1.55 eV.[105]

While ITN (**8**) had been initially obtained by the high-temperature catalytic dehydrogenation of its 1,3-dihydro derivative **6**,[89] in 1971 Cava et al. have described a simpler procedure allowing the preparation of **8** in high yield by dehydration of the sulfoxide **7**[106–108] (Scheme 6).

The electrochemical polymerization of **8** was initially reported to be rather delicate. Thus, the use of electrolytes such as $Bu_4NClO_4$ or $Bu_4NBF_4$ in MeCN, commonly employed for the electrodeposition of PTs, led to a white precipitate of poly(dihydroisothianaphthene) as the main product.[90] However, polymerization could be achieved by indirect oxidation of **8** by electrogenerated chlorine or bromine.[90,92,109] More recently, it has been shown that satisfactory results could be obtained by the application of repetitive potential scans to solutions containing classical electrolytes such as $Et_4NBF_4$ or $Bu_4NBF_4$ in MeCN.[110–112] Furthermore, whereas the CVs of PITN prepared by the indirect method were difficult to interpret due to the lack of the redox system corresponding to the reduction (n-doping) of the polymer,[92,93] complete and well-defined CVs have been obtained on films produced by means of the improved electrodeposition procedure,[110–112] (Figure 2).

Poly(**8**) has also been prepared by means of chemical syntheses. Thus oxidation of the dihydro derivative **6** with atmospheric oxygen, $FeCl_3$[113] sulfuric choride,[114] or *N*-chlorosuccinimide,[115] leads directly to the doped conducting polymer. It has also been reported that poly(**8**) could be directly obtained from phthalic anhydride or phthalide by reaction with $P_4S_{10}$.[116]

## B. Substituted Isothianaphthenes

These initial investigations on poly(**8**) have been followed by a large amount of work devoted to the synthesis of substituted analogs of **8**. This work was motivated by the desire to achieve both a further reduction of $E_g$ and the development of soluble analogs of poly(**8**).

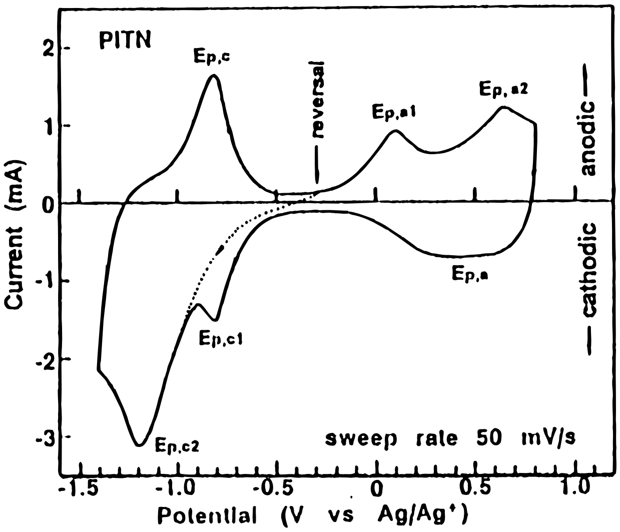


**Figure 2.** Cyclic voltammogram of poly(**8**) obtained after several redox cycles in 0.2 mol L$^{-1}$ $Bu_4NBF_4/CH_3CN$, scan rate 50 mV s$^{-1}$. (Reprinted from ref 112. Copyright 1995 Elsevier Science SA, Lausanne, Switzerland.)

A first step in this direction involved the synthesis of poly(5,6-(methylenedioxy)isothianaphthene) **9**.[117] This compound was prepared from 1,2-bis(chloromethyl)-4,5-(methylenedioxy)benzene according to a synthetic route similar to that in Scheme 6. While the CV of the monomer revealed a slight decrease in the oxidation potential from 0.85 V/Ag$^+$/Ag for **8** to 0.65 V, as expected from the electron-releasing effect of the methylenedioxy substituent, this effect was not observed in the CV of the polymer which, in constrast, showed an oxidation potential slightly higher than poly(**8**). Furthermore, whereas the bandgap was comparable to that of poly(**8**), the conductivity of both the chemically and electrochemically prepared polymers (3–6 10$^{-2}$ S cm$^{-1}$) was considerably lower than that of poly(**8**) (50 S cm$^{-1}$).[117]

Soluble analogs of poly(**8**) have been prepared by grafting long alkyl chains onto the phenyl ring. Thus, poly(5-decylisothianaphthene) has been synthesized by chemical polymerization of **10** using $FeCl_3$.[118] The polymer was soluble in common organic solvents. Polymer solutions showed a $\lambda_{max}$ at 512 nm while a solution-cast film exhibited an optical bandgap of 1.0–1.3 eV. Other soluble alkyl derivatives of poly(**8**) have also been mentioned in a patent.[119] Poly(5-*tert*-butylisothianapthene) has recently been synthesized.[120] 5-Methylisothianaphthene (**11**) was reported to electropolymerize at a lower potential than unsubstituted **8**, however, the resulting polymer oxidizes at a higher potential than poly(**8**).[121]

Halogen substitution of the phenyl ring (**12**–**14**) induces considerable changes in the onset potential for n-doping which shifts from −1.1 V/SCE for **8** and **11** to −0.2 V for the dichloro derivative **14** (Figure 3). However, the expected reduction of the bandgap was not definitively confirmed by the red shift of the electronic absorption spectrum which was smaller than expected.[122]

While introduction of fluorine at the 5-position (**12**) leads to a positive shift of the onset potential for

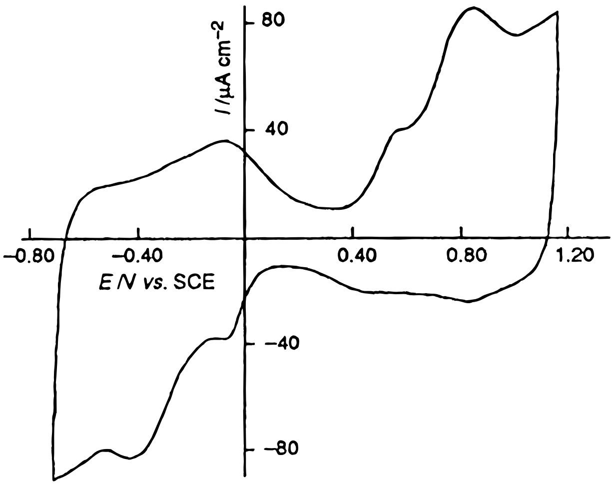
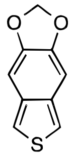


**Figure 3.** Cyclic voltammogram of poly(**14**) on ITO, electrolytic medium 0.2 mol L$^{-1}$ $Et_4NBF_4/CH_3CN$, scan rate 50 mV s$^{-1}$. (Reprinted from ref 111 Copyright 1992 Royal Society of Chemistry, UK.)

n-doping, substitution at the 4-position (**13**) produces the reverse effect, presumably for steric reasons.[122] Whereas theoretical works have predicted the bandgap to be independent of substitution,[94] full substitution by fluorine **15** produces a considerable increase of $E_g$ from 1.10 to 2.10 eV, which has been attributed to both electronic and steric effects of substitution.[123]



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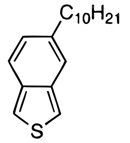

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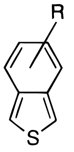
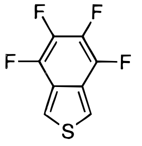


**11** R = 5- Me
**12** R = 5-F
**13** R = 4-F
**14** R = 5,6-Cl



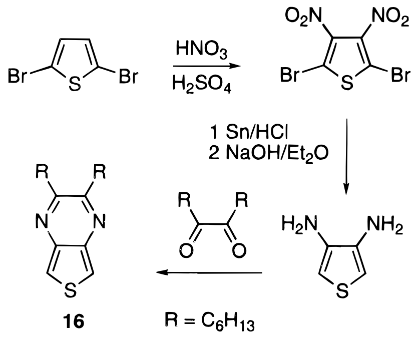
**15**

## C. Thienopyrazine

Parallel to the direct substitution of various positions of the phenyl ring, annelation of the thiophene ring with other moieties capable of producing further reduction of $E_g$ has been undertaken by several groups. This approach was first illustrated by the synthesis of poly(thieno[3,4-*b*]pyrazine (**16**) (Scheme 7).[124]

This polymer was designed on the basis of theoretical calculations predicting a bandgap smaller than that of poly(**8**) (0.70 eV vs 0.80 eV).[97] Furthermore, reduced steric interaction between adjacent monomer units was also expected. The monomer 2,3-dihexylthieno[3,4-*b*]pyrazine (**16**) was synthesized according to Scheme 7 and chemically polymerized using $FeCl_3$. The undoped polymer was dissolved in chloroform and dialized ($M_w$ cutoff 3500) against chloroform. The electronic spectrum showed an absorption maximum at 875 nm (in $CHCl_3$ solution) and at 915 nm for a solution cast film with a bandgap of 0.95 eV. Films cast after doping with $NOBF_4$ in solution exhibited a maximum four-probe conductivity of 3.6 10$^{-2}$ S cm$^{-1}$.[124]

**Scheme 7**



More recently, other polymers derived from **16** with various alkyl chain lengths have been investigated by Raman spectroscopy, and it was concluded that the polymer has a quinoid ground-state geometry in the neutral state and an aromatic one in the doped state.[125]

## D. Fused Thiophenes

The results obtained with PITN derivatives led to interest in other fused ring systems as potential precursors of small gap CPs. In particular thieno[2,3-*b*]thiophene (**17**),[126] thieno[3,2-*b*]thiophene (**18**),[127] dithieno[3,2-*b*:2′,3′-*d*]thiophene (**19**),[128] and the corresponding electrogenerated polymers have all been investigated in recent years.[129−132] Contrary to theoretical expectations, these polymers show bandgaps slightly larger than PT.[133]

In fact, it has been shown that the red shift of $\lambda_{max}$ vs the number of carbons in the conjugated path of the related thienoacene series is comparable to that observed in the corresponding oligothiophenes,[134] suggesting that the mode of annelation in thienoacene is not particularly propitious for the reduction of $E_g$.

Until now dithieno[3,4-*b*:3′,4′-*d*]thiophene (**20**)[128] is the only thienothiophene precursor leading to a small bandgap polymer. The polymer was initially synthesized by electropolymerization[135,136] but a photochemical method has recently been reported.[137] It was claimed that the polymer was transparent in the visible spectral region in its doped form while the low energy absorption edge of the undoped neutral state indicates a bandgap of 1.10−1.20 eV (Figure 4).

As a result of its small gap, poly(**20**) can be easily n-doped at moderately negative potentials, a property which has been considered with regard to applications in redox supercapacitors.[138] Finally it is worth noting that polymerization of **20** can occur at the free α-positions of each terminal thiophene ring thus opening up the possibility of reaching polymers of higher dimensionality.

Thieno[3,4-*c*]thiophenes with a 10-electron system and sulfur in the formal oxidation state +4 (**21**) have been the subject of synthetic and theoretical interest for more than 20 years.[139−141] However, until now only a few examples of this class of compounds have been synthesized while many of them, and in particular the unsubstituted derivative (**21**, R = H) are unstable and have only been detected by trapping experiments as cycloaddition products.[141]

The corresponding oligomers and polymer have been theoretically evaluated but there was little

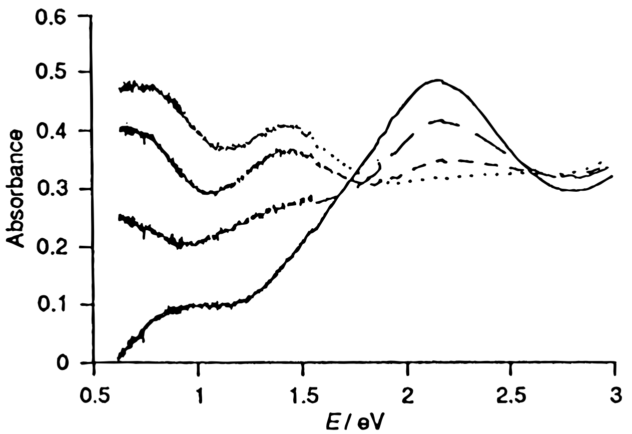
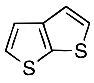
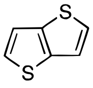
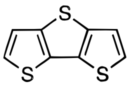


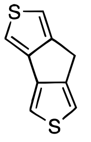
**Figure 4.** Electronic absorption spectra of poly(**20**) film recorded in situ during the electrochemical doping: (—) (neutral, (···) full doped. (Reprinted from ref 137. Copyright 1994 Royal Society of Chemistry, UK.)

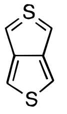
agreement between the reported results which predicted that the bandgap would be smaller,[95] or larger[142,143] than that of poly(**8**). However, owing to the very limited stability of **21** it may take time before this polymer can be effectively synthesized. Thieno[3,4-*b*]thiophene (**22**) was synthesized 20 years ago by Wynberg et al.[144] This compound which was unstable in air exhibited a *ca.* 0.50 eV red shift of the absorption edge compared to the parent molecules **17** and **18.** While the corresponding polymer is still to be synthesized, it has already been theoretically considered and bandgaps of 1.54 and 1.63 eV have been calculated for the aromatic and quinoid forms respectively.[142]

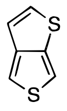

**17**


**18**


**19**


**20**


**21**


**22**

## V. *π*-Conjugated Precursors

The use of conjugated oligomers as precursors for the electrochemical synthesis of PT has been considered early.[11,12] This approach is motivated by two main reasons. First, since the starting molecule already contains exclusive α−α′ linkages, the resulting polymer can be expected to contain fewer α−β′ conjugation defects than that prepared from a monomeric precursor. Second, as the oxidation potential of the precursor decreases with conjugation and hence with chain length,[145] electropolymerization will require less positive potentials, thus limiting possible side reactions of the cation radical, or overoxidation of the deposited polymer at high potentials.[146,147] However, both theory and experiment have shown that the increase in conjugation in the precursor molecule results in a rapid loss of reactivity of the corresponding cation radical,[148,149] and thus in progressive inhibition of electropolymerization.[150−154]

With these limits in mind, the conjugated precursor approach presents several advantages such as the possibility of designing sophisticated precursor structures combining building blocks with different electronic properties.

### A. Terthienyls

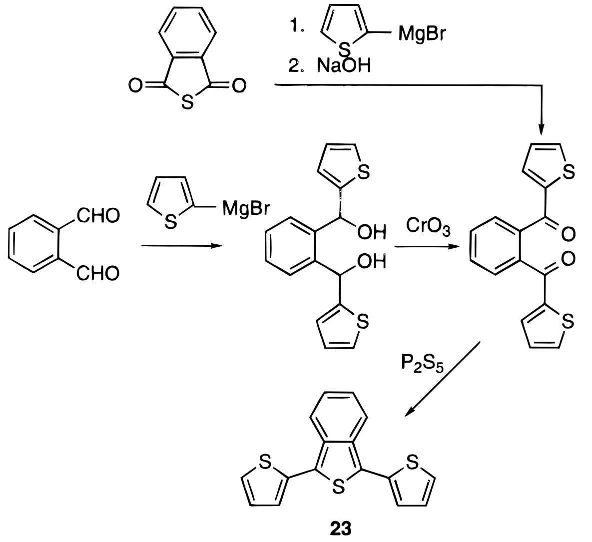
The use of terthienyls as precursors for electropolymerization has been widely investigated.[12] While noticeable improvement in effective conjugation and conductivity have recently been achieved by the grafting of solubilizing side chains,[154,155] or by the use of chemical polymerization,[155,156] it is generally acknowledged that terthienyls are not the most appropriate precursors for improving the structural definition and conductivity of PTs.[148−154] In spite of these inherent reactivity problems, trimeric precursors have drawn renewed attention in the context of small bandgap polymers. In fact, the insertion of a tailored ring system into the middle of a trimeric precursor presents several advantages such as the construction of alternate donor and acceptor moieties or the stabilization of rather unstable fused ring systems. This allows an initial evaluation of their impact on the electronic properties of the LCS.

An early application of this idea was illustrated by **23** in which ITN is used as the median ring system. The synthesis of **23** was reported almost simultaneously by four groups, according to the procedures depicted in Scheme 8.[101,157−159]

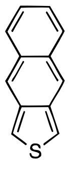
The oxidation potential of **23** was lower than that of terthienyl (0.80 vs 1.05 V/SCE) and the CV exhibited some reversibility indicative of a rather stable cation radical. Electropolymerization by repetitive potential scans led to a poorly conductive polymer ($\sigma = 5 \times 10^{-3}$ to $10^{-2}$ S $cm^{-1}$)[157,159] as is generally observed for poly(terthienyls).[150,152] The absorption edge of the neutral polymer led to an estimated bandgap of 1.70 eV,[157,159] a value intermediate between those of PT and PITN.

Poly(isonaphthothiophene) (poly(**24**)) has been considered in several theoretical works. There is how-

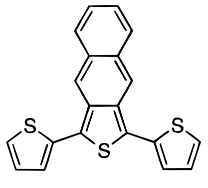
**Scheme 8**



ever little agreement among the various predicted bandgap values that extend from 0.10 to 1.55 eV.[96,143,160−163] While this polymer is still to be synthesized, a terthienyl containing a central isonaphthothiophene (**25**) was recently prepared using the general route employed for the synthesis of **23**.[164]



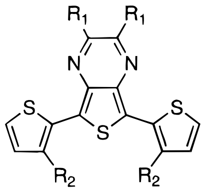
**24**



**25**

Compared to the parent **23**, **25** exhibits a considerable shift of $\lambda_{max}$ (546 vs 427 nm) and a much lower oxidation potential (0.62 vs 0.87 V respectively). Furthermore the CV waves appear rather symmetric which is characteristic of a stable cation radical. Electrodeposition was performed by repetitive potential scans. The CV of the resulting polymer was similar to that of poly(**23**) and suggests an incomplete polymerization. Although a bandgap as low as 0.65 eV has been claimed, in agreement with some theoretical predictions,[161,162] this result was not unequivocally confirmed by the optical spectra.

In order to reduce steric interactions between the fused benzene ring and the adjacent thiophene rings in **23**, Yamashita et al. have synthesized a series of trimers containing a median thieno[3,4-*b*]pyrazine ring system (**26**−**30**).[165] These compounds were prepared from 3′,4′-dinitroterthienyl using a procedure similar to that used for the synthesis of **16**.[124]



**26** $R_1 = R_2 = H$
**27** $R_1 = Me, R_2 = H$
**28** $R_1 = C_6H_{13}, R_2 = H$
**29** $R_1 = C_{13}H_{27}, R_2 = H$
**30** $R_1 = R_2 = C_6H_{13}$

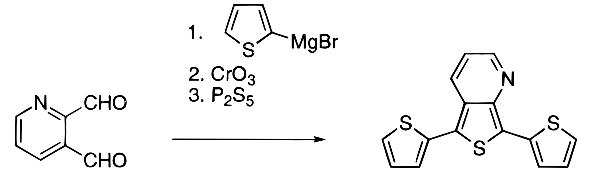
The electronic absorption spectra of **26**−**30** show appreciable red shifts compared to **23** with $\lambda_{max}$ ranging from 484 nm for **30** to 529 nm for the unsubstituted **26.** These compounds are irreversibly oxidized at 0.80−1.00 V/SCE, depending on substitution and reversibly reduced in the −1.10 to −1.50 V region. These moderately negative reduction potentials have been attributed to the electron-withdrawing effects of the thieno[3,4-*b*]pyrazine moiety.[165]

Except for **30** in which the alkyl chains ($R_2$) induce a large steric hindrance to planarity, all compounds could be electropolymerized by repetitive potentials scans and the bandgaps of the polymers estimated from electrochemical and optical data were in the range of 1.00−1.50 eV.[165]

The problem of steric interactions in this particular system has been analyzed in more detail by Ferraris et al. who synthesized 2,5-di(2-thienyl)pyridino[*c*]thiophene **31** (Scheme 9).[166]

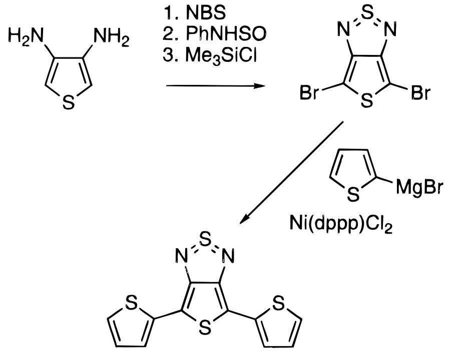
The single-crystal X-ray structure of **31** revealed a small dihedral angle between the median moiety and the thiophene ring on the nitrogen side (*ca.* 3.5°) and a much wider angle of 39° on the CH side. This result confirmed that introduction of nitrogen in the six-member heterocycle reduces steric interactions with adjacent thiophene rings. This compound oxidizes at 0.52 V/SCE, *i.e.* 0.28 V less positive than **23**. Polymerization by repetitive potential scans led to a polymer with a bandgap of 1.40 eV.[166]

**Scheme 9**



**31**

**Scheme 10**



**32**

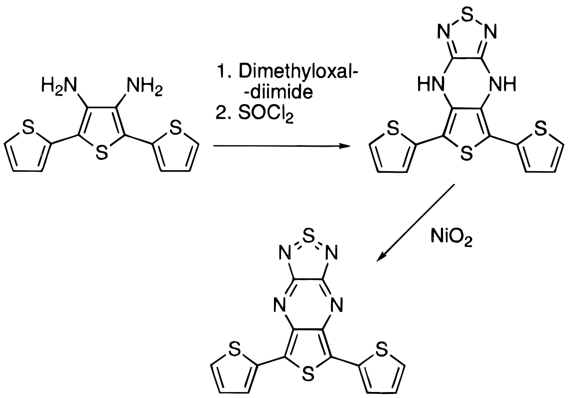
Yamashita et al. have synthesized another trimeric fused-ring system built around a thieno[3,4-*c*][1,2,5] thiadiazole median ring (**32**) (Scheme 10).[167] This system was selected on the basis of the lower HOMO−LUMO gap of thienothiadiazole (TTD) compared to isothianaphthene **8**. Thus TTD shows its lowest $\pi-\pi^*$ transition at 415 nm instead of 343 nm for **8**.[89,139] Furthermore, it was expected that the short intermolecular S···N contacts already observed in the solid state for other series of compounds containing the thiadiazole unit[168] could contribute to controling the structural order in the polymer.

The X-ray structure of **32** shows that the three rings in the molecule are nearly coplanar with intramolecular distances between the nitrogen atoms and the sulfur of the adjacent thiophene (3.13 Å) shorter than the sum of the van der Waals radii (3.35 Å). The molecule showed small $\Delta E$ with the lowest $\pi-\pi^*$ transition at 618 nm and oxidation and reduction potentials at +0.85 and −0.93 V/SCE, respectively. Electropolymerization produced a polymer with a $\lambda_{max}$ at 934 nm in the neutral state and a bandgap of *ca.* 0.90 eV. This small $E_g$ value was confirmed by CV which showed oxidation and reduction peaks at +0.70 V and −1.10 V/SCE with a 0.90 V difference between the threshold potentials for p- and n-doping.[167]

These authors have extended this approach to the synthesis of other trimeric precursors. Thus, **33** in which a tricyclic median ring system was used as electron-deficient unit was described in a short conference paper (Scheme 11).[169]

This compound exhibits an even smaller $\Delta E$ value than the parent **32** with the lowest $\lambda_{max}$ at 990 nm and oxidation and reduction potentials at +0.87 and −0.19 V/SCE. The reduced form shows spectral

**Scheme 11**



**33**

features quite comparable to terthienyl thus underlining the major influence of the pyrazine moiety in the internal charge-transfer process. As expected, the resulting electrogenerated polymer exhibits a very narrow electrochemical bandgap with a *ca.* 0.30 V potential difference between the onset for oxidation and reduction (Figure 5).

The low-energy absorption edge of the optical spectrum was observed below 0.50 eV which is the smallest bandgap value reported so far.

More recently the same group reported the synthesis of **34** (Scheme 12), in which a benzobis(1,2,5-thiadiazole) acts as the electron-withdrawing moiety.[170]

Compound **34** exhibits a larger HOMO−LUMO gap than **33** with a $\lambda_{max}$ at 702 nm and oxidation and reduction potentials at +0.95 and −0.53 V/SCE, respectively. However, the electronic absorption spectrum of the polymer electrodeposited on ITO was quite similar to that of poly(**33**) with a bandgap equal to or slightly lower than 0.50 eV.[170]

These various examples show that trimeric precursors offer interesting opportunities to built up complex molecular architectures combining moieties of different electronic properties and in some cases of limited stability. This approach has been successfully applied to several hybrid ring systems leading to polymers with bandgaps among the smallest so far reported.

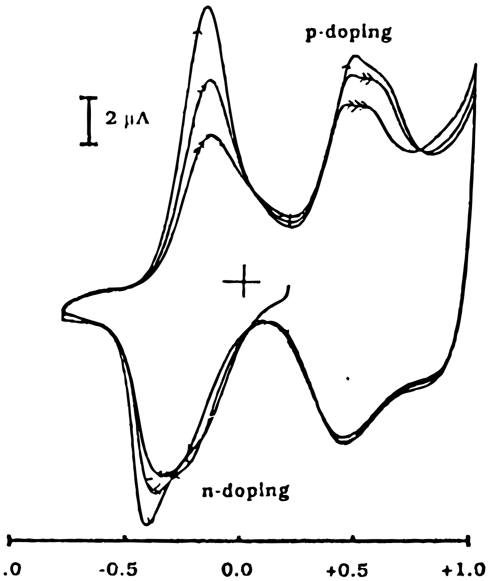
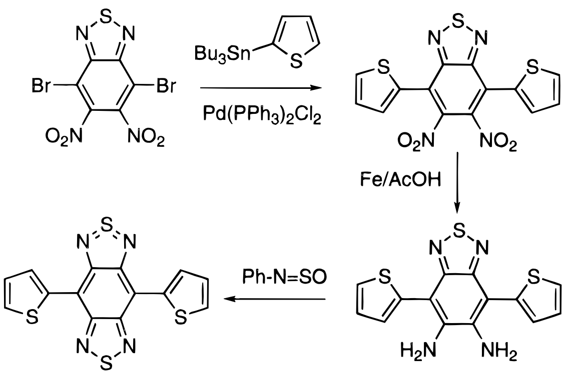


**Figure 5.** Cyclic voltammogram of poly(**33**) at a Pt electrode in 0.1 mol L$^{-1}$ $Bu_4NClO_4$/PhCN, scan rate 10 mV s$^{-1}$. (Reprinted from ref 167. Copyright 1995 Elsevier Science SA, Lausanne, Switzerland.)

**Scheme 12**



**34**

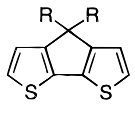
However, the scope of this approach has two important limitations. On the one hand the poor reactivity of the radical cation derived from conjugated precursors with high-lying HOMO level can limit the efficiency of electropolymerization. On the other hand, the dilution effect resulting from the insertion of the active moiety between two thiophene rings (*i.e.* four in the resulting polymer) may in some cases, limit the reduction of $E_g$ to values intermediate between those of the two constitutive building blocks.

## B. Bithienyls

Bithiophene (BT), which was the first thiophene derivative to be electropolymerized,[11] remains an interesting precursor combining good film-forming properties with a moderate oxidation potential (1.30 V/SCE).

Until now, BT-based precursors of electrogenerated small bandgap CPs have been limited to a few examples built on bridged bithiophenes.

Cyclopenta[2,1-*b*:3′,4′-*b*′]dithiophene (**35**), was synthesized in the late 1960s by two groups.[171,172]

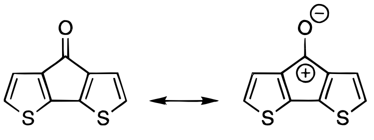


R = alkyl

**35**

The electropolymerization of unsubstituted **35** has been briefly mentioned in two papers that underline its low oxidation potential and the relatively high conductivity of the resulting polymer.[173,174] Recently, the synthesis of derivatives of **35** substituted by alkyl chains at the bridging carbon has been reported and the detailed characterization of the resulting electrogenerated polymers confirmed the extensively conjugated structure of these materials.[175] While this work was conducted for a quite different purpose, the reported electrochemical and optical characteristics of these polymers revealed that they have smaller bandgaps than poly(BT), thus providing a first clue on the effects of bridging the two thiophene rings.

Bithiophenes gained a renewed interest as precursors in 1991 when Ferraris et al. reported that electropolymerization of cyclopenta[2,1-*b*:3′,4′-*b*′]-dithiophen-4-one (**36a**) led to a polymer with a bandgap of 1.10−1.20 eV.[176]



**36a** **36b**

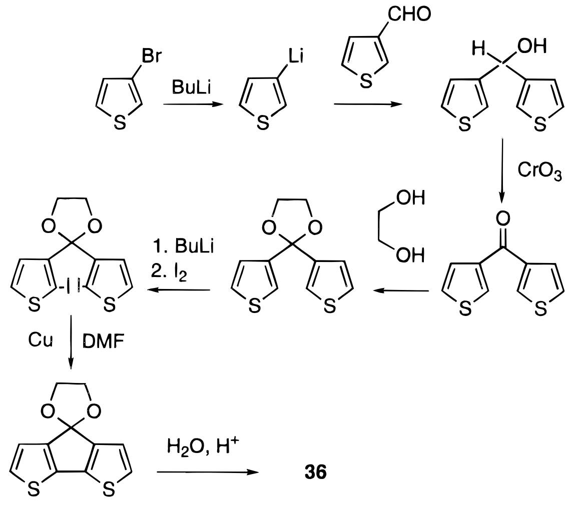
This approach was based on the idea that the electron-withdrawing effects of the ketone group and contribution of the primary resonance form **36b** should decrease the aromaticity of the system and hence increase the quinoid character of the polymer. In fact the wavelength of the lowest $\pi-\pi^*$ transition of **36** at 474 nm indicates a smaller $\Delta E$ than for BT ($\lambda_{max} = 300$ nm).[177] The oxidation potential of **36** was slightly higher (40−60 mV) than that of bithiophene,[176,178] indicating that the carbonyl group has only a moderate effect on the energy level of the HOMO. Similar small differences were found between the oxidation potentials of the electrodeposited polymers namely 0.85 vs 1.00 V/SCE for poly(bithiophene).[176,178] The bandgap value determined by spectroelectrochemical experiments was 1.10−1.20 eV,[176] a value confirmed by CV.[178]

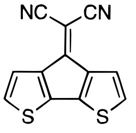
Ketone **36**, synthesized in 1970 by Wynberg et al.[179] (Scheme 13) now occupies a special position since all bithiophenic precursors of small bandgap PTs reported so far are derivatives of this molecule.

The first example involved the electropolymerization of 4-(dicyanomethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**37**), prepared by Knoevenagel condensation of **36** with malononitrile.[180]

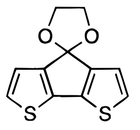
Compared to **36**, the stronger electron-withdrawing effects of the dicyanomethylene group lowers the LUMO level and leads to a decrease in $\Delta E$ confirmed by the 100 nm red shift of the longest absorption maximum. This absorption band was assigned to a $\pi-\pi^*$ transition by analogy with **36** and also on the basis of solvatochromic effects.[180] The optical spectrum of poly(**37**) was strongly reminiscent of that of poly(**36**) with the emergence of a new absorption band extending to the near IR and with a long wavelength band edge at *ca.* 0.80 eV (Figure 6). The small difference observed between the onset potential for p- and n-doping was consistent with this low gap value.[180]

**Scheme 13**

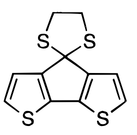




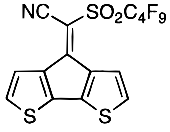
**37**



**38**



**39**



**40**

Theoretical calculations on a geometric structure optimized by semiempirical techniques led to the conclusion that introduction of the dicyanomethylene group at the sp$^2$-bridging carbon induces major geometrical changes within each ring resulting in a structure which can be viewed as a combination of aromatic and quinoid geometries.[181] The small $E_g$ value calculated for poly(**37**) (0.59 eV) was related to HOMO and LUMO levels located between those of aromatic and quinoid PT chains.[181] On the basis of the same methodology, it has been suggested that poly[(dicyanomethylene)cyclopentadicyclopentadiene] should exhibit an even smaller bandgap of 0.16 eV.[182]

The synthesis of 4-[cyano[(nonafluorobutyl)sulfonyl]methylidene]cyclopenta[2,1-*b*:4,3-*b*′]dithiophene (**40**) was recently described.[183] Similar to poly(**36**) and poly(**37**), the electronic absorption spectrum of the neutral electrogenerated poly(**40**) exhibits a bathochromic extension toward the near IR leading to an estimated bandgap of 0.67 eV.[183]

The above results may lead to the conclusion that a significant reduction of $E_g$ in this type of polymer requires introduction of strong electron-withdrawing group at the sp$^2$-bridging carbon. This hypothesis is however contradicted by several recent examples. Thus, omission of the last hydrolysis step during the synthesis of ketone **36** (Scheme 13) afforded the dioxolane **38** which had not been isolated so far. This compound can be easily electropolymerized and the CV of the resulting polymer exhibits a potential difference betwen oxidation and reduction consider-

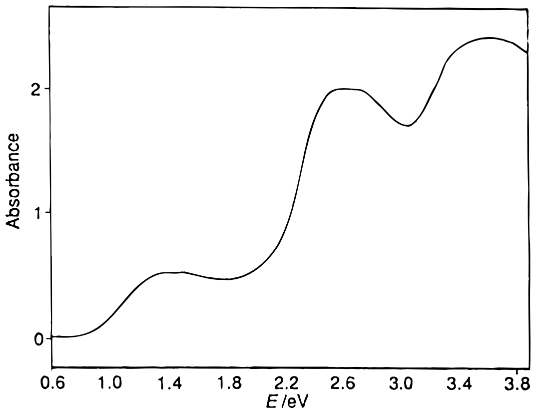


**Figure 6.** Electronic absorption spectrum of poly(**37**) on ITO. (Reprinted from ref 180. Copyright 1991 Royal Society of Chemistry, UK.)

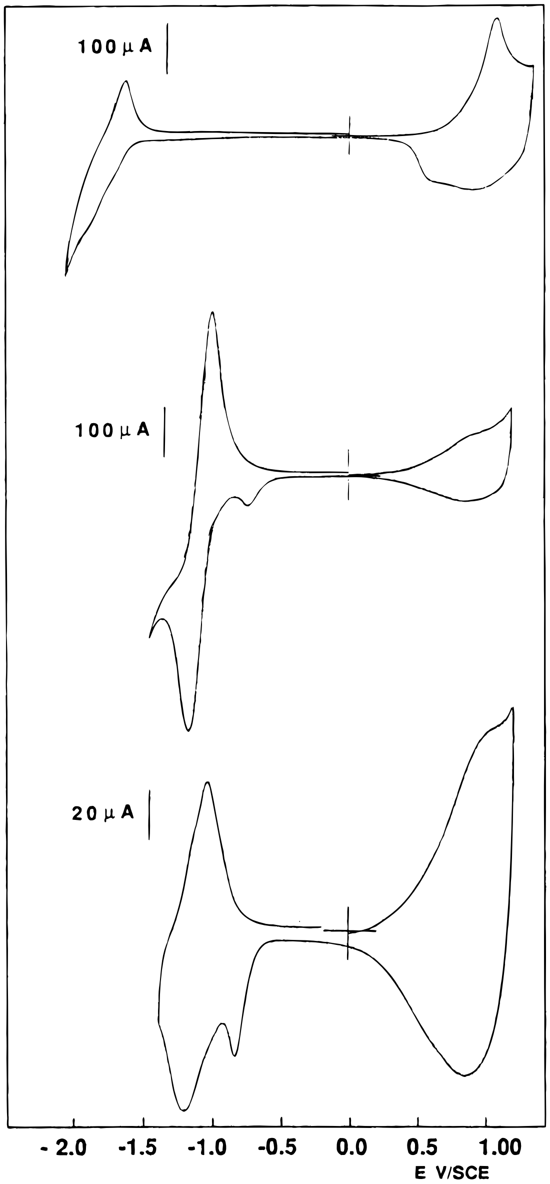


**Figure 7.** Cyclic voltammogram recorded in 0.10 mol $L^{-1}$ $Bu_4NPF_6$/MeCN, scan rate 100 mV $s^{-1}$: (top) PBT; (middle) poly(**36**); (bottom) poly(**38**). (Reprinted from ref 178. Copyright 1994 Royal Society of Chemistry, UK.)

ably smaller than for poly(bithiophene) (PBT) and even poly(**36**) (Figure 7).[178]

This small electrochemical gap is partly due to the low oxidation potential of poly(**38**) (0.70 V/SCE vs 0.85 V for poly(**36**), which suggests that the dioxolane group has less influence on the HOMO level than the ketone or dicyano group in **36** and **37**. The narrow bandgap of poly(**38**) is confirmed by its optical spectrum which shows a large red shift of the main absorption band compared to poly(BT) and a low energy absorption edge at 1.10−1.20 eV similarly to poly(**36**) (Figure 8).

As already observed for polyether substituted PTs,[184] the introduction of the dioxolane group leads to a considerable increase in hydrophilicity of the polymer. Consequently, poly(**38**) remains fully electroactive in aqueous medium in striking contrast to PBT and poly(**36**).[185] Compound **39** was prepared by dithioacetalization of ketone **36**. Similar to other thiophenic precursors containing sulfide groups,[186,187] electropolymerization of **39** was difficult and proceeded with low yield. Nevertheless, the electrochemical data of poly(**39**) suggest a bandgap of about 1.40 eV.[185]

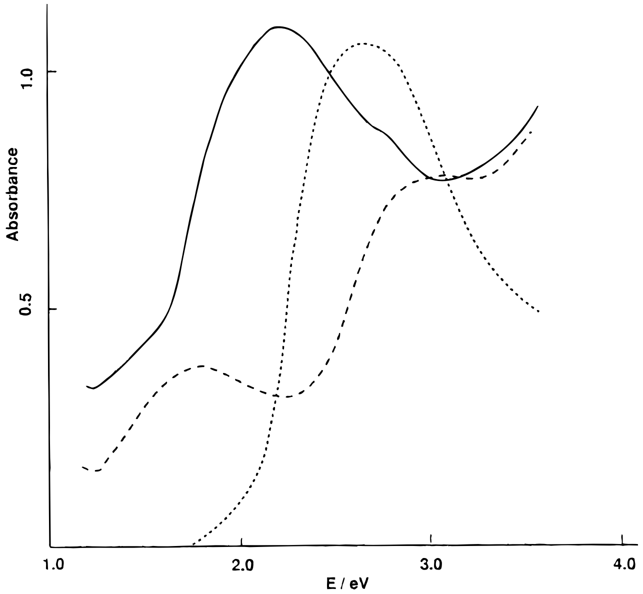
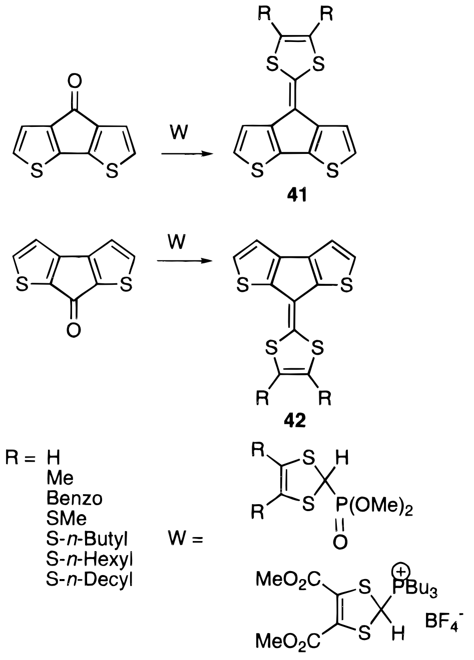


**Figure 8.** Electronic absorption spectra of undoped polymers on ITO: (···) Dotted PBT; (- -) poly(**36**); (—) poly(**38**). (Reprinted from ref 178. Copyright 1994 Royal Society of Chemistry, UK.)

**Scheme 14**



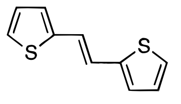
Bithiophenes **41** and **42** have been synthesized by Wittig−Horner or Wittig olefination of thienocyclopentanones with appropriate phosphonates esters or phosphonium salts (Scheme 14).[188−190]

As expected, introduction of the 1,3-dithiole moiety leads to a 0.30−0.50 V decrease in the oxidation potential compared to BT and to a 100 nm red shift of $\lambda_{max}$.[188] Similar trends were observed for the corresponding electrogenerated polymers. However, polymers derived from **42** show higher oxidation potentials and blue-shifted absorption maxima than those derived from **41**.[190] These differences probably reflect the lack of α-conjugation of the two thiophene rings in **42**. Polymers derived from **41** absorb at much longer wavelengths than PBT, (up to 689 nm for R = $CO_2Me$) and exhibit $E_g$ values down to 1.40 eV for R = (*S*)-*n*-hexyl. Some of these polymers show high conductivites, up to 50 S $cm^{-1}$, that have been attributed to the consequences of intermolecular S···S interactions.[190]

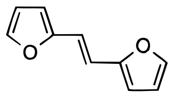
These results as well as those obtained for poly(**38**) and poly(**39**) pose several interesting problems. As a matter of fact, the arguments developed for poly(**36**) and poly(**37**) about the electron-withdrawing effects of the CO and $(CN)_2$ groups cannot be invoked here, and the reduction of $E_g$ must have another origin. Whereas an alternate explanation involving the enhanced planarity and possible decrease of BLA caused by the rigidification of the π-conjugated system has been suggested,[178,191] this question is not fully elucidated yet.

## C. Dithienylethylenes

Conjugated polymers obtained by the electropolymerization of dithienylethylene (**43**)[192,193] or difurylethylene (**44**)[194] have attracted increasing interest recently. As a matter of fact, these polymers constitute interesting models of the corresponding poly(heteroarenevinylenes) while preserving the advantages of electropolymerization in terms of rapidity and straightforward electrochemical and spectroelectrochemical characterization. As for poly(arylenevinylenes) or poly(heteroarylenemethines) (see section VI), these polymers can be viewed as a combination of the structures of $(CH)_x$ and polyaromatic CPs.



**43**

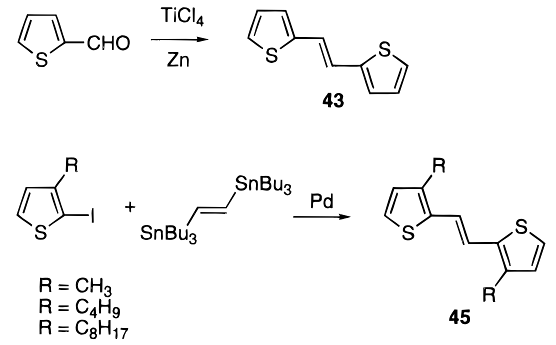


**44**

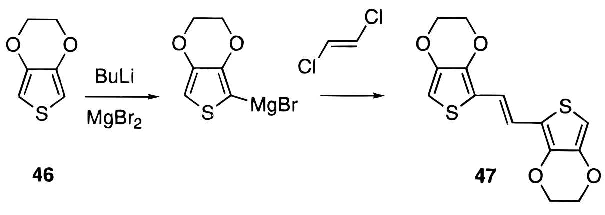
As already discussed, a major drawback of extensively π-conjugated precursors lies in the enhanced stability of the corresponding radicals which exerts deleterious consequences for the electropolymerization process. Thus, electropolymerization of **43** was initially reported as producing only poorly conductive powdery deposits.[195] Optimized electrodeposition conditions, low current densities, and the use of propylene carbonate as solvent led to free-standing films with conductivities up to 15 S $cm^{-1}$ and a bandgap of 1.80 eV.[196,197]

While **43** was obtained by McMurry coupling of thiophene-2-carboxaldehyde,[192,193] 3-alkyl substituted analogs (**45**) have been synthesized by Pd-catalyzed coupling of 1,2-bis(tri-*n*-butylstannyl)ethene with the appropriate 3-alkyl-2-iodothiophene[198] (Scheme 15). These precursors were polymerized either electrochemically or chemically using $FeCl_3$ leading to soluble polymers. Electrogenerated films presented better optical characteristics with an optical bandgap of 1.70 eV.[198,199] Analysis of the thermochromic properties of these polymers did not provide evidence for temperature-dependent distortion of the conjugated backbone, thus confirming that these polymers are as expected, more rigid than poly(3-alkylthiophenes).[200]

**Scheme 15**



**Scheme 16**



3,4-(Ethylenedioxy)thiophene (**46**) was initially synthesized in 1970 as a potentially active anticarcinogen agent.[201] This compound has recently become a focus of considerable attention when it was shown that the corresponding polymer exhibits an exceptional stability in the doped state associated with high conductivity and a low optical bandgap (1.60−1.70 eV).[202,203]

(*E*)-1,2-Bis-[3,4-(ethylenedioxy)thiophen-2-yl]ethylene (**47**) has been prepared by nickel-cataylzed coupling of the Grignard reagent of **46**, obtained by transmetalation of the 2-lithio derivative, with *trans*-dichloroethylene (Scheme 16).[204] Electropolymerization afforded an electroactive polymer with an optical bandgap of 1.40 eV (Figure 9).

It has been shown that introduction of an electron-withdrawing cyano group at the olefinic linkage of poly(phenylenevinylene) led to polymers with high electron affinity.[205−207] This property has been used in the fabrication of electroluminescent diodes in which electron injection could be ensured by stable metal electrodes.[19,20,208] Using a similar approach, a further reduction of the bandgap of poly(**43**) was recently accomplished by the synthesis of diheteroareneethylene precursors with a cyano group at the ethylene linkage **48**−**50**. These compounds were

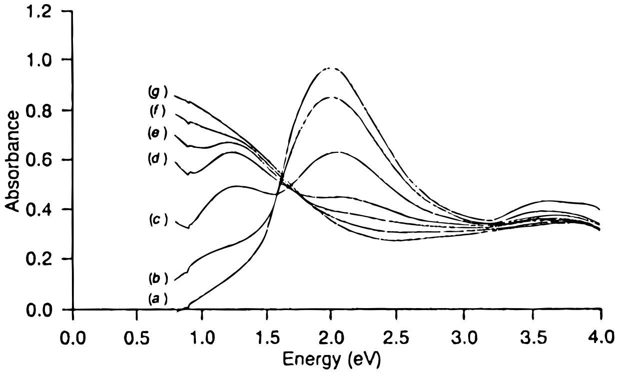
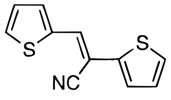
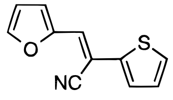
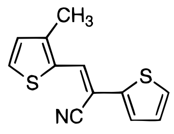


**Figure 9.** Electronic absorption spectra of poly(**47**) on ITO taken at (a) −1.3, (b) 0.0, (c) 0.1, (d) 0.2, (e) 0.3, (f) 0.4, (g) 0.5 V vs Ag/Ag$^+$. (Reprinted from ref 204. Copyright 1995 Royal Society of Chemistry, UK.)

obtained by Knoevenagel condensation of 2-thiopheneacetonitrile with the appropriate thiophene- or furan-2-carboxaldehyde.[209]


**48**


**49**


**50**

While the presence of a methyl group on the thiophene ring (**50**) has deleterious consequences for the electropolymerization, incorporation of furan into the structure (**49**) greatly improves the film-forming properties allowing deposition of free-standing films with a conductivity of 4.8 S $cm^{-1}$. This value, which is considerably higher than those reported for poly(**44**),[210,211] shows that the association with thiophene contributes to limiting the anodic overoxidation of furan. Poly(**48**−**50**) show a significant bandgap decrease compared to poly(**43**) or poly(**44**) with $E_g$ values of 1.40−1.50 eV for poly(**49**) and poly(**50**) (Table 1). However, the most significant results were obtained with poly(**48**) which exhibits an extension of the absorption edge down to *ca.* 0.50 eV (Figure 10). The potential difference between the onset for oxidation and reduction (less than 0.30 V) is one of the smallest observed so far for a conjugated polymer (Figure 11).[209]

**Table 1. Main Electrochemical and Optical Characteristics of Poly(diarylethylenes)**

| precursor | $E_{ox}$[a] | $E_{red}$[a] | $E_{gap}$ (eV)[b] | σ S ($cm^{-1}$) | ref |
|---|---|---|---|---|---|
| **43** | | | 1.80 | 15 | 196 |
| **43** | 0.98 | | 1.80 | $10^{-2}$ | 197 |
| **44** | 0.74[c] | | >2.50 | $10^{-6}$ | 210 |
| **44** | 0.58 | | 2.20 | 0.32 | 211 |
| **45** | | | 1.70 | $10^{-1}$ | 199 |
| **47** | | | 1.40 | | 204 |
| **48** | 0.55 | −0.10 | 0.50−0.60 | 0.07 | 209 |
| **49** | 1.00 | −1.06 | 1.40 | 4.8 | 209 |
| **50** | 0.60 | −0.50 | 1.50 | | 209 |
| **58** | 0.58 | | 1.40 | $10^{-2}$−$10^{-1}$ | 197 |

[a] In V vs SCE. [b] Optical. [c] vs Ag/AgCl.

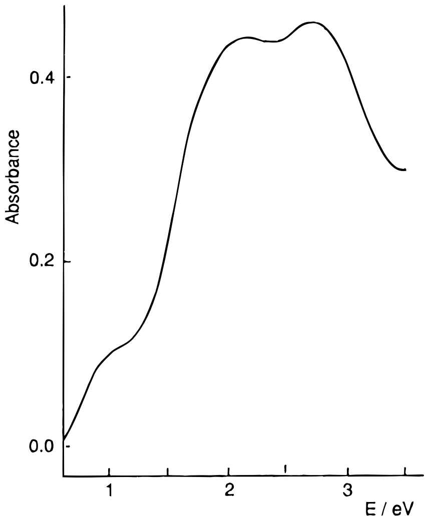


**Figure 10.** Electronic absorption spectrum of undoped poly(**48**) on ITO. (Reprinted from ref 209. Copyright 1995 Royal Society of Chemistry, UK.)

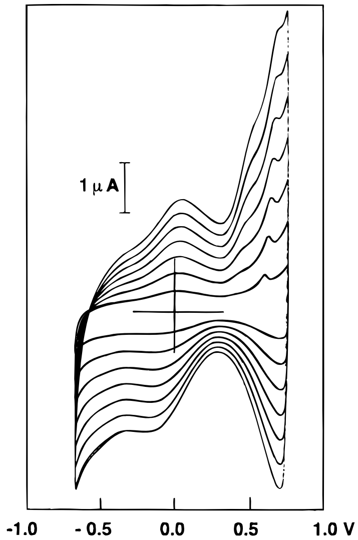
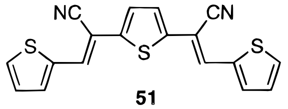
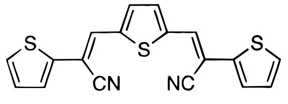
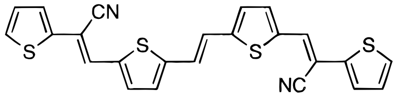


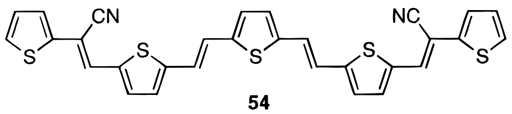
**Figure 11.** Cyclic voltammograms of poly(**48**) on Pt in 0.1 mol $L^{-1}$ $Bu_4NPF_6$/MeCN, scan rate 50−300 mV $s^{-1}$ by increment of 50 mV $s^{-1}$. (Reprinted from ref 209. Copyright 1995 Royal Society of Chemistry, UK.)

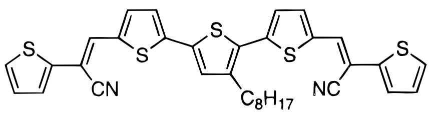
A recent extension of this strategy has concerned the synthesis of oligomers **51**−**56**. All these compounds undergo electrochemical reduction at moderately negative potentials (*ca.* −1.10 V/SCE) however, the position of the CN group and the extent of conjugation strongly affect the electroreduction behavior.

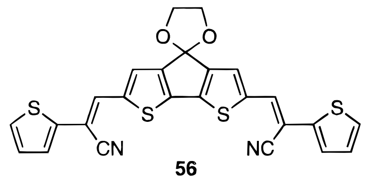

**51**


**52**


**53**


**54**


**55**


**56**

Thus, whereas reduction of **51** is irreversible, **52** is reversibly reduced to the dianion state through two successive one-electron steps, while for the longer oligomers **53**−**56**, these two waves merge into a

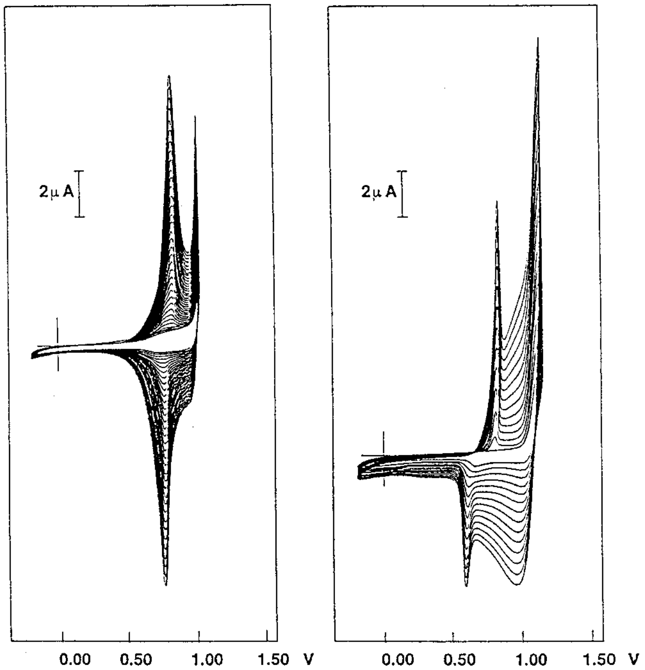
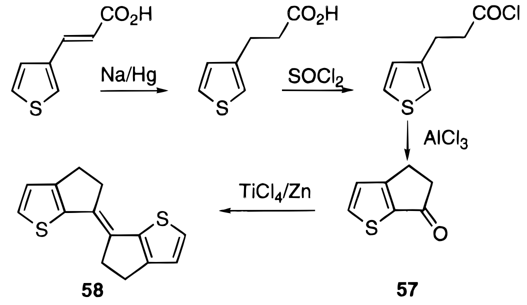


**Figure 12.** Potentiodynamic electrodeposition curves for **56** (left) and **55** (right), $10^{-3}$ M in $10^{-1}$ M $Bu_4NPF_6/CH_2Cl_2$, $v = 100$ mV $s^{-1}$. (Reprinted from ref 212.)

**Scheme 17**



single step two-electron transfer.[212] Furthermore, whereas **51**−**54** are difficult to polymerize due to their conjugated structure, the grafting of solubilizing alkyl or dioxolane side groups into **55** and **56** combined with the activating effects of the CN substituents allows their facile electropolymerization (Figure 12) into highly cathode-active polymers with a moderate bandgap ($E_g$ = 1.50 eV).[212]

Another interesting approach to reducing the bandgap of poly(**43**) consists in the rigidification of the dithienylethylene molecule by covalent bridging of each thiophene ring with the central double bond as exemplified by **58**.[197] This compound was synthesized by McMurry coupling of the cyclic ketone **57**, obtained in three steps from 3-thienylacrylic acid[213] (Scheme 17).

As could be expected, the bridging of the molecule produces a strong enhancement of the resolution of the vibronic fine structure in the optical spectrum of **58**,[214] and a red-shifted extension of the absorption to *ca.* 460 nm (Figure 13). These changes are accompanied by a decrease in the oxidation potential from 1.10 V to 0.72 V. Compared to poly(**43**), poly(**58**) exhibits a strong decrease in the oxidation potential from 0.98 to 0.58 V and a considerable improvement of reversibility. As shown by the optical spectrum of the polymers (Figure 13), this 0.40 V negative shift of the oxidation potential corresponds to an equal reduction of the bandgap from 1.80 to 1.40 eV. This correlation suggests that the reduction of $E_g$ in this system reflects essentially an increase of the HOMO level.[197]

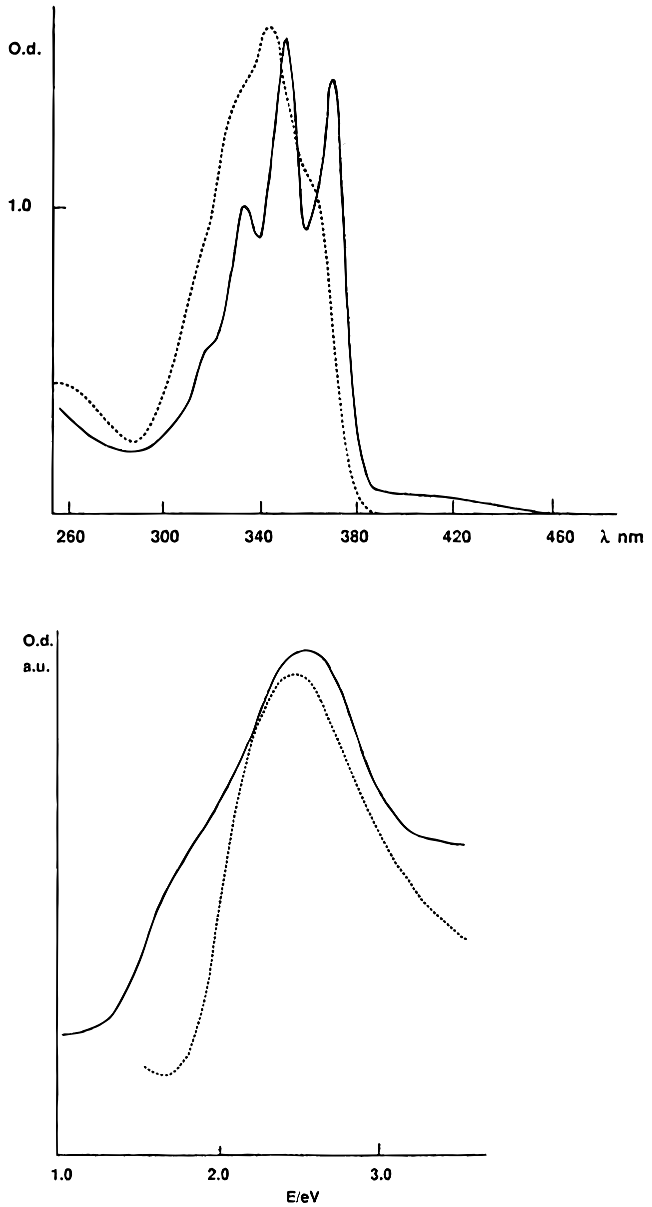


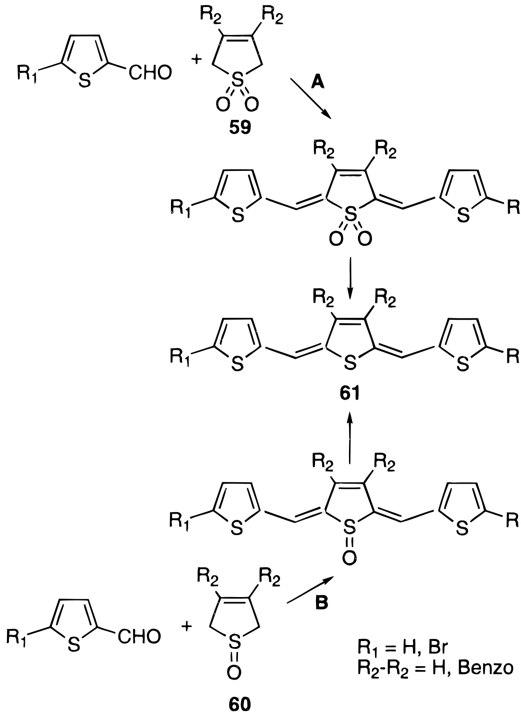
**Figure 13.** Top: UV−vis absorption spectra of **43** (···) and **58** (—) in $CH_2Cl_2$. Bottom: Electronic absorption spectra of undoped poly(**43**) (···) and poly(**58**) (—) on ITO. (Reprinted from ref 197. Copyright 1994 Royal Society of Chemistry, UK.)

The main electrochemical and optical data of poly(diheteroarene-ethylenes) (Table 1) show that with the exception of **48**−**50**, reduction of the bandgap in these systems results from an increase of the HOMO level which leads to $E_g$ values in the range of 1.40 eV. This value which corresponds to the bandgap of $(CH)_x$ has been proposed as the lowest limit of $E_g$ for these polymers.[196] On the other hand, conductivities remain rather low, which reflects the rather delicate electropolymerization of these compounds due, as for other conjugated precursors, to the limited reactivity of their cation radicals.

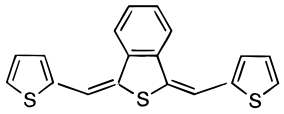
### D. Diheteroarylene Methines

Parallel to the synthesis of poly(heteroarylenemethines) by various elimination routes (see section VI.B), Hanack et al. have developed another approach based on the preparation of short chain conjugated precursors already containing the desired methine linkage.[215−219] These precursors have been synthesized by Knoevenagel type condensation of thiophene or pyrrole-2-carboxaldehyde with dihydrothiophene sulfones **59** (Scheme 18, route A) or with sulfoxides **60**, (route B) possibly substituted at the 3- and 4-positions.

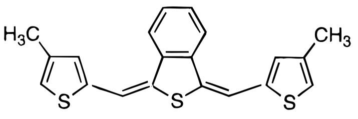
**Scheme 18**



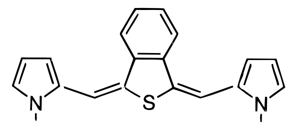
In the case of unsubstituted sulfones, reduction to the sulfide state (**61**) could not be achieved and the sulfoxide route was the preferred one.[215] Whereas a large number of precursors have been synthesized,[216,217] only a few examples of the corresponding polymers have been briefly described.[218,219]



**62**



**63**



**64**

Compounds **62**−**64** were polymerized electrochemically. However, as indicated by the quasireversibility of their oxidation CV, these extensively conjugated precursors lead to rather stable cation radicals. Consequently, electropolymerization appears essentially limited to the formation of a dimer containing significant amounts of starting material. This conclusion is confirmed by the similarity of the optical spectra of the polymer and of the precursor, that both exhibit a $\lambda_{max}$ around 450 nm and an $E_g$ value of *ca.* 2.0 eV.[219]

While the properties of these polymers are far from exciting, in contrast the small $\Delta E$ values of the precursors look very promising and clearly demonstrate the efficiency of the incorporation of methine linkages into the LCS.

To summarize, conjugated precursors are interesting models that have established the impact of multiple structural modifications on the bandgap of LCSs. Furthermore, as shown by several examples, this approach allows the incorporation into the conjugated chain of rather unstable ring systems capable of strongly influencing the magnitude of the bandgap. However, the counterpart of this efficiency at the level of the precursor molecule is a considerable loss in reactivity of the resulting cation radicals which results in incomplete or even fully inhibited electropolymerization. The conjugated precursor approach appears therefore a contradictory strategy. The more effective it is at the molecular level the less efficient it is at the macromolecular polymer scale. Consequently, in view of the considerable reduction of $\Delta E$ observed in some tailored conjugated precursors, it seems that a chemical synthesis of oligomers containing a limited number of these precursor molecules would probably be much more efficient in terms of gap reduction than their electropolymerization.

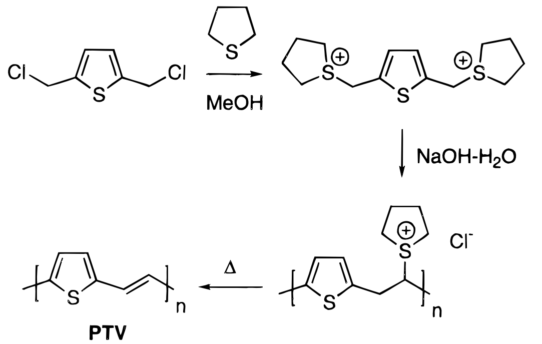
## *VI. Polymeric Precursors*

Polymers involving various associations of olefinic and aromatic substructures such as poly(arylenevinylenes) and poly(arylenemethines) form important classes of CPs that have undergone considerable developments. In spite of their different structures these polymers have the fact in common that they are generally synthesized by means of an elimination reaction from a polymeric nonconjugated polymer.

### A. Poly(arylenevinylenes)

The discovery of electroluminescence in poly(phenylenevinylenes) (PPVs)[16] has justified the wide current interest in these polymers and in their smaller bandgap parent poly(thienylenevinylene) (PTV) and poly(furylenevinylene) (PFV). PPVs were initially prepared by means of the polymerization of bis[(halomethyl)benzenes][220] by Wittig olefination[207,221,222] or Knoevenagel condensation.[206] However, these various routes gave essentially low molecular weight insoluble and infusible materials. An important step in the development of these polymers occurred with the soluble precursor route.[223−226] This method which was then extended to other polymers such as PTV[227−229] and PFV,[230] involves the synthesis of a polyelectrolytic nonconjugated polymer by condensation of 2,5-bis(chloromethyl)thiophene or -furan

**Scheme 19**



with tetrahydrothiophene followed by thermal conversion to the corresponding conjugated polymer (Scheme 19).

An alternative method involving hydrogen abstraction from poly(2,5-thienyleneethylene) has also been reported.[231] While more recently a PTV dimethoxy-substituted at the vinylene linkage has been prepared by benzoin condensation of thiophene dicarbaldehyde followed by deprotonation and oxymethylation.[232] Another soluble PTV derivative obtained by McMurry coupling of 3,4-dibutoxythiophene-2,5-dicarbaldehyde has also been described.[233]

Several works have shown that PTV and PFV exhibit smaller bandgaps than their purely polyaromatic parent PT and poly(furan). Thus PTV shows a bandgap of 1.70−1.80 eV[227,234] *ca.* 0.4 eV smaller than PT and close to the value of 1.60 eV calculated using the VEH method.[235] A bandgap of 1.76 eV has been reported for PFV,[230] considerably smaller than that of poly(furan).[236]

Whereas in the case of furan-based polymers this difference is mainly due to the overoxidation of the furan ring in poly(furan), the smaller PTV bandgap compared to that for PT is the result of two effects (i) a decrease in the overall aromatic character of the $\pi$-conjugated system, allowing a better delocalization of $\pi$-electrons over the whole polymer chain, and (ii) a limitation in rotational disorder due to the presence of ethylenic linkages of defined configuration. Attempts at reducing the PTV bandgap have given rise to various structural modifications, and it has been shown that introduction of an alkoxy group at the 3- or 3- and 4-positions of the thiophene ring could lead to a significant decrease of $E_g$.[237] Thus, as has been reported recently, the electronic absorption spectra of poly(3,4-dibutoxythienylenevinylene) and other dialkoxy substituted PTVs synthesized by an improved thermal elimination route exhibit a marked red shift of $\lambda_{max}$ to 700 nm and a broad absorption band extending into the near IR and leading to an estimated bandgap of 1.20 eV (Figure 14).[238]

## B. Poly(heteroarylenemethines)

Poly(heteroarylenemethines) are another class of LCSs based on the association of aromatic and olefinic moieties. These polymers differ from poly(arylenevinylenes) in that a variable proportion of the aromatic moieties are converted into a quinoid form. These polymers were proposed as low bandgap LCSs by Jenekhe in 1986.[239] The idea was based on theoretical considerations which led to the conclusion that the quinoid form of PT should possess a significantly smaller bandgap than the aromatic form[33,240] and that poly(arylenemethines) should exhibit small bandgaps.[241,242] Thus, by forcing some parts of the $\pi$-conjugated system to adopt a quinoid geometry and by mixing the aromatic and quinoid forms in variable proportions, one should, in principle, be able to tune the bandgap between the two limiting values.[239] The small bandgap expected for this class of conjugated polymers has been confirmed in a number of theoretical works,[243−247] while much effort has been devoted to their synthesis. Since the initial reports on poly(methines), thiophene derivatives have been used as substrates because of the relatively small PT bandgap.[239] Poly(thiophenemethylidenes) were obtained by the condensation of a thiophene oligomer with an aldehyde followed by an elimination reaction (Scheme 20). A bandgap as low as 0.75 eV, which was at that time the smallest known value of $E_g$ for an organic polymer, was claimed.[239] However, the structure of the polymer obtained and the reality of bandgap reduction have been subject to controversy and, since dehydrogenation was achieved with bromine,[248] it has been suggested that the resulting polymers were partially brominated and doped with bromine.[249,250] Nevertheless, the effectiveness of this synthetic route has been demonstrated by the synthesis of poly(terthiophenemethylenes) by acid-catalyzed polymerization of terthiophene with aldehydes.[251] This method was recently extended to the synthesis of 20 new polymers containing one to four α-thiophene rings connected by an sp$^3$ carbon bearing variously substituted phenyl groups (**65**).[252] The methylene bridge was preserved only for the polymers containing bithiophenes or higher oligomers, while in the case of single thiophene rings, considerable and even complete dehydrogenation occurred (Scheme 20).[252]

These precursor polymers were then converted into the corresponding poly(thienylenemethines) (**66**) by dehydrogenation using DDQ. The conversion process was effective only for precursors containing bithiophene units, whereas the structure of polymers incorporating longer oligomers remained uncertain.[253]

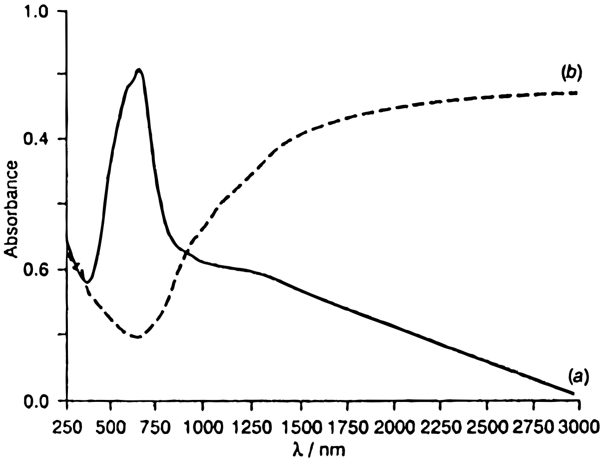
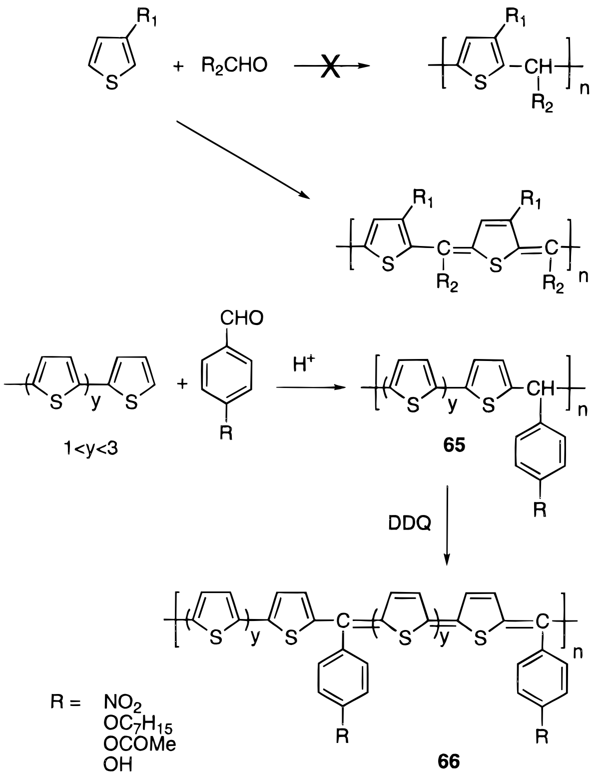


**Figure 14.** Electronic absorption spectra of poly(3,4-dibutoxythienylenevinylene) on ITO: (a) neutral and (b) doped. (Reprinted from ref 238. Copyright 1995 Royal Society of Chemistry, UK.)

**Scheme 20**

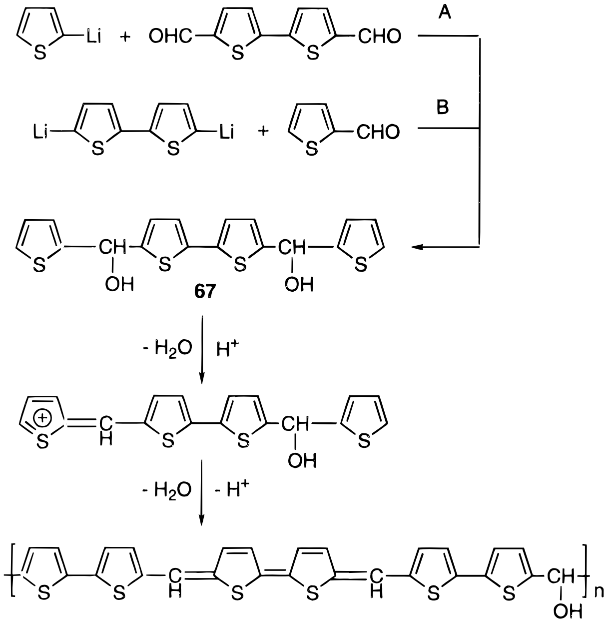


The determination of the polymers bandgaps by electrochemical and optical methods gave consistent results. Polymers with single thiophene rings show $\lambda_{max}$ in the 460−500 nm region and $E_g$ values similar or slightly smaller than that of PT. Incorporation of bithiophene units results in a red shift of $\lambda_{max}$ (580−650 nm) and in a reduction of $E_g$ down to 1.14−1.45 eV, depending on the substitution of the phenyl ring. Compared to hydrogen, *para* substitution by electron-releasing groups leads to smaller $E_g$ while introduction of electron-withdrawing groups has opposite effects. As shown by electrochemical data, the decrease of $E_g$ results mainly from a 0.45−0.60 V decrease of the oxidation potential while the positive shift of the reduction potential was much smaller (*ca.* 0.30 V).[253]

Other groups have developed alternative synthetic routes toward poly(arylenemethines). Early works used the condensation of 2-(chloromethyl)-5-formylfuran with pyrrole or thiophene, or the reaction of α,α,α′-trichloro-*p*-xylene with aromatic compounds in the presence of Friedel−Crafts catalysts.[254] However, the resulting insoluble polymers exhibit a considerable amount of structural defects and low conductivity after doping.[254] Another strategy developed by the same group involved the condensation of 2-lithiothiophene with 2,5′-dithiophenedicarboxaldehyde (Scheme 21 route A) or that of 2,5-dilithiobithiophene with 2-formylthiophene (route B) to give a dicarbinol **67**.[255] Addition of protonic or Lewis acids to solutions of **67** leads to the precipitation of an insoluble black solid which was interpreted as a polymerization of the cation resulting from the monodehydration of the dicarbinol.[255]

Various thiophene- and *N*-methylpyrrole-based polymers have been prepared according to this procedure. The optical spectra of solution-cast films exhibit absorption features in the 800−1500 nm region with absorption edges down to 1600 nm. The polymers were shown to be photoelectrically active with a spectral dependence of photoconductivity following the absorption spectrum. However, owing to uncertainty regarding their exact oxidation state, it was difficult to conclude unequivocally that these polymers have small intrinsic bandgaps.[255] More recently, these authors reported an improved procedure involving the use of a thienyl aryl ketone instead of 2-formylthiophene and isolation of the dicarbinol intermediate.[256] Films were then cast from solutions of the dicarbinols, and after removal of the solvent, the films were treated with trifluoroacetic acid. This process, which led to immediate color change from colorless to deep blue, was interpreted as resulting from a polycondensation reaction as in Scheme 21, although acid doping is also a possibility.[257,258] The optical spectra of the resulting materials show absorption edges as low as 0.60−0.80 eV for aryl-susbstituted polymers. However, the spectrum of the electrochemically reduced polymer showed that the bandgap is probably closer to 1.30−1.40 eV.[256]

**Scheme 21**



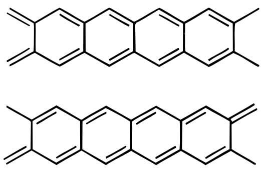
## VII. Ladder Polymers

The synthesis of ladder-conjugated polymers as a mean of reaching low bandgap polymers has been considered in early works.[259,260] Such polymers that can be considered as 1D graphite ribbons, represent a possible strategy for increasing the dimensionality of low dimensional $\pi$-conjugated polymers and hence counterbalance the effects of BLA and Peierls instability.[22,23,30−34]

### A. Polyacenes

Polyacene (**68**) is probably the most famous member of this class of materials. Interest in this material is based on theoretical considerations and also on experimental results obtained for the first members of the oligomer series.[259]

Polyacene can be viewed as a combination of two parallel chains of *trans* $(CH)_x$ fastened together. Due

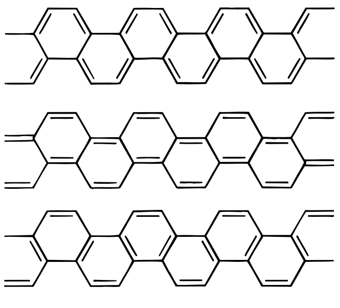


**68**

to its unique structure, this polymer has been the focus of much theoretical interest.[260−267] Kivelson and Chapman proposed that **68** should be metallic and could possibly exhibit superconducting properties.[261] Other works concluded that **68** would not be subject to Peierls distortion and should have a metallic band structure.[262,263] A bandgap of 0.50 eV was calculated by Yamabe et al.[262] while a zero bandgap was predicted by Brédas et al.[264] and Pomerantz et al.,[265] and a value of 0.20 eV was calculated by Kao and Lilly.[266]

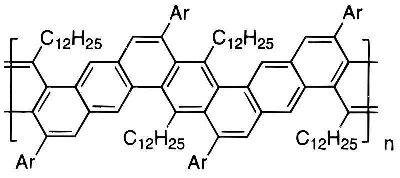
Oligomers of the acene series have been synthesized up to heptacene.[268] Examination of the redox potential and the HOMO−LUMO gap of the first members of the series reveals a sharp decrease of $\Delta E$ from naphthalene to heptacene which suggests that increasing chain length could lead to a very small and perhaps vanishing bandgap.[259,269] Until now heptacene remains the longest known member of the series and despite several attempts leading to materials of unspecified structure,[270−273] the development of a straighforward and unequivocal synthesis of polyacene remains an open question. More recent attempts have been directed toward the synthesis of precursors by means of repetitive Diels−Alder additions,[274,275] while the synthesis of polyacene *via* the cyclization of polybutadiyne has been studied theoretically.[276] Preparation of **68** by means of the LB method has also been considered,[277] while oligomers with a polyacene-based structure have recently been prepared by heating diphenyldiacetylene under high pressure.[278,279]

The search for other rigid systems possibly devoid of Peierls distortion has led to consideration of different structures in which fastened parallel $\pi$-conjugated chains of $(CH)_x$ are combined in different ways. Thus, polyphenanthrene (**69**) can be viewed as the result of various combinations of *cis*-$(CH)_x$ chains. This polymer was predicted as having a very large bandgap of 10.6 eV. However, due to the considerable overestimation inherent in the employed method of calculation, the authors estimated the real gap to be around 4−5 eV.[262]



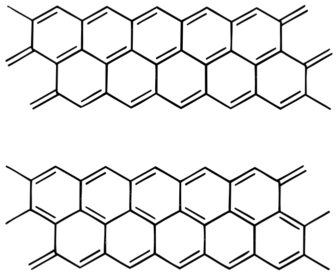
**69**

A polymer with a structure close to that of **69** was recently synthesized by an electrophilic-induced cyclization reaction (**70**).[280] The spectral characterisitics of this polymer ($\lambda_{\max} = 360$ nm, $E_g = 2.60$ eV) appear in qualitative agreement with the large bandgap value predicted for polyphenanthrene.



**70**

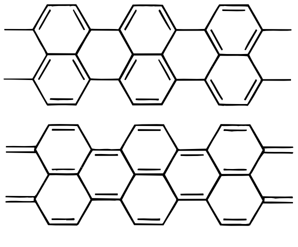
Polyacenacene (**71**) is another one-dimensional graphite involving three parallel *trans*-$(CH)_x$ chains. This polymer has been considered theoretically and predicted to have a metallic band structure with no bandgap.[263,281] Of the three envisioned structures, the "aromatic one", namely that with no BLA, was predicted to be the most energetically stable.[281]



**71**

## B. Poly(perinaphthalene)

Poly(perinaphthalene) (**72**) has been of interest for more than 15 years. Similar to **68**, **69**, and **71**, this polymer can be viewed as a combination of $(CH)_x$ chains. In a first publication, Kaplan et al. reported a conductivity of 250 S cm$^{-1}$ for a material obtained by pyrolysis of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) at 700−900 °C in vacuum.[282] The films obtained when pyrolysis was performed in the presence of niobium as dopant were claimed to be superconducting with an onset $T_c$ of 12 K.[282] Subsequent work established that poorly conducting material ($\sigma = 5\ 10^{-4}$ S cm$^{-1}$) could also be produced by electron beam or argon ion beam irradiation of PTCDA.[283,284]



**72**

Using the same precursor but a modified synthetic procedure, Iqbal et al. obtained **72** as whiskers with pellet conductivities ranging from $10^{-2}$ to 15 S cm$^{-1}$ depending on the pyrolysis temperature.[285] Much higher conductivities (up to 1100 S cm$^{-1}$) were reported by Murakami et al.[286,287] however in both cases the hydrogen content of the material was much lower than that expected for **72**, suggesting that significant graphitization took place during the pyrolysis process. More recently thin films of **72** with conductivity of $5.7 \times 10^{-4}$ S cm$^{-1}$ were obtained by chemical vapor deposition using PTCDA as the precursor. The activation energy determined from the temperature dependence of the conductivity was found to be 0.18 eV.[288]

The electronic properties and band structure of PPN have been investigated using different theoretical approaches.[265,285,289−296] It has been pointed out that **72** has a zero topological bandgap and as for $(CH)_x$ the bandgap is not related to the connectivity of the conjugated backbone but appears basically as a consequence of the Peierls distortion and electron−electron interaction.[292] The band structure of **72** has been analyzed by several authors. On the basis of the assumption of a slightly quinoid structure, Brédas et al. have obtained a bandgap of 0.44 eV for a single chain and of 0.29 eV for the crystal assuming a crystal structure similar to that of perylene.[293] A more recent study has underlined the fact that the bandgap is governed to a great extent by the degree of BLA,[294] and a larger bandgap was predicted (0.56 eV) in satisfying agreement with the values extrapolated from experimental data obtained on short chain oligomers that range between 0.92−0.98[295] and 1.32 eV.[296]

Despite the interest of these various works, the synthetic problems posed by the preparation of a polymer with well-defined structure has remained unsolved due, among other things, to the intractability of the materials obtained by pyrolysis. As happened for PT, this situation has triggered a high interest in shorter chain oligomers as model compounds. While the first members of the oligorylene series *e.g.* terylene and quaterylene have been known for several decades,[297,298] their extremely low solubility has prevented any attempt at direct characterization by conventional methods. Recently, Müllen et al. reported the synthesis of the first examples of soluble oligorylenes **77**.[299] The preparation of these compounds involved the palladium-catalyzed coupling of 2,7-di-*tert*-butylnaphthalene boronic acid **73** with dibromo compounds **74** and **75**, to afford the polynaphthalene **76** which was then cyclized into the target molecules by treatment with potassium and oxidation with anhydrous cadmium chloride (Scheme 22). In the case of the longest compounds ($n = 2$) a further cyclization reaction using Kovacic conditions[9] ($CuCl_2/AlCl_3/CS_2$) was needed to achieve complete cyclization.[299]

As expected, the increase in the degree of annelation leads to a large bathochromic shift of $\lambda_{max}$ and to a strong decrease of the first oxidation potential down to a value as low as 0.23 V/SCE. These changes result in a large reduction of the HOMO−LUMO gap $\Delta E$ down to 1.80 eV for $n = 2$ (Table 2). Furthermore, the number of accessible redox states increases with $n$ and for $n = 2$, the system can be oxidized to the tetracationic and reduced to the trianionic state.[299]

**Scheme 22**

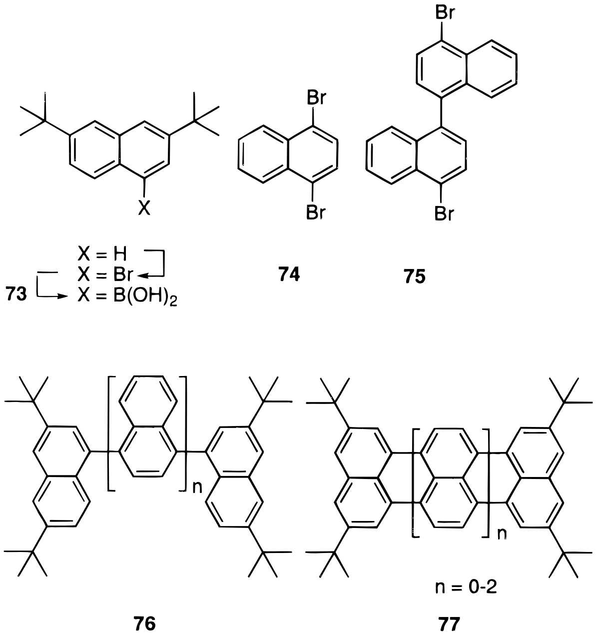


**Table 2. Main Optical and Electrochemical Data for Oligorylenes 77 as a Function of the Degree of Annelation**

| $n$ | $\lambda_{max}$ (nm) | $E_{ox}$[a] | $E_{red}$[a] | $\Delta E_{elec}$ (eV) | $\Delta E_{Opt}$ (eV) | $\Delta E_{theor}$ (eV) |
|---|---|---|---|---|---|---|
| 0 | 439 | 0.78 | −1.99 | 2.77 | 2.67 | 2.78 |
| 1 | 560 | 0.43 | −1.57 | 2.00 | 2.14 | 2.19 |
| 2 | 660 | 0.23 | −1.42 | 1.64 | 1.80 | 1.84 |

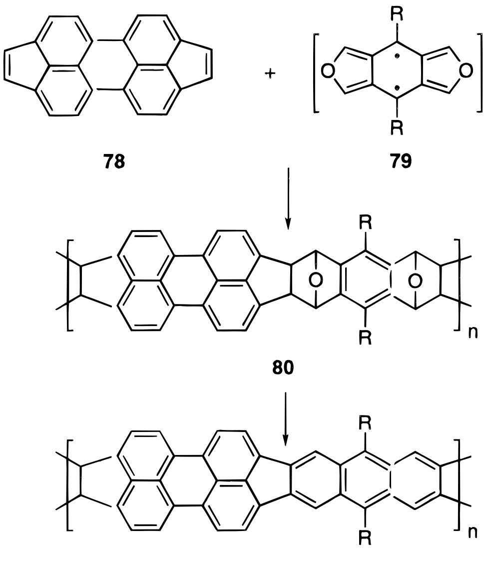
[a] In V vs SCE (ref 299).

The $\Delta E$ value obtained (1.60−1.80 eV for $n = 2$) is already significantly smaller than that for poly(*p*-phenylene) (3.40 eV) and poly(*p*-phenylenevinylene) (2.50 eV) and comparable to that for $(CH)_x$ (1.40 eV). Compounds **77** become conductive upon doping with iodine. Their powder conductivities reached 5 S cm$^{-1}$ for $n = 2$. An EPR study of the radical anions of **77** has revealed that considerable spin density prevails at both ends of the molecules, making them interesting models for the elaboration of molecular electronic devices.[300,301] Extrapolation of experimental results obtained for **77** led to estimated values of 0.80−0.98 eV for the bandgap of **72** which falls within the range of several theoretical predictions.[293,294]

Very recently, Schlüter et al. have described the synthesis of a new type of ladder polymer constructed by combining **68** and **72**. The resulting structure is reminiscent of the open-chain analog of the belt region of $C_{60}$.[302] These polymers were prepared by Diels−Alder reaction of the dienophile **78** with the *in situ*-generated bis-diene **79,** to give a partially saturated precursor **80** which was then converted into the target polymer **81** by dehydration with *p*-toluenesulfonic acid (Scheme 23).

While the first members of this new class of polymers were poorly soluble, further work has led to soluble polymers or oligomers with variable proportions of acene vs rylene moieties in the structure.[303,304] Theoretical calculations for a polymer based on a succession of naphtalene and anthracene units predicted a bandgap of 2.15 eV, which is in excellent agreement with experiment.[303]

**Scheme 23**



81

## C. Polyquinoxalines and Related Polymers

While several of the above structures are in fact ladder polymers, this term is more generally employed in the literature on conjugated polymers, to designate polymers already existing in nonbridged form e.g. polyaniline or poly(*p*-phenylene).

Ladder-type polymers can be prepared by two main general strategies. The first employs the polymerization of multifunctional monomers in which both strands of the ladder structure are generated in a single reaction, while the second is based on the cyclization of a suitably substituted single stranded open chain.[305]

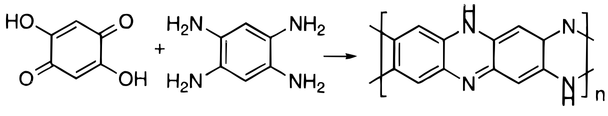
Polyquinoxalines (**82**) are probably one of the first class of ladder polymers to be investigated. These materials have initially been developed because of their high tensile strength and excellent thermal stability.[306,307] Recently, their electronic properties have drawn renewed attention when it was suggested that the rigidification of the structure represented an interesting approach for the improvement of the electronic properties of the polymers with respect to electronic and nonlinear optical applications.[308-310]

Polyquinoxalines have been prepared by the condensation of a dihydroxy diketone with aromatic polyamines (Scheme 24).[306-308]

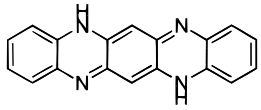
The analysis of the electronic properties of a model compound 5,12-dihydro-5,7,12,14-tetraazapentacene (**83**) has shown that this compound absorbs down to 600 nm and can form a conductive crystalline complex with methanesulfonic acid.[308,309]

Other related structures involve rigid oligomers with the heteroacene skeleton such as oligophenothiazines (**84**) obtained by direct thionation of various anilino derivatives.[311] Oxidation of the leuco (L) form afforded the quinoid (Q) form which exhibited a strong absorption with maxima at 521 and 556 nm. Surprisingly, the highest conductivity (*ca.* 5 × $10^{-7}$ S $cm^{-1}$) was found for the L form while the Q form was found to be insulating.[311]

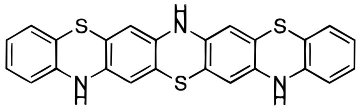
**Scheme 24**



**82**



**83**



**84**

A semiconducting ladder polymer was obtained by polycondensation of 2,3,5,6-tetrachlorobenzoquinone and a 3,7-diaminophenazinium chloride. The polymer was reported to have an intrinsic conductivity ranging from 7.2 × $10^{-8}$ to 8 × $10^{-6}$ S $cm^{-1}$, depending on the method of preparation. However, there was no increase in conductivity upon doping.[312] Recently the synthesis of ladder polyanilines was attempted through the electropolymerization of *o*-phenylenediamines[313-316] or *o*-aminophenols.[317,318] However, the resulting polymers exhibited low molecular masses and low conductivities and their structure was not unequivocally ascertained.[313-318]

## D. Poly(phenylenes)

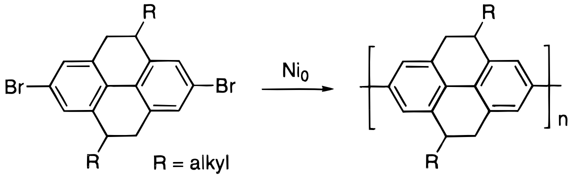
More conclusive results have been obtained concerning the preparation of ladder poly(*p*-phenylene) (PPP). A first step in this direction involved the synthesis of poly(tetrahydropyrene) **85** from a dibromo precursor (Scheme 25).[319]

This polymer can be viewed as a partially rigidified PPP in which the presence of the two ethano bridges should improve planarity. In fact a recent analysis of the evolution of the optical properties of oligomers as a function of chain length has shown that for an equal number of six benzene rings, oligomers of the **85** series absorb at a significantly longer wavelength (352 vs 308 nm) (Table 3), thus confirming that partial planarization markedly increases the effective conjugation length.[320]

The first fully planarized ladder PPP (**86**) was synthesized in 1991 by Scherf and Müllen.[321] This polymer was obtained by Suzuki coupling[322] of an aromatic dibromo diketone with an aromatic diboronic acid (Scheme 26).

After polymerization, reduction of the keto groups afforded a polyalcohol which was readily converted into the ladder polymer **86** by Friedel–Crafts alkylation.[323] The soluble polymer was obtained with a molecular weight $M_n$ of 20 000 (about 45–50 phen-

**Scheme 25**

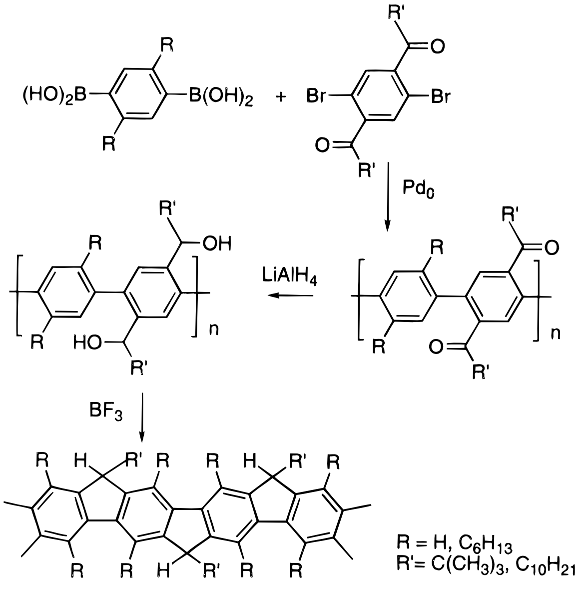


**85**

**Table 3. Longest Wavelength Absorption Maxima of PPP Oligomers (from ref 320)**

| no. of benzene rings | PPP | **85** | **86** |
|---|---|---|---|
| 3 | 279 | | 335 |
| 4 | 292 | 329 | |
| 5 | 299 | | 390 |
| 6 | 308 | 352 | |
| 7 | | | 414 |
| 8 | | 364 | |
| 10 | | 370 | |
| 12 | | 375 | |

**Scheme 26**



**86**

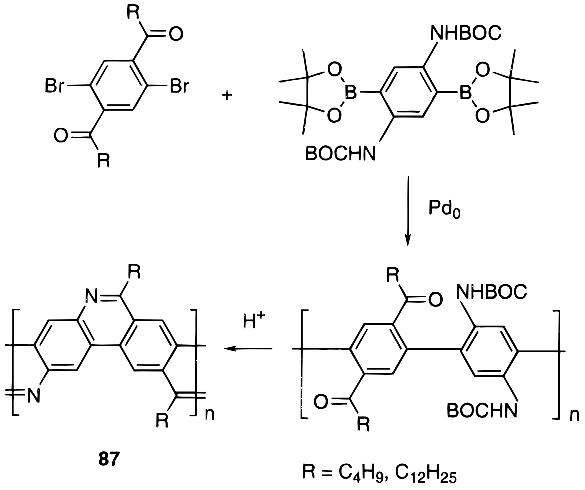
ylene units). As shown by a study of the corresponding oligomers, for an equal number of benzene rings, fully bridged oligomers absorb at a considerably longer wavelength (Table 3),[320] thus confirming that planarization significantly increases the effective conjugation. In fact comparison of the optical spectra of PPP and of its ladder version has confirmed that the latter shows a smaller bandgap *i.e.* 2.70 vs 2.90–3.20 eV for conventional PPP.[324]

Due to their rigid and regioregular structure, ladder PPPs undergo low-energy losses by nonradiative decay and thus exhibit a high quantum efficiency of photoluminescence (>60%) which has been used in the fabrication of light-emitting diodes.[325–327] More recently the photovoltaic properties of **86** were also investigated.[328] Various topological isomers of ladder PPP have been considered from a theoretical viewpoint and the calculated bandgaps were in the range of 2.40–2.50 eV, in good agreement with experiment.[329,330]

Using a different approach, Tour et al. synthesized ladder PPPs in which consecutive phenyl rings are bridged by an imine group.[331] The polymers were synthesized by Pd(0)-catalyzed coupling of a dibromo diketone with a diboronic derivative of a protected diamine. After polymerization, treatment of the polymer with trifluoroacetic acid afforded the ladder polymers **87** (Scheme 27).

The polymers were reported to be soluble in their noncyclized form while the cyclized polymers showed

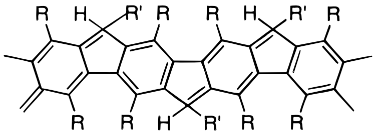
**Scheme 27**



**87**

$\lambda_{max}$ in the range of 463–490 nm in the solid state.[331]

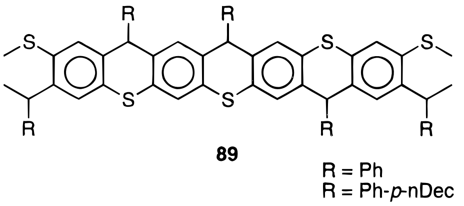
In order to achieve a further bandgap decrease, the conversion of ladder PPP into ladder type poly(arylenemethide) (**88**) has been investigated.[332,333] However, dehydrogenation with DDQ was possible only in the case of a ladder PPP having a majority of *meta* linkages, while for purely *para*-linked polymer, dehydrogenation was carried out by lithiation of the benzylic positions followed by oxidation using cadmium chloride.[333]



**88**

While the resulting polymer exhibited a series of absorption peaks characterisitic of oligo(phenylenemethide) segments ($\lambda_{max}$ = 544, 687, 828, and 940 nm), structural irregularities were present in the material.[333]

Ladder polymers with an heteroacene skeleton corresponding to a rigid polyphenylene sulfide with alternant *meta* and *para* linkages **89** have been described recently.[334,335] These polymers exhibit wide gaps with $\lambda_{max}$ at 306 nm; however, they are easily converted into aromatically stabilized near-IR absorbing polycations.[335]



**89**

As demonstrated by several of the above examples, rigidification of LCSs into ladder systems represents an efficient strategy to reducing the bandgap of conjugated polymers. However, until now this approach has been essentially applied to phenylene-based structures which, owing to the high resonance energy of the benzene ring might not be the most appropriate substrate for achieving very small bandgap values.

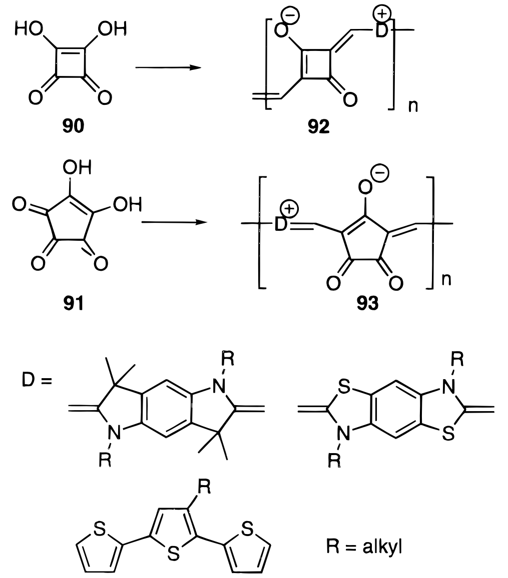
## VIII. Molecular Linear π-Conjugated Systems

Despite the broad variety of structures and synthetic routes considered in the previous sections, these different approaches resort in fact to two main strategies namely the design of a precursor molecule, in general extensively conjugated, already involving the structural features expected to produce a decrease of $E_g$ and the synthesis of polymers in which a small $E_g$ results essentially from the topology imposed on the LCS. While many of the above examples have demonstrated the efficiency of these two strategies, they do present however, some important drawbacks. Thus, whereas tailored precursors have made it possible to establish the role of several structural factors in the control of $E_g$, some of them possess an extensively conjugated structure which results in poorly reactive cation radicals and hence in incomplete polymerization. On the other hand, although the synthesis of ladder polymers has allowed a significant reduction in the bandgap, the lowest values reached so far on phenylene-based systems, are still in the range of 2.0 eV.

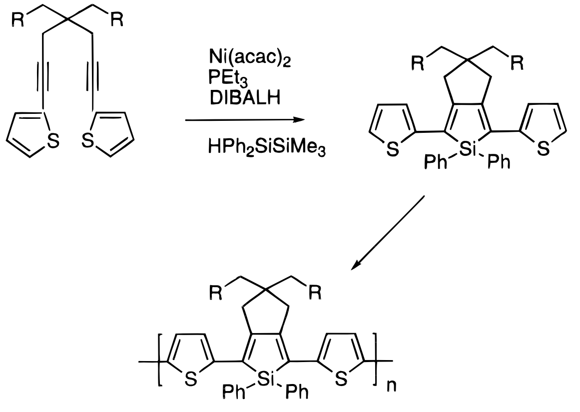
This situation leads to the conclusion that the design of molecular LCSs based on the combination of the two above approaches can represent an interesting new strategy for the synthesis of small bandgap LCSs. In recent years, the control of the electronic properties of molecular LCSs with view to synthesizing molecules and materials for quadratic and cubic nonlinear optics has attracted keen attention.[336−338] In this regard, thiophene-based LCSs are of particular interest due to their stability, structural versatility, and moderate $\Delta E$.[339−341] In fact, this recent development parallels the broad fundamental[12,37−46] and technological[58,342−344] interest in thiophene oligomers (*n*Ts). Although the synthesis of NLO molecules and that of small bandgap LCSs have different aims, the common feature is that both require the design of a conjugated π-system showing optimal electron transmission properties.

A first possible approach to reducing the $\Delta E$ in *n*Ts involves the insertion of electron acceptor groups into the conjugated path in order to create alternate donor and acceptor moieties. Although this idea was already implicit in earlier works,[176,180] it was only in 1992 that this concept was proposed explicitly as an alternative route toward small bandgap polymers.[345] Thus, condensation of squaric acid (**90**) and croconic (**91**) acids with various bifunctional electron donor analogs of donors in squaraine dyes,[346−348] such as benzodipyrrolines or benzodithiazoles, led to polysquaraines and polycroconaines, **92** and **93** (Scheme 28), with bandgaps down to 0.5 eV.[345] Shortly after, this strategy was extended to include other donors like terthienyls. However, the resulting polymers exhibited larger gaps (1.1−1.4 eV).[349] More recently the same group reported water-soluble polymers of type **92** and **93** formed by substituting the donor moiety by alkanesulfonate groups. The polymers had optical bandgaps as low as 0.7 eV which were correlated to the photoconductivity bandgap.[350]

**Scheme 28**



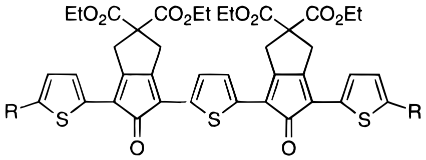
**Scheme 29**



**94** R = OSiMe$_2$-*t*-Bu

Another application of this concept involved the thiophene−silole hybrid system **94**. The basic trimeric structure was prepared by nickel-catalyzed intramolecular cyclization of diacetylenic precursors (Scheme 29).

The resulting trimers were then converted into higher oligomers or polymers by palladium cross coupling of organotin and halo derivatives of the basic unit.[351] While these hybrid structures have smaller gaps than *n*Ts and even PT, the decrease in $\Delta E$ remains limited since the $\lambda_{max}$ of compound **94** containing 33 heterocycles ($n = 11$) reaches only 615 nm.[351] Recently, it has been shown that replacement of the silole ring by cyclopentadienone with stronger electron-withdrawing effects allows a further decrease in $\Delta E$ with $\lambda_{max}$ reaching 706 nm for **95.**[352]

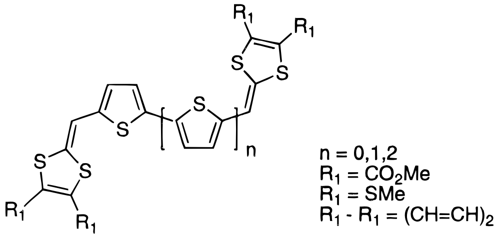


R = H, Me

**95**

While introduction of electron-withdrawing groups aims to reduce $E_g$ by lowering the LUMO level, the alternative approach based on the raising of the HOMO level by incorporation of electron-releasing groups into the electronic structure, has also been developed. Thus, substitution of the end thiophene rings of *n*Ts by alkoxy groups has been shown to lead to a decrease in oxidation potential and to a $\lambda_{max}$ red shift.[353,354]

Tetrathiafulvalene derivatives (TTFs) rank among the most effective $\pi$-electron donors which have given rise to several organic superconducors.[355,356] It was therefore interesting to take advantage of these $\pi$-donor properties by synthesizing hybrid conjugated systems combining some structural features and properties of both *n*Ts and TTF.[357−361] Hybrid *n*T-TTFs built around $\pi$-conjugated spacers of 1, 2, or 3 conjugated thiophene rings (**96**) have been synthesized by Wittig or Wittig−Horner olefination of the appropriate dialdehyde, although some of them have also been prepared by electrochemical synthesis.[361]



n = 0,1,2
$R_1 = CO_2Me$
$R_1 = SMe$
$R_1 - R_1 = (CH{=}CH)_2$

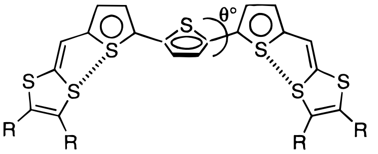
**96**

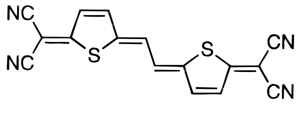
The electrochemical and optical properties of *n*Ts-TTFs show that $\Delta E$ depends on substituents $R_1$ and on the length of the *n*T spacer. However, although *n*Ts-TTFs exhibit smaller $\Delta E$ values than their constitutive building blocks,[359,360] the increase of the length of the *n*T conjugated bridge leads, already for $n = 1$, to a saturation of effective conjugation.[360] In this case $\Delta E$ reaches at best 2.30 eV, a value comparable to that of sexithienyl.[362] This moderate value is, however, larger than expected in view of the apparent conjugation length. X-ray studies have revealed that the strong S···S interactions between the sulfur atoms of the thiophene and 1,3-dithiole rings rigidify the lateral parts of the molecule (Scheme 30).[360]

This leads to the conclusion that the observed convergence of $\Delta E$ results essentially from the rotational disorder in the *n*T spacer. Consequently further reduction of $\Delta E$ in these systems should not resort to a lengthening of the *n*T spacer but rather to the minimization or suppression of rotational disorder.

This question has been approached in several ways. A first solution involves the substitution of both ends of the molecule by functional groups capable of imposing a quinoid geometry on the whole $\pi$-conjugated system. This is exemplified by **97** in which the two dicyanomethylene groups stabilize the quinoid form of the LCS.[363] These compounds, developed as conjugated electron acceptors, are characterized by a red-shifted absorption (up to 557 nm) and by the occurrence of their first reduction in the +0.02 to −0.13 V vs Ag/AgCl potential range.

**Scheme 30**





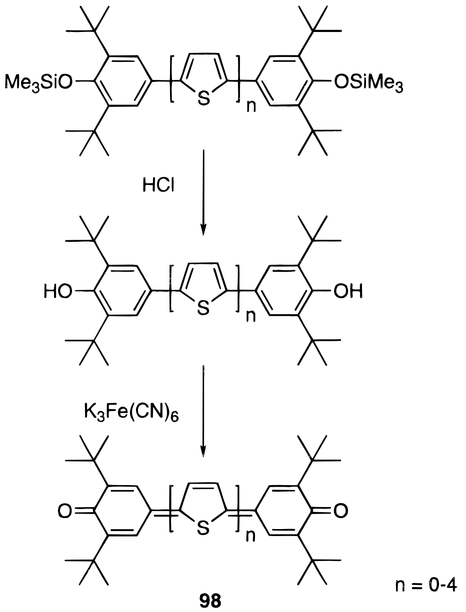
**97**

Extensively conjugated *p*-diphenoquinone analogs **98** (Scheme 31) represent another illustration of this strategy.[364−367]

The *n*Ts conjugated system was constructed by successive Pd-catalyzed cross-coupling reactions leading to disiloxanes which were subsequently converted into the target compounds by hydrolysis and oxidation (Scheme 31). This last step leads to the dearomatization of the thiophene rings with formation of a fully quinoid $\pi$-conjugated system. The electrochemical properties of compounds **98** show that the first oxidation potential $E_{ox}1$ decreases from 1.20 V/SCE for $n = 1$ to 0.55 V for $n = 4$ while concurrently, the first reduction potential $E_{red}1$ shifts from −0.46 V to −0.20 V. For $n = 4$ this leads to a potential difference $E_{sum} = E_{ox}1 - E_{red}1$ of 0.75 V which lies among the smallest reported for molecular LCS.[365] This small $\Delta E$ is confirmed by the considerable red shift of $\lambda_{max}$ (558 to 830 nm) produced by the increase of *n* from 1 to 4. The effects of the substitution of the end phenyl rings have been analyzed and it has been shown that $E_{ox}1$ and $E_{red}1$ correlate with Hammett $\sigma_p$ constants.[365,366] More recently, replacement of thiophene by tellurophene (for $n = 1$) has been shown to decrease $E_{sum}$ from 1.66 to 1.31 eV.[367]

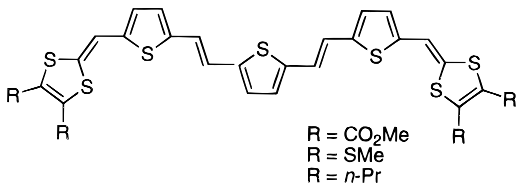
Rotational disorder in *n*Ts-TTFs can be minimized by another approach involving the replacement of the *n*T spacer by an oligo(thienylenevinylene) (TV) one in which the olefinic linkages of defined configuration will limit the possible rotations. Futhermore, incor-

**Scheme 31**



**98**

poration of double bonds into the conjugated spacer will decrease its overall aromatic character which can be expected to improve its electron transmission properties.



**99**

The synthesis of the first examples of extended TTF analogs built according to this approach (**99**) has confirmed these hypotheses and in contrast to **96**, no effective conjugation saturation was observed when increasing the length of the TV spacer. Thus, for $n = 3$, a $\Delta E$ value of 2.0 eV, already smaller than the bandgap of PT, was obtained.[368] Furthermore, as shown by their CV, even for $n = 1$, these compounds are directly oxidized into their dication state through a single-step two-electron process, thus confirming the weak Coulombic repulsion in these systems.[368] A further chain extension of these systems has been accomplished by grafting solubilizing alkyl chains on the thiophene rings of the oligo(thienylenevinylene) spacer (**100** and **101**).[369] These compounds exhibit a further decrease in oxidation potential and the dication can be formed directly at less than 0.20 V while the tetracation is reached around 1.00 V (Figure 15). This increase of the HOMO level results in a further decrease of $\Delta E$ down to 1.85 eV.[369]

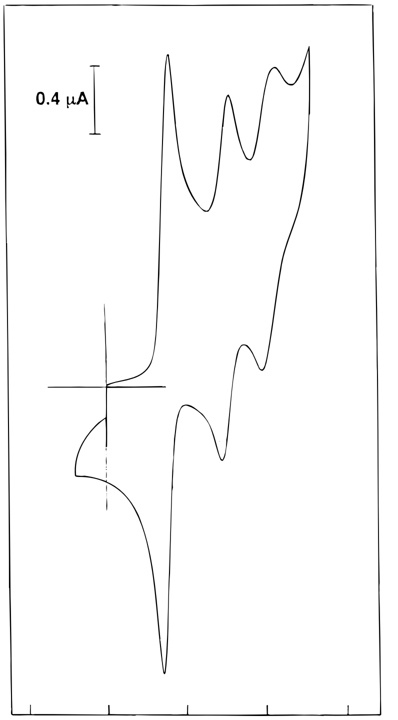
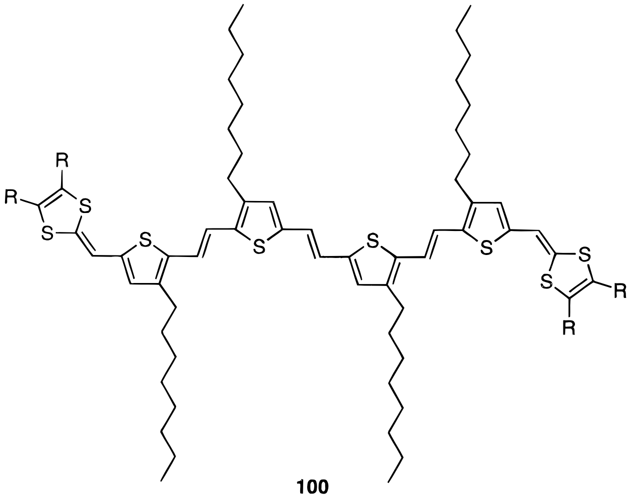
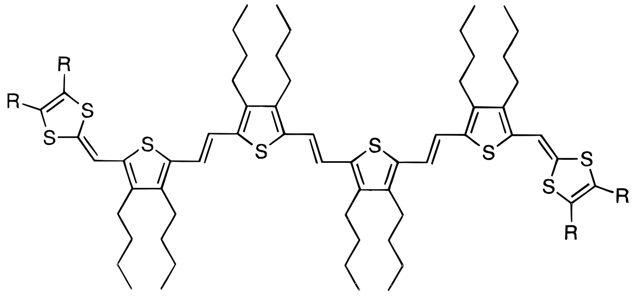


**Figure 15.** Cyclic voltammograms of **100** (R = SMe), ($10^{-3}$ mol L$^{-1}$) in 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$/CH$_2$Cl$_2$, scan rate 100 mV s$^{-1}$ (from ref 369).



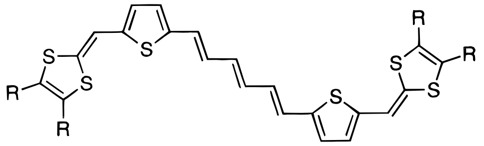
**100**



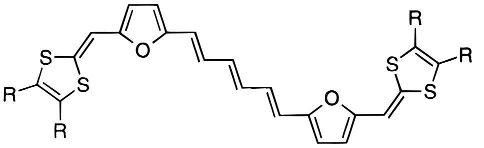
**101**

R = SMe
R = n-propyl

A recent analysis of the effects of the number of double bonds inserted between the two heterocycles in the dithienyl and difuryl polyene systems **102** and **103** has shown that $\Delta E$ depends on the nature of the heteroatom, on the length of the conjugated spacer and on R. A judicious combination of these structural variables allows a considerable increase of the HOMO level and leads to oxidation potentials among the lowest so far reported for hybrid TTF systems.[370]



**102**



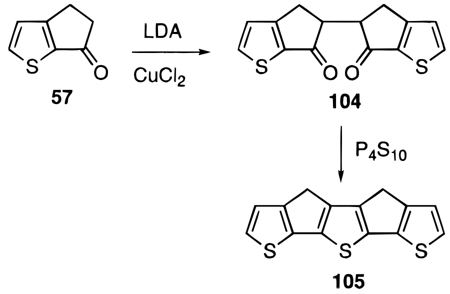
**103**

R = CO$_2$Me, SMe, n-Pr

A much more drastic approach for the suppression of rotational disorder involves the full rigidification of the conjugated system by the bridging of the monomer units. While the use of bridged bithienyl precursors represented a first step in this direction,[173–178,180] a more decisive step has been accomplished by the synthesis of a fully rigid terthienyl, **105**. This compound has been prepared by oxidative coupling of the enolate[371] of ketone **57**, followed by cyclization of the resulting 1,4-diketone **104** (Scheme 32).[372]

A comparison of the CV of **105** and terthienyl (3T) shows that the bridging of the thiophene rings

**Scheme 32**



induces a negative shift of the first oxidation peak corresponding to the formation of the cation radical from 1.07 to 0.60 V. Furthermore, whereas reduction of 3T requires very negative potentials, (−2.00 V in DMF)[38] that of **105** occurs at −0.75 V in MeCN (Figure 16), while in THF reversible reduction to the anion radical and dianion states are observed at −1.00 and −1.15 V. These shifts result in decrease of $\Delta E$ from 3.20 to 1.35 eV.[372]

The fact that effects of such magnitude are observed already for a trimer indicates that rigidification of *n*Ts is a powerful approach, and these early results strongly suggest that extension of this strategy to longer oligomers could lead to very small bandgaps.

Other recent examples of rigid LCSs involve extended TTF hybrid systems built around rigid bithienyls bearing various substituents at the bridging carbon **106**−**108**.[373] Compared to their nonrigid analogs **96**, the CV of these compounds reveal a decrease in the oxidation potential to 0.38 V for **106** and **107** and 0.18 V for **108** while the reduction potential undergoes a positive shift up to −0.56 and −0.52 V for **106** and **107**, respectively. Consequently, these compounds can be reversibly charged to their tricationic and trianionic states in a relatively narrow potential range (Figure 17).

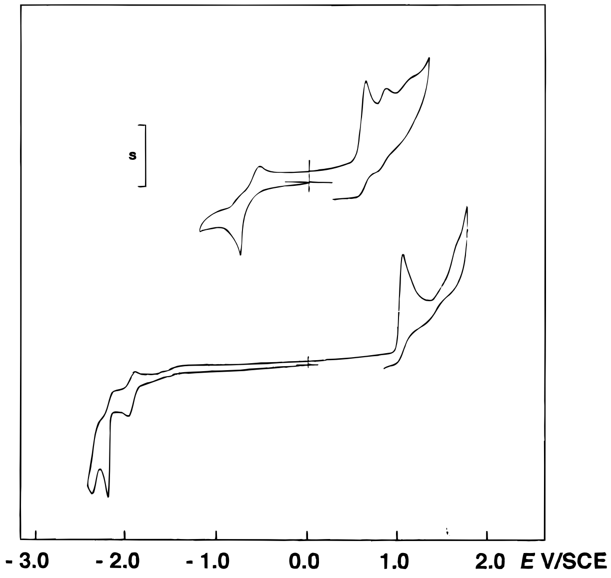


**Figure 16.** Top: Cyclic voltammogram of **105** ($10^{-3}$ mol $L^{-1}$) in 0.1 mol $L^{-1}$ $Bu_4NPF_6$/MeCN, scan rate 100 mV $s^{-1}$, $s = 2\ \mu A$ (from ref 191). Bottom: Cyclic voltammogram of terthienyl, oxidation in $Bu_4NPF_6$/MeCN, $s = 2\ \mu A$ (from ref 191), reduction in $Bu_4NI$/DMF $s = 4\ \mu A$. (Reprinted from ref 38. Copyright 1991 American Chemical Society.)

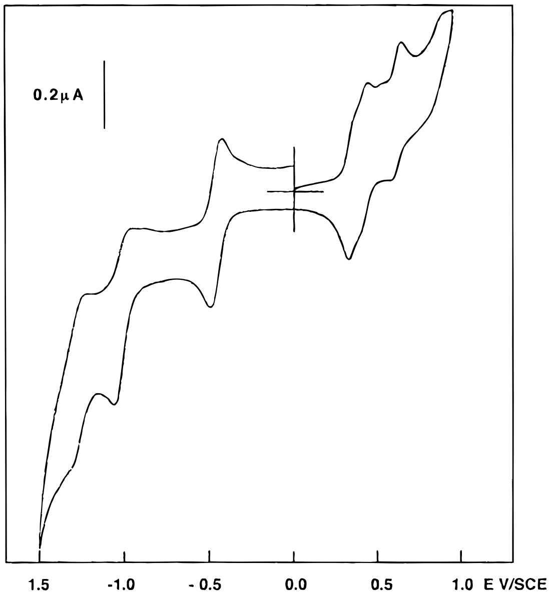
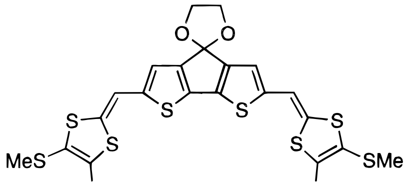
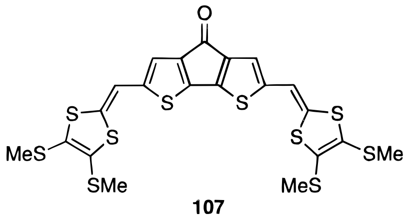


**Figure 17.** Cyclic voltammograms of **106** ($10^{-3}$ mol $L^{-1}$) in 0.1 mol $L^{-1}$ $Bu_4NPF_6/CH_2Cl_2$, scan rate 100 mV $s^{-1}$. (Reprinted from ref 373. Copyright 1994 Royal Society of Chemistry, UK.)

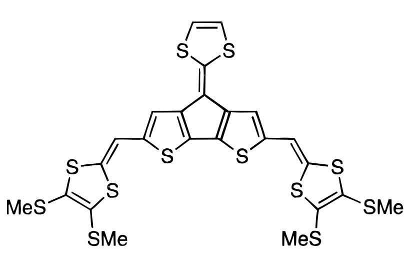
These considerable changes lead to electrochemical $\Delta E$ values as low as 0.90 eV in the case of **106**, in satisfying agreement with optical data.[373]



**106**



**107**



**108**

These low gap values have been confirmed by the electronic absorption spectrum of a vacuum sublimed thin film of **106** which exhibits an absorption onset around 1.10−1.20 eV (Figure 18). This result confirms that the small $\Delta E$ values observed in solution are effectively associated with narrow bandgaps of the corresponding materials in the solid state.[185]

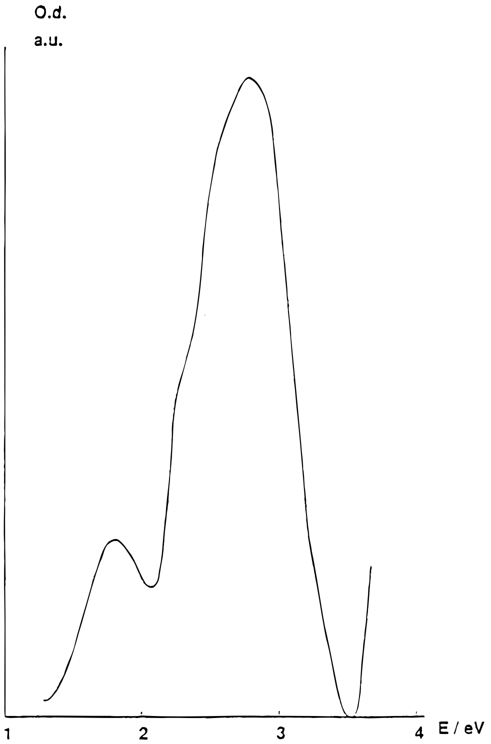


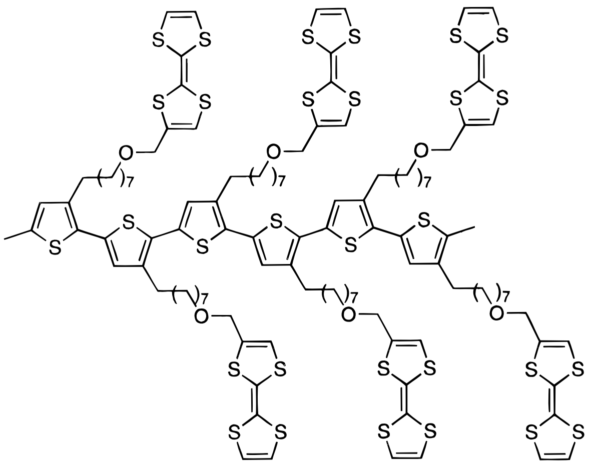
**Figure 18.** Solid-state electronic absorption spectrum of **106** vacuum sublimed on glass (from ref 191).

## IX. Supramolecular Bandgap Control

While many of the above recent examples show that it is now possible to tailor individual molecules with small $\Delta E$ values, the similarity of the $\Delta E$ and $E_g$ values of **106** show that intermolecular interactions are weak in the condensed phase. However, this is far from being a general rule and in many cases such interactions can significantly influence the magnitude of the bandgap. A detailed survey of the different strategies involved in crystal engineering and supramolecular chemistry is of course beyond the scope of this review. Therefore, in this last section, only a few representative examples of possible approaches capable of contributing to a supramolecular control of the electronic properties of materials derived from LCSs will be briefly discussed.

Although for CPs this question has theoretically been considered at an early stage,[54] works aimed at the control of the supramolecular organization have remained scarce. Until now most attempts in this direction have been based on the same general strategy. Substituents with a strong tendency to self-assemble or to stack are covalently attached to the $\pi$-conjugated spine in order that interactions among these substituents exert an indirect control on the structure and electronic properties of the LCS in the condensed phase. Although such indirect substituent effects have already been invoked to account for the extended conjugation observed for some 3-substituted PTs,[70,74,75] their deliberate use to control the organization of CPs is relatively recent. In the case of PT, an early example of application of this strategy involved substitution by phenyl groups sterically and electronically decoupled from the conjugated backbone. The optical and electrochemical properties of these polymers showed that interactions among the substituted phenyl groups lead to considerable enhancement of the resolution of the vibronic fine structure in the optical spectrum and to an increase of the n-doping level. These changes are indicative of a more rigid $\pi$-conjugated system.[72]

Other attempts in the same direction involve 3-substitution of the thiophene ring by perfluoroalkyl chains,[374-376] or by mesogenic groups.[377-379] However, the efficiency of these various approaches for controlling the electronic properties of the polymers remains to be demonstrated.



**109**

An interesting related strategy concerns the grafting of TTF derivatives onto conjugated polymers.[377,380] Thus, when TTF is grafted on the PT backbone through a spacer group of appropriate length (**109**), the CV of the resulting polymer exhibits a splitting of the TTF first reduction wave, typical of the occurrence of the mixed-valence dimer $(TTF)_2^{+}$,[381] which indicates that self-assembly of the oxidized TTF moieties already takes place in the material (Figure 19).[380]

More recently, attempts to synthesize conjugated systems of higher dimensionality have been reported. The first model involved spiro-fused oligothiophenes that have been synthesized as models for molecular

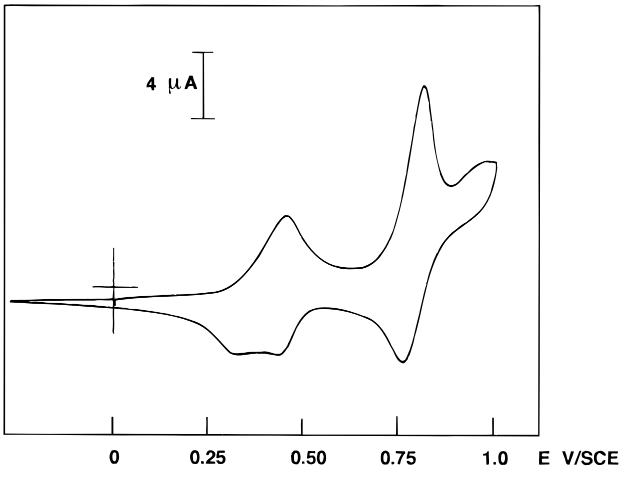
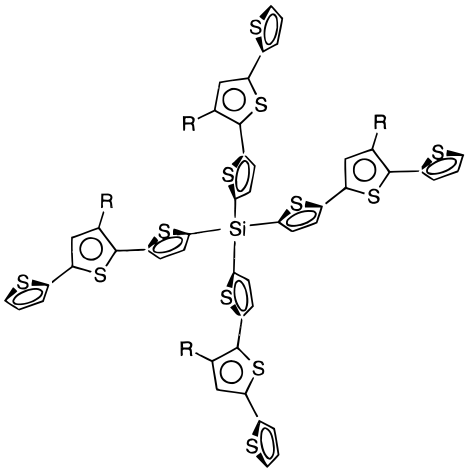


**Figure 19.** Cyclic voltammograms of poly(**109**) electrodeposited on Pt, in 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$/MeCN, scan rate 10 mV s$^{-1}$. (Reprinted from ref 380. Copyright 1993 American Chemical Society.)

logic.[3,382] From a different viewpoint, the first example of a tetrahedral precursor with four polymerizable terthienyl groups linked to a central silicon atom (**110**) has been synthesized.[383]



**110**

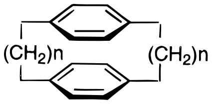
Electrooxidation of **110** leads to the deposition of a tetrakis-cation radical salt which can be subsequently converted into a material containing sexithienyl units by further electrooxidation.[383] Whereas electrochemical, spectroscopic, and analytical data of the resulting material are consistent with the expected 3D structure, further work is still needed to definitively confirm this conclusion.

As shown by these few examples, the supramolecular control of the electronic properties of CPs and LCSs-based materials is still very rudimentary. Consequently, the actual potentialities of this emerging field of research are difficult to evaluate at this early stage of development.

The control of the supramolecular organization is considerably more advanced where molecular conductors and in particular charge transfer salts of TTF derivatives are concerned. Unlike most of the oligomeric and polymeric LCSs, TTF salts can be obtained as single crystals which makes it possible to use crystal engineering rules.[384] While the prominent role of intermolecular S···S interactions in the organization of crystals of TTF derivatives or of their cation radical salts is well known,[385,386] other directing effects such as hydrogen bonding[387] or lipophilic interactions[388−390] have also been demonstrated. The use of interactions between long alkyl chains as molecular fasteners has been demonstrated by Inokuchi et al. who have shown that single crystals of alkylthio-substituted TTF, exhibited intrinsic conductivities as high as $10^{-5}$ S cm$^{-1}$, correlated to a decrease in the ionization potential and an increase of the charge carriers mobility.[389] The invariance of the electronic properties of individual molecules has led to the conclusion that the observed phenomena reflected a collective behavior resulting from a closer packing of the TTF molecules in the crystal.

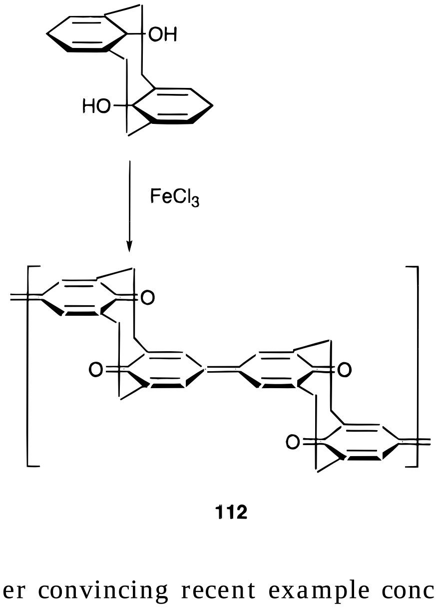
Examples of similar effects remain scarce in the case of LCSs, and whereas the effects of substitution by alkyl chains on the optical properties of sexithienyl have been discussed,[391] no changes in the bandgap have been reported yet.

Perhaps one of the most promising ways to achieving supramolecular control of the bandgap is to bring LCSs together at short intermolecular distances by means of covalent bonds. As a matter of fact, several examples in the literature have shown that when stacks of aromatic systems are fastened by short covalent linkages, frontier orbital overlap induces an increase of the HOMO level. This process is similar to the formation of conducting bands in the $\pi$-stacks of conducting organic crystals. This phenomenon was clearly demonstrated with cyclophanes **111** for which the shortening of the inter-ring distance by a decrease in *n* produced a considerable red shift of the absorption edge.[392−394]



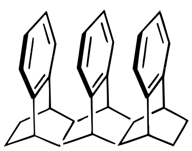
**111**

A related CPs example concerns the poly(cyclophane) **112** obtained by oxidative polymerization of a bis-phenolic precursor. The electronic absorption spectrum of this polymer was similar to that of 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone but red shifted by about 70 nm, with an optical gap of 1.80 eV.[395]



**112**

Another convincing recent example concerns the synthesis of a covalently linked molecular $\pi$-stack **113**.[396] The better $\pi$-orbital overlap resulting from the fastening of the benzene rings produces drastic changes in the CV of **113** which exhibits two reversible oxidation waves at 1.28 and 1.74 V vs Ag/AgCl. These changes represent a decrease of more than 1.20 V in the oxidation potential of benzene thus confirming that covalent fastening of $\pi$-electrons systems can represent a powerful approach for the control of their electronic properties.



**113**

## X. Conclusions and Perspectives

The persistent problems related to the unsatisfactory level of performance for exisiting CPs for bulk utilization, together with their rapidly expanding advanced electronic and photonic applications have triggered a strong intensification of research on small bandgap LCSs in the past five years.

In polyaromatic systems, the search for a quinoid geometry has long remained the archetypal approach widely illustrated by numerous experimental and theoretical works on poly(isothianaphthene).

In recent years this strategy has been enriched by the emergence of new approaches based on two main routes namely the electropolymerization of tailored extensively conjugated precursors and the creation of $\pi$-conjugated systems by means of elimination reactions on non-conjugated precursor polymers.

By allowing the incorporation into the conjugated chain of rather unstable ring systems capable of strongly influencing the magnitude of the bandgap, the electropolymerization of $\pi$-conjugated precursors has led to materials that exhibit some of the smallest bandgaps reported so far. However, in many cases, the scope of this aproach is limited by the low reactivity of the cation radicals produced by the electrooxidation of extensively conjugated systems. Further progress in this area could resort in the elaboration of longer oligomers by means of chemical synthesis or in the control of the reactivity of the linking sites of oligomeric precursors by appropriate structural modification.

The soluble precursor route has been successfully applied to the preparation of several CPs. However, the efficiency of this approach for the synthesis of small bandgap LCSs is less evident and the bandgap of the poly(arylenemethines) prepared by this method are still much larger than expected. The main problem here is probably related to the control of the elimination reaction in order to produce a defect-free fully conjugated polymer chain.

The preparation of ladder polymer is a challenging task as evidenced by the fact that the synthesis of the most famous member of this class of polymers, namely polyacene, has resisted all attempts so far. Whereas the first results obtained in the oligorylene or ladder PPP series look very promising and confirm the efficiency of the rigidification of the LCS for the reduction of the bandgap, the smallest gap values reached by these systems are still in the range of 2.0 eV. The high aromatic resonance energy of the benzene ring is probably an important factor.

In spite of their specific limitations, all these approaches have greatly contributed to improving our knowledge of the relevant structural parameters that control the electronic properties and the magnitude of the gap in LCSs. In this context, the recent development of small bandgap molecular LCSs appears particularly interesting. As a matter of fact, the use of well-defined model structures allows a refinement of the study of the structural/electronic property relationships and the analysis of the effects of subtle structural variations. On the other hand, being the most recent, this approach has the enormous advantage of benefiting from all the previous experience. Thus, the substitution and/or rigidification of thiophene oligomers has allowed the development of molecular LCSs with bandgaps approaching the smallest values reached so far. These results are important as they suggest that the extension of these concepts to longer molecular LCSs or even to polymers could lead to materials with very small or perhaps vanishing gaps.

However, the synthesis of such small gap LCSs is only half the solution of synthesizing intrinsically conducting materials. The proper organization of these elemental bricks into a 3D supramolecular architecture is also required. Furthermore, the potential industrial use of such material will be conditioned by the possibility of preparing them in processable forms. This question is far from trivial since, for example, rigidity and solubility are often contradictory. In this respect, recent advances in various fields such as composite materials,[397,398] gels,[399,400] and dendrimers[401,402] will certainly open up exciting new perspectives.

## XI. Acknowledgments

Professors A. Gorgues and M. Jubault are gratefully acknowledged for their critical reading of the manuscript and for many useful comments.

## XII. References

(1) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 90.
(2) *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982.
(3) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687.
(4) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.
(5) Ito, T.; Shirakawa, H.. Ikeda, S. *J. Polym. Sci. Chem. Ed.* **1974**, *12*, 11.
(6) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.
(7) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635.
(8) Diaz, A. F.; Lacroix, J. C. *New J. Chem.* **1988**, 12, 171.
(9) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.
(10) Genies, E. M. *New J. Chem.* **1989**,
(11) Diaz; A. F. *Chem. Scr.* **1981**, *17*, 142.
(12) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(13) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.
(14) Mertz, A. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1990; Vol. 152, p 49.
(15) Deronzier, A.; Moutet, J. C. *Acc. Chem. Res.* **1989**, *22*, 249.
(16) Burroughes, J. H.; Bradey, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(17) Proceedings of ISCM '94. *Synth. Met.* **1995**, Vols. 69−72.
(18) Rudge, A.; Davey, J.; Gottesfeld, S.; Ferraris, J. P. *Proc. Electrochem. Soc.* **1993**, *93*, 74.
(19) Baigent, D. R.; Hamer, P. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1995**, *71*, 2175.
(20) Greeham, NC.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
(21) Little W. A. *Phys. Rev.* **1964**, *134*, A1416.
(22) Wennerström, O. *Macromolecules* **1985**, *18*, 1977.
(23) Peierls, R. E. *Quantum Theory of Solids*; Oxford University Press: London, 1956.
(24) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98.
(25) Lyons, L. E. *Aust. J. Chem.* **1980**, *33*, 1717.
(26) Loutfy, R. O.; Cheng, Y. C. *J. Chem. Phys.* **1980**, *73*, 2902.
(27) Kaufman, J. H.; Chung, T. C.; Heeger, A. J. *Solid State Commun.* **1983**, *47*, 585.

(28) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702.
(29) Kaner, R. B.; Porter, S. J.; Naims, D. P.; MacDiarmid, A. G. *J. Chem. Phys.* **1989**, *90*, 5102.
(30) Kertez, M.; Koller, J.; Azman, A. *J. Chem. Phys.* **1977**, *67*, 1180.
(31) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698.
(32) Lowe, J. P.; Kafafi, S. A. *J. Am. Chem. Soc.* **1984**, *106*, 5837.
(33) Brédas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808.
(34) Lee, Y-S.; Kertesz, M. *J. Chem. Phys.* **1988**, *88*, 2609.
(35) Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41.
(36) Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M. *J. Chem. Phys.* **1985**, *83*, 1323.
(37) Alberti, A.; Favaretto, L.; Seconi, G. *J. Chem. Soc., Perkin Trans. 2* **1990**, 931.
(38) Jones, D.; Guerra, M.; Favaretto, L.; Modelli, A.; Fabrizio, M.; Distefano, G. *J. Phys. Chem.* **1990**, *94*, 5761.
(39) Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *Adv. Mater.* **1993**, *5*, 834.
(40) Distefano, G.; Da Colle, M.; Jones, D.; Zambianchi, M.; Favaretto, L.; Modelli, A. *J. Phys. Chem.* **1993**, *97*, 3504.
(41) Chadwick, J. E.; Kohler, B. E. *J. Phys. Chem.* **1994**, *98*, 3631.
(42) Belletête, M.; Leclerc, M.; Durocher, G. *J. Phys. Chem.* **1994**, *98*, 9450.
(43) Orti, E.; Viruela, P. M.; Sanchez-Marin, J.; Tomas, F. *J. Phys. Chem.* **1995**, *99*, 4955.
(44) Horne, J. C.; Blanchard, G. J.; LeGoff, E. *J. Am. Chem. Soc.* **1995**, *117*, 955.
(45) ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887.
(46) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.
(47) Sato, M.; Hiroi, M. *Synth. Met.* **1995**, *71*, 2085.
(48) Hernandez, V.; Castiglioni, C.; Del Zopo, M.; Zerbi, G. *Phys. Rev. B* **1994**, *50*, 9815.
(49) Mintmire, J. W.; White, C. T.; Lelert, M. L. *Synth. Met.* **1987**, *16*, 235.
(50) Kürti, J.; Surjan, P. R.; Kertesz, M.; Frapper, G. *Synth. Met.* **1993**, *55*−57, 4338.
(51) Yon, S. Y.; Kwon, S. J.; Kim, S. C. *J. Chem. Phys.* **1995**, *103*, 1871.
(52) Zhou, Z.; Parr, G. *J. Am. Chem. Soc.* **1989**, *111*, 7371.
(53) Soos, Z. G.; Hayden, G. W. *Synth. Met.* **1989**, *28*, D543.
(54) Grant, P. M.; Batra, I. P. *Solid State Commun.* **1979**, *29*, 225.
(55) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 9.
(56) Lin, J. W. P.; Dudek, L. P. *J. Polym. Sci.* **1980**, *18*, 2869.
(57) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
(58) Bäuerle, P. *Adv. Mater.* **1993**, *5*, 879.
(59) Roncali, J.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1987**, *18*, 139.
(60) Furukawa, Y.; Akimoto, M.; Harada, I. *Synth. Met.* **1987,** *18*, 189.
(61) Delabouglise, D.; Roncali, J.; Garreau; R.; Lemaire, M. *New J. Chem.* **1988**, *12*, 155.
(62) Sauvajol, J. L.; Chenouni, D.; Lère-Porte, J. P.; Chorro, C., Moukaia, B.; Petrissans, J. *Synth. Met.* **1990**, *38*, 1.
(63) Sato, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1986**, *14*, 279.
(64) Roncali, J.; Garnier, F. *New J. Chem.* **1986**, *4*−5, 237.
(65) Hotta, S. *Synth. Met.* **1988**, 22, 103.
(66) Roncali, J.; Yassar, A.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1988**, 581.
(67) Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804.
(68) Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1983**, *87*, 2289.
(69) Roncali, J.; Yassar, A.; Garnier, F. *J. Chim. Phys.* **1989**, *86*, 85.
(70) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.
(71) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1989**, 679.
(72) Roncali, J.; Korri Youssoufi, H.; Garreau, R.; Garnier, F.; Lemaire, M. *J Chem. Soc., Chem. Commun.* **1990**, 414.
(73) Roncali, J.; Marque, P.; Garreau, R.; Garnier, F.; Lemaire, M. *Macromolecules* **1990**, *23*, 1347.
(74) Roncali, J.; Li, H. S.; Garnier, F. *J. Phys. Chem.* **1991**, *95*, 8983.
(75) Li, H. S.; Garnier, F., Roncali, J. *Solid State Commun.* **1991**, *77*, 811.
(76) Li, H. S.; Garnier, F.; Roncali, J. *Macromolecules* **1992**, *25*, 6425.
(77) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
(78) Lemaire, M.; Roncali, J.; Garnier, F.; Garreau, R.; Hannecart, E. French Pat. 86.04744, April 4 1986.
(79) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
(80) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.
(81) McCullough, R. D.; Williams, S. P.; Tristam-Nagle, S.; Jayaraman, M.; Ewbank, P. C.; Miller, L. *Synth. Met.* **1995**, *69*, 279.
(82) Tamao, K.; Odama, S.; Nakasima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *8*, 3347.
(83) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.
(84) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.
(85) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem*., **1993**, *58*, 904.
(86) Chen, T.-A.; Wu, X.; Rieke, R. D. *Synth. Met.* **1993,** *60*, 175
(87) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233
(88) Thémans, B.; André, J. M.; Brédas, J. L. *Synth. Met.* **1987**, *21*, 149.
(89) Meyer, R.; Kleinert, H.; Richter, S.; Gewald, K. *J. Prakt. Chem.* **1963**, *20*, 244.
(90) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382.
(91) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985.
(92) Colaneri, N.; Kobayashi, M.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1986**, *14*, 45.
(93) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.
(94) Brédas, J. L.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1986**, *85*, 4673.
(95) Brédas, J. L.; Thémans, B.; André, J. M.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *11*, 343.
(96) Lee, Y. S.; Kertesz, M. *Int. J. Quantum Chem. Symp.* **1987**, *21*, 163.
(97) Nayak, K.; Marynick, D. S. *Macromolecules* **1990**, *23*, 2237.
(98) Kürti, J.; Surjan, P. R. *J. Chem. Phys.* **1990**, *92*, 3247.
(99) Karpfen, A.; Kertesz, M. *J. Phys. Chem.* **1991**, *95*, 7680.
(100) Hoogmartens, I.; Adriaensens, P.; Vanderzande, D.; Gelan, J.; Quattrochi, C.; Lazzaroni, R.; Brédas, J. L. *Macromolecules* **1992**, *25*, 7347.
(101) Hoogmartens, I.; Adriaensens, P.; Carleer, R.; Vanderzande, D.; Martens, H.; Gelan, J. *Synth. Met.* **1992**, *51*, 219.
(102) Kiebooms, R.; Hoogmartens, I.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Macromolecules* **1995**, *28*, 4961.
(103) Kertesz, M. *Synth. Met.* **1995**, *69*, 641.
(104) Zerbi, G.; Magnoni, M. C.; Hoogmartens, I.; Kiebooms, R.; Carleer, R.; Vanderzande, D.; Gelan, J. *Adv. Mater.* **1995**, *7*, 1027.
(105) Quattrochi, C.; Lazzaroni, R.; Brédas, J. L.; Kiebooms, R.; Vanderzande, D.; Gelan, J.; Van Meervelt, L. *J. Phys. Chem.* **1995**, *99*, 3932.
(106) Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *36*, 3932.
(107) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266.
(108) Cava, M. P.; Pollack, N. M. *J. Am. Chem. Soc.* **1966,** *88*, 4112.
(109) Yashima, H.; Kobayashi, M.; Lee, K.-B; Chung, T. C.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* **1987**, *134*, 46.
(110) Christensen, P. A.; Kerr, J. C. H.; Higgins, S. J.; Hamnet, A. *Faraday Discuss. J. Chem. Soc.* **1989**, *88*, 261.
(111) Dale, S. M.; Glide, A.; Hillman, A. R. *J. Mater. Chem.* **1992**, *2*, 99.
(112) Onoda, M.; Nakayama, H.; Morita, S.; Kawai, T.; Yoshino, K. *Synth. Met.* **1995**, *69*, 605.
(113) Jen, K.-Y.; Elsenbaumer, R. L. *Synth. Met.* **1986**, *16*, 379.
(114) Rose, T. L.; Liberto, M. C. *Synth. Met.* **1989**, *31*, 395.
(115) Hoogmartens, I.; Vanderzande, D.; Martens, H.; Gelan, G. *Synth. Met.* **1992**, *47*, 367.
(116) van Asselt, R.; Hoogmartens, I.; Vanderzande, D.; Gelan, J.; Froehling, P. E.; Aussems, M.; Aagaard, O.; Schellekens, R. *Synth. Met.* **1995**, *74*, 65.
(117) Ikenoue, Y.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1991**, *40*, 1.
(118) Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *Synth. Met.* **1993**, *55*−*57*, 960.
(119) Funatsu, E. Jpn Pat. 02 252 727, 11 Oct. 1990; *Chem Abstr.* **1991**, *114*, 197730q.
(120) Burbridge, S. J.; Page, H.; Drury, A.; Davey, A. P.; Callaghan, J.; Blau, W. *J. Mod. Opt.* **1994**, *41*, 1217.
(121) King, G.; Higgins, S. J. *J. Chem. Soc., Chem. Commun.* **1994**, 825.
(122) King, G.; Higgins, S. J. *J. Mater. Chem.* **1995**, *5*, 447.
(123) Swann, M. J.; Broke, G.; Bloor, D. *Synth. Met.* **1993**, *55*−*57*, 281.
(124) Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1672.
(125) Kastner, J.; Kuzmany, H.; Vegh, D.; Landl, M.; Cuff, L.; Kertesz, M. *Macromolecules* **1995**, *28*, 2922.
(126) Gronowitz, S.; Persson, B. *Acta Chem. Scand.* **1967**, *21*, 812.
(127) Litvinov, V. P.; Gol'dfarb, Y. L. *Adv. Heterocycl. Chem.* **1976**, *19*, 123.
(128) De Jong, F.; Janssen, M. J. *J. Org. Chem.* **1971**, *36*, 1645.
(129) Danieli, R.. Taliani, C.; Zamboni, R.; Giro, G.; Biserni, M.; Mastragostino, M.; Testoni, A. *Synth. Met.* **1986**, *13*, 328.
(130) Jow, T. R.; Jen, K. Y.; Elsenbaumer, R.; Shacklette, L. W. *Synth. Met.* **1986**, *14*, 53.
(131) Di Marco, P.; Mastragostino, M.; Taliani, C. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 241.
(132) Biserni, M.; Marinangeli, A. M.; Mastragostino, M. *J. Electrochem. Soc.* **1985**, *132*, 1597.
(133) Taliani, C.; Zamboni, R.; Danieli, R.; Ostoja, P.; Porzio, W.; Lazzaroni, R.; Brédas, J. L. *Phys. Scr.* **1989**, *40*, 781.

(134) Mazaki, Y.; Kobayashi, K. *Tetrahedron Lett.* **1989**, *30*, 3315.
(135) Bolognesi, A.; Catellani, M.; Destri, S.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1988**, 246.
(136) Taliani, C.; Ruani, G.; Zamboni, R.; Bolognesi, A.; Catellani, M.; Destri, S.; Porzio, W. *Synth. Met.* **1989**, *28*, C507.
(137) Catellani, M.; Caronna, T.; Valdo Meille, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1911.
(138) Arbizzani, C.; Catellani, M.; Mastragostino, M.; Mingazzini, C. *Electrochim. Acta* **1995**, *40*, 1871.
(139) Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139.
(140) Cava, M. P.; Lakshmikantham, M. V. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds; Pergamon Press: New York, 1984; Vol. 4, p 1037.
(141) Beye, N.; Cava, M. P. *J. Org. Chem.* **1994**, *59*, 2223 and references therein.
(142) Hong, S. Y.; Marynick, D. S. *Macromolecules* **1992**, *25*, 4652.
(143) Lee, Y. S.; Kertesz, M.; Elsenbaumer, R. L. *Chem. Mater.* **1990**, *2*, 526.
(144) Wynberg, H.; Zwaneneburg, D. J. *Tetrahedron Lett.* **1967**, 761.
(145) Diaz, A. F.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electroanal. Chem.* **1981**, *121*, 355.
(146) Marque, P.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1987**, *218*, 107.
(147) Krische B.; Zagorska, M. *Synth. Met.* **1989**, *28*, C257.
(148) Waltman, R. J.; Bargon, J. *Tetrahedron* **1984**, *40*, 3963.
(149) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76.
(150) Roncali, J.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1986**, *14*, 323.
(151) Berlin, A.; Wernet, W.; Wegner, G. *Makromol. Chem.* **1987**, *188*, 2963.
(152) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183.
(153) Roncali, J.; Giffard, M.; Jubault, M.; Gorgues, A. *J. Electroanal. Chem.* **1993**, *361*, 185.
(154) Roncali, J.; Gorgues, A.; Jubault, M. *Chem. Mater.* **1993**, *5*, 1456.
(155) Wang, C.; Benz, M. E., LeGoff, E.; Schindler, J. L.; Albritton-Thomas, J.; Kannewurf, C. R.; Kanatzidis, M. *Chem. Mater.* **1994**, *6*, 401.
(156) Visy, C.; Lukkari, J.; Kankare, J. *Macromolecules* **1994**, *27*, 3322.
(157) Lorcy, D.; Cava, M. P. *Adv. Mater.* **1992**, *4*, 562.
(158) Bäuerle, P.; Götz, G.; Emerle, P.; Port, H. *Adv. Mater.* **1992**, *4*, 564.
(159) Musinanni, S.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1993**, 172.
(160) Brédas, J. L. *Synth. Met.* **1987**, *17*, 115.
(161) Bakhshi, A. K.; Ladik, J. *Solid State Commun.* **1987**, *63*, 1157.
(162) Kurti, J.; Surjan, P. R.; Kertesz, M. *J. Am. Chem. Soc.* **1991**, *113*, 9865.
(163) Hong, S. Y.; Marynick, D. S. *J. Chem. Phys.* **1992**, *96*, 5797.
(164) Lakshmikantham, M. V.; Lorcy, D.; Scordilis-Kelley, C.; Wu, X-L.; Parakka, J. P.; Metzger, R. M.; Cava, M. P. *Adv. Mater.* **1993**, *5*, 723.
(165) Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1585.
(166) Ferraris, J. P.; Bravo, A.; Kim, W.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1994**, 991.
(167) Tanaka, S.; Yamashita, Y. *Synth. Met.* **1993,** *55−57*, 1251.
(168) Suzuki, T.; Fujii, H.; Yamashita, Y.; Kabuto, C.; Tanaka, S.; Harasawa, H.; Mukai, T.; Miyashi, T. *J. Am. Chem. Soc.* **1992**, *114*, 3034.
(169) Tanaka, S.; Yamashita, Y. *Synth. Met.* **1995**, *69*, 599.
(170) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791.
(171) Kraak, A.; Wieserma, A. K.; Jordens, P.; Wynberg, H. *Tetrahedron* **1968,** *24*, 3381.
(172) Jeffries, A. T.; Moore, K. C.; Ondeyka, D. M.; Sringsteen, A. W.; Mac Dowell, D. W. H. *J. Org. Chem.* **1981**, *46*, 2885.
(173) Cunningham, D. D.; Gaa, A.; Pham, C. V.; Lewis, E. T.; Burkhardt, A.; Davidson, L. L.; Kansah, A. N.; Ataman, O. Y.; Zimmer, H.; Mark, H. B. *J. Electrochem. Soc.* **1988**, *135*, 2750.
(174) Berlin, A.; Brenna, E.; Pagani, G. A.; Sannicolo, F. *Synth. Met.* **1992**, *51*, 287.
(175) Zotti, G.; Schiavon, G.; Berlin, A.; Fontana, G.; Pagani, G. *Macromolecules* **1994**, *27*, 1938.
(176) Lambert, T. M.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1991**, 752.
(177) Sease, J. W.; Zechmeister, L. *J. Am. Chem. Soc.* **1947**, *69*, 270.
(178) Brisset, H.; Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1305.
(179) Jordens, P.; Rawson, G.; Wynberg, H. *J. Chem. Soc. C* **1970**, 273.
(180) Ferraris, J. P.; Lambert, T. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1268.
(181) Toussaint, J. M.; Brédas, J. L. *Synth. Met.* **1993**, *61*, 103.
(182) Toussaint, J. M.; Brédas, J. L. *Synth. Met.* **1995**, 69, 637.
(183) Ferraris, J. P.; Henderson, C.; Torres, D.; Meeker, D. *Synth. Met.* **1995**, *72*, 147.
(184) Roncali, J., Li, H. S.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1990**, *36*, 267.
(185) Roncali, J.; Brisset, H.; Thobie-Gautier, C.; Jubault, M.; Gorgues, A. *J. Chim. Phys.* **1995**, *92*, 771.
(186) Roncali, J.; Garreau, R.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1500.
(187) Ruiz, J. P.; Nayack, K.; Marynick, D. S.; Reynolds, J. R. *Macromolecules* **1989**, *22*, 1231.
(188) Kozaki, M.; Tanaka, S.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1500.
(189) Kozaki, M.; Tanaka, S.; Yamashita, Y. *Chem. Lett.* **1993,** 533.
(190) Kozaki, M.; Tanaka, S.; Yamashita, Y. *J. Org. Chem.* **1994**, *59*, 442.
(191) Roncali, J.; Thobie-Gautier, C.; Brisset, H.; Jubault, M.; Gorgues, A. *J. Chim. Phys.* **1995**, *92*, 767.
(192) Kellogg, R. M.; Groen, M. B.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 3093.
(193) Loader, L. E.; Timmons, C. J. *J. Chem. Soc.* **1967**, 1677.
(194) Kossmehl, G.; Härtel, M.; Manecke, G. *Makromol. Chem.* **1970**, *131*, 15.
(195) Tanaka, S.; Sato, M.; Kaeriyama, K. *Makromol. Chem.* **1985**, *186*, 1685.
(196) Martinez, M.; Reynolds, J. R.; Basak, S.; Black, D. A.; Marynick, D. S.; Pomerantz, M. *J. Polym. Sci. B*, **1988**, *26*, 911.
(197) Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E.; Frère, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2249.
(198) Catellani, M.; Luzzati, S.; Speroni, F. *Synth. Met.* **1993**, *55−57*, 1188.
(199) Catellani, M.; Luzzati, S.; A. Musco, A.; Speroni, F. *Synth. Met.* **1994**, *62*, 223.
(200) Speroni, F.; Catellani M.; Luzzati, S.; Musco, A. *Synth. Met.* **1993**, *55−57*, 94.
(201) Gogte, V. N.; Shah, L. G.; Tilak, B. D.; Gadekar, K. N.; Sahasrabudhe, M. B. *Tetrahedron*, **1967**, *23*, 2437.
(202) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87.
(203) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *Electrochim. Acta*
(204) Sotzing, G. A.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1995**, 703.
(205) Lenz, R. W.; Hanlovits, C. E. *J. Org. Chem.* **1960**, *25*, 813.
(206) Hörhold, H. H.; Opferman, J. *Makromol. Chem.* **1970**, *131*, 105.
(207) Hörhold, H. H.; Helbig, M. *Makromol. Chem. Makromol. Symp.* **1987**, *12*, 229.
(208) Friend, R. H.; Greeham, N. C.; Grüner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117.
(209) Ho, H. A.; Brisset, H.; Frère, P.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1995**, 2309.
(210) Kossmehl, G.; Greczmiel, T.; Plieth, W. *Macromol. Chem. Phys.* **1994**, *195*, 3655.
(211) Benahmed-Gasmi, A.; Frère, P.; Roncali, J. *J. Electroanal. Chem.* **1996**, *406*, 231.
(212) Ho, H. A.; Brisset, H.; Elandaloussi, E.; Frère, P.; Roncali, J. *Adv. Mater.* **1996**, *8*, 990.
(213) MacDowell, D. W. H.; Patrick, T. B.; Frame, B. K.; Ellison, D. L. *J. Org. Chem.* **1967**, *32*, 1227.
(214) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; John Wiley and Sons: New York, 1962.
(215) Hanack, M.; Hieber, G.; Dewald, G.; Ritter, H. *Synth. Met.* **1991**, *41−43*, 507.
(216) Hanack, M.; Schmid, U.; Echinger, S.; Teichert, F.; Hieber, J. *Synthesis* **1993,** 634.
(217) Ritter, H.; Mangold, K-M.; Röhrig, U.; Schmid, U.; Hanack, M. *Synth. Met.* **1993**, *55−57*, 1193.
(218) Echinger, S.; Schmid, U.; Teichert, F.; Hieber, J..; Ritter, H.; Hanack, M. *Synth. Met.* **1993**, *61*, 163.
(219) Hanack, M.; Hieber, G.; Mangold, K-M.; Ritter, H.; Röhrig, U.; Schmid, U. *Synth. Met.* **1993**, *55−57*, 827.
(220) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci. A-1* **1966**, *4*, 1337.
(221) Kossmehl, G.; Härtel, M.; Menecke, G. *Makromol. Chem.* **1970,** *131*, 15.
(222) Kossmehl, G.; Härtel, M.; Menecke, G. *Makromol. Chem.* **1970,** *131*, 37.
(223) Wessling, R. A.; Zimmerman, R. G. US Patents 3,401,152, 1968; and 3,706,677, 1972; *Chem. Abstr.* **1968**, *69*, 87735q; and **1973**, *78*, 85306n.
(224) Wessling, R. A. *J. Polym. Sci. Polym. Symp.* **1985**, *72*, 55.
(225) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polymer* **1987**, *28*, 567.
(226) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, 25, 387.
(227) Jen, K.-Y.; Maxfield, M. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309.
(228) Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1448.
(229) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1987**, 28, 229.
(230) Jen, K.-Y.; Jow, T. R.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1113.
(231) Iwatsuki, S.; Kubo, M.; Yamashita, H. *Chem. Lett.* **1989**, 729.
(232) Peeters, L.; Eevers, W.; Van Der Borght, Jacobs, S.; Geise, H. J. *Polymer* **1993**, 34, 4589.

(233) Iwatsuki, S.; Kubo, M.; Itoh, Y. *Chem. Lett.* **1993**, 1085.
(234) Barker, J. *Synth. Met.* **1989**, *32*, 43.
(235) Brédas, J. L.; Elsenbaumer, R. J.; Chance, R. R.; Silbey, R. *J. Chem. Phys.* **1983**, *78*, 5656.
(236) Glenis, S.; Benz, M.; LeGoff, E.; Schindler, J. L.; Kannewurf, C. R.; Kanitzidis, M. *J. Am. Chem. Soc.* **1993**, 115, 12519.
(237) Eckhardt, H.; Shacklette, L. W.; Jen, K.-Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303.
(238) Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1451.
(239) Jenekhe, S. A. *Nature* **1986**, *322*, 345.
(240) Brédas, J. L. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 49.
(241) Brédas, J. L.; Boudreaux, D. S.; Chance, R. R.; Silbey, R. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 323.
(242) Boudreaux, D. S.; Chance, Elsenbaumer, R. L.; Frommer, J. E.; Brédas, J. L.; Silbey, R. *Phys. Rev.* **1985**, *31*, 652.
(243) Kertesz, M.; Lee, Y. S. *J. Phys. Chem.* **1987**, *91*, 2690.
(244) Toussaint, J. M.; Brédas, J. L. *Macromolecules* **1993**, *26*, 5240.
(245) Musso, G. F.; Dellepiane, G.; Cuniberti, C.; Rui, M.; Borghesi, A. *Synth. Met.* **1995**, *72*, 209.
(246) Toussaint, J. M.; Thémans, B.; André, J.; Brédas, J. L. *Synth. Met.* **1989**, *28*, C205.
(247) Toussaint, J. M.; Brédas, J. L. *Synth. Met.* **1991**, *41*–*43*, 3555.
(248) Jenekhe, S. A. *Macromolecules* **1986**, *19*, 2663.
(249) Patil, A. O.; Wudl, F. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1987**, *28*, 341.
(250) Patil, A. O.; Wudl, F. *Macromolecules* **1988**, *21*, 540.
(251) Jenekhe, S. A. *Macromolecules* **1990**, *23*, 2848.
(252) Chen, W.-C.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 454.
(253) Chen, W.-C.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 465.
(254) Jira, R.; Braunling, H. *Synth. Met.* **1987**, *17*, 691.
(255) Bräunling, H.; Blöchl, G.; Becker, R. *Synth. Met.* **1991**, *41*–*43*, 487.
(256) Bräunling, H.; Becker, R.; Blöchl, G. *Synth. Met.* **1993**, *55*–*57*, 833.
(257) Han, C. C.; Elsenbaumer, R. L. *Synth. Met.* **1989**, *30*, 123.
(258) Giffard, M.; Alonso, P.; Garin, J.; Gorgues, A.; Nguyen, T. P.; Richomme, P.; Robert, A.; Roncali, J.; Uriel, S. *Adv. Mater.* **1994**, *6*, 298.
(259) Meier, H. *Organic Semiconductors*; Verlag Chemie: Weinheim, 1974.
(260) André, J. M.; Gouverneur, L.; Leroy, G. *Bull Soc. Chim. Belg.* **1967,** *76*, 661.
(261) Kivelson, S.; Chapman, O. L. *Phys. Rev. B.* **1983**, *28*, 7236.
(262) Tanaka, K.; Ohzeki, K.; Nankai, S.; Yamabe, T.; Shirakawa, H. *J. Phys. Chem. Solids* **1983**, *44*, 1069.
(263) Kertesz, M.; Hoffmann, R. *Solid State Commun.* **1983**, *47*, 97.
(264) Brédas, J. L.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1982**, *76*, 3673.
(265) Pomerantz, M.; Cardona, R.; Rooney, P. *Macromolecules* **1989**, *22*, 304.
(266) Kao, J.; Lilly, A. C., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4149.
(267) Lowe, J. P.; Kafafi, S. A.; LaFemina, J. P. *J. Phys. Chem.* **1986**, *90*, 6602.
(268) Bailey, W. J.; Liaio, C.-W. *J. Am. Chem. Soc.* **1955**, *77*, 992.
(269) Simon, J.; Tournilhac, F.; André, J. J. *New. J. Chem.* **1987**, *11*, 383.
(270) Edwards, G. A.; Goldfinger, G. *J. Polym. Sci.* **1955**, *16*, 589.
(271) Bohlmann, F.; Inhoffen, B. *Chem. Ber.* **1956**, *89*, 1276.
(272) Pohl, H. A.; Engelhart, E. H. *J. Phys. Chem.* **1962**, *66*, 2085.
(273) Teyssie, P.; Korn-Girard, A. *J. Polym. Sci. A* **1964**, *2*, 2849.
(274) Vogel, T.; Blatter, K.; Schlüter, A. D. *Makromol. Chem., Rapid Commun.* **1989,** *10*, 427.
(275) Ashton, P. R.; Mathias, J. P.; Stoddart, J. F. *Polym. Prep.* **1991**, *32*, 419.
(276) Tanaka, K.; Yamashita, S.; Koike, T.; Yamabe, T. *Synth. Met.* **1989**, *31*, 1.
(277) Ozaki, M.; Ikeda, Y.; Nagoya, I. *Synth. Met.* **1989**, *28*, C801.
(278) Kojima, Y.; Tsuji, M.; Matsuoka, T.; Takahashi, H. *Macromolecules* **1994**, *27*, 3735.
(279) Kojima, Y.; Matsuoka, T.; Sato, N.; Takahashi, H. *Macromolecules* **1995**, *28*, 2893.
(280) Goldfinger, M. B.; Swager, T. *J. Am. Chem. Soc.* **1995**, *116*, 7895.
(281) Yamabe, T.; Tanaka, K.; Ohzeki, K.; Ata, S. *Solid State Commun.* **1982**, *44*, 823.
(282) Kaplan, M. L.; Schmidt, P. H.; Chen, C.-H.; Walsh, W. M., Jr. *Appl. Phys. Lett.* **1980**, *36*, 867.
(283) Schmidt, P. H.; David C.; Kaplan, M. L.; Feldmann, W. L. *Appl. Phys. Lett.* **1982**, *40*, 93.
(284) Forrest, S. R.; Kaplan, M. L.; Schmidt, P. H.; Venkatesan, T.; Lovinger, A. J. *Appl. Phys. Lett.* **1982**, *41*, 708.
(285) Iqbal, Z.; Ivory, D. M.; Marti, J.; Brédas, J. L.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 103.
(286) Murakami, M.; Yoshimura, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1649.
(287) Murakami, M.; Yoshimura, S. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 95.
(288) Kamo, H.; Yudasaka, M.; Kurita, S.; Matsui, T.; Kikuchi, R.; Ohki, Y.; Yoshimura, S. *Synth. Met.* **1994**, *68*, 61.
(289) Bozovic, I. *Phys. Rev. B*, **1985**, *32*, 8136.
(290) Tanaka, K.; Ueda, K.; Koike, T.; Yamabe, T. *Solid State Commun.* **1984**, *51*, 943.
(291) Bakhshi, A. K.; Ladik, J. *Synth. Met.* **1989**, *30*, 115.
(292) Karabunarliev, S.; Baumgarten, Müllen, K.; Tyutyulkov, N. *Chem. Phys.* **1994**, *179*, 421.
(293) Brédas, J. L.; Baughman, R. H. *J. Chem. Phys.* **1985**, *83*, 1316.
(294) Viruela-Martin, R.; Viruela-Martin, P. M.; Orti, E. *J. Chem. Phys.* **1992**, *97*, 8470.
(295) Müllen, K.; Koch, K.-H. *Chem. Ber.* **1991**, *124*, 2091.
(296) Tyutyulkov, N.; Tadjer, A.; Mintcheva, I. *Synth. Met.* **1990**, *38*, 313.
(297) Clar, E.; Kelly, R.; Laird, R. M. *Monatsh. Chem.* **1956**, *80*, 391.
(298) Clar, E.; Schmidt, W. *Tetrahedron* **1978**, *34*, 3219.
(299) Bohnen, A.; Koch, K.-H.; Lüttke, W.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 525.
(300) Baumgarten, M.; Koch, K. H; Müllen, K. *J. Am. Chem. Soc.* **1994**, *116*, 7341.
(301) Baumgarten, M.; Anton, U.; Gherghel, L.; Müllen, K. *Synth. Met.* **1993**, *55*–57, 4807.
(302) Schlüter, A.-D.; Löfter, M.; Enkelmann, V. *Nature* **1994**, *368*, 331.
(303) Löffler, M.; Schlüter, A.-D.; Gessler, K.; Saenger, W.; Toussaint, J. M.; Brédas, J. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2209.
(304) Schlicke, B.; Schirmer, H.; Schlüter, A.-D. *Adv. Mater.* **1995**, *7*, 544.
(305) Baumgarten, M.; Bunz, U.; Scherf, U.; Müllen, K. In *Molecular Engineering for Advanced Materials*; Becher, J., Schaumburg, K., Eds.; Kluwer Academic Publishers: Dordrecht, 1995; p 159.
(306) Stille, J. K.; Mainen, E. L. *Macromolecules* **1968**, *1*, 36.
(307) DeSchryver, F.; Marvel, C. S. *J. Polym. Sci. A* **1967**, *5*, 545.
(308) Jenekhe, S. A. *Macromolecules* **1991**, *24*, 1.
(309) Foot, P. J. S.; Montgomery, V.; Rhodes, C. J.; Spearman, P. *Mol. Cryst. Liq. Cryst.* **1993**, *236*, 199.
(310) Cao, X. F.; Jiang, J. P.; Bloch, D. P.; Hellwarth, R. W.; Yu, L. P.; Dalton, L. *J. Appl. Phys.* **1989**, *65*, 5012.
(311) Della Casa, C.; Andreani, F.; Costa Bizzarri, P.; Fiorini, M., Salatelli, E.; Grossi, L.; Porzio, W. *Synth. Met.* **1989**, *29*, E477.
(312) Bandara, A. J; Curley, J.; Pritchard, G. *Synth. Met.* **1995**, *72*, 1.
(313) Chiba, K.; Ohsaka, T.; Ohnuki, Y.; Oyama, N. *J. Electroanal. Chem.* **1987**, *219*, 117.
(314) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1990**, *2*, 649.
(315) Oyama, N.; Sato, M.; Ohsoka, T. *Synth. Met.* **1989**, *29*, E501.
(316) Goyette, M. A.; Leclerc, M. *J. Electroanal. Chem.* **1995**, *382*, 7.
(317) Kunimura, S.; Ohsaka, T.; Oyama, N. *Macromolecules* **1988**, *21*, 894.
(318) Barbero, C.; Silber, J. J.; Sereno, L. *J. Electroanal. Chem.* **1990**, *291*, 81.
(319) Chmil, K.; Scherf, U. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 217.
(320) Grimme, J.; Kreyenschmidt, M.; Uckert, F.; Müllen, K.; Scherf, U. *Adv. Mater.* **1995**, *7*, 292.
(321) Scherf, U.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489.
(322) Myaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.
(323) Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* **1930**, *52*, 2881.
(324) Graupner, W.; Mauri, M.; Stampfl, J.; Leising, G.; Scherf, U.; Müllen, K. *Solid State Commun.* **1994**, *91*, 7.
(325) Huber, J.; Müllen, K.; Salbeck, J.; Schenk, H.; Scherf, U.; Stehlin, T.; Stern, R. *Acta Polym.* **1994**, *45*, 244.
(326) Grüner, J.; Hamer, P. J.; Friend, R. H.; Huber, H. J.; Scherf, U.; Holmes, A.B. *Adv. Mater.* **1994**, *6*, 748.
(327) Grüner, J.; Wittmann, H. F.; Hamer, P. J.; Friend, R. H.; Huber, H. J.; Scherf, U.; Müllen, K.; Moratti, S. C.; U.; Holmes, A. B. *Synth. Met.* **1994**, *67*, 181.
(328) Kölher, A.; Grüner, J.; Friend, R. H.; Müllen, K.; Scherf, U. *Chem. Phys. Lett.* **1995**, *243*, 456.
(329) Kertesz, M.; Hughbanks, T. R. *Synth. Met.* **1994**, *69*, 699.
(330) Kertesz, M. *Macromolecules* **1995**, *28*, 1475.
(331) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935.
(332) Scherf, U.; Müllen, K. *Polymer Commun.* **1992**, *33*, 2443.
(333) Scherf, U. *Synth. Met.* **1993**, *55*–57, 767.
(334) Freund, T.; Scherf, U.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2424.
(335) Freund, T.; Müllen, K.; Scherf, U. *Macromolecules* **1995**, *28*, 547.
(336) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustcich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.
(337) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.
(338) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341.
(339) Rao, V. P.; Cai, Y. M.; Jen, A. K.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1689.
(340) Gilmour, S.; Marder, S. R.; Perry, J. W.; Cheng, L.-T. *Adv. Mater.* **1994**, *6*, 494.
(341) Jen, A. K.-Y.; Rao, V. P.; Drost, K. J.; Wong, K. Y.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2057.
(342) Fichou, D.; Nishikitani, Y.; Horowitz, G; Roncali, J.; Garnier, F. *Synth. Met.* **1989**, *28*, C729.
(343) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.

(344) Geiger, F.; Stoldt, M.; Schweizer, H.; Bäuerle, P.; Umbach, E. *Adv. Mater.* **1993**, *5*, 922.

(345) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119.

(346) Maahs, G.; Hegenberg, P. *Angew. Chem., Int. Ed. Engl.* **1966,** *5*, 888.

(347) Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677.

(348) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.

(349) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, *55*−*57*, 299.

(350) Havinga, E. E.; Pomp, A.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1995**, *69*, 581.

(351) Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867.

(352) Tamao, K.; Yamaguchi, S.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 229.

(353) Zotti, G.; Gallazzi, M. C.; Zerbi, G.; Meille, S. V. *Synth. Met.* **1995**, *73*, 217.

(354) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013.

(355) *The Physics and Chemistry of Organic Superconductors*; Saito, G., Kagoshima, S., Eds.; Springer Verlag: London, 1990.

(356) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355.

(357) Benahmed-Gasmi, A.; Frère, P.; Garrigues, B.; Gorgues, A.; Jubault, M.; Carlier, R.; Texier, F. *Tetrahedron Lett.* **1992**, *33*, 6457.

(358) Hansen, T. K.; Lakshmikantham, M. V.; Cava, M. P.; Niziurski-Mann, R. E.; Jensen, F.; Becher, J. *J. Am. Chem. Soc.* **1992**, *114*, 5035.

(359) Roncali, J.; Giffard, M.; Frère, P.; Jubault, M.; Gorgues, A. *J. Chem. Soc., Chem. Commun.* **1993**, 689.

(360) Roncali, J.; Rasmussen, L.; Thobie-Gautier, C.; Frère, P.; Brisset, H.; Sallé, M.; Becher, J.; Simonsen, O.; Hansen, T. K.; Benahmed-Gasmi, A.; Orduna, J.; Garin, J.; Jubault, M.; Gorgues, A. *Adv. Mater.* **1994**, *6*, 841.

(361) Benahmed-Gasmi, A.; Frère, P.; Roncali, J.; Elandaloussi, E.; Orduna, J.; Garin, J.; Jubault, M.; Gorgues, A. *Tetrahedron Lett.* **1995**, *36*, 2983.

(362) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.

(363) Fujii, M.; Aso, Y.; Otsubo, T.; Ogura, F. *Synth. Met.* **1993**, *55*−*57*, 2136.

(364) Takahashi, K.; Suzuki, T. *J. Am. Chem. Soc.* **1989**, *111*, 5483.

(365) Takahashi, K.; Suzuki, T.; Akiyama, K.; Ikegami, Y.; Fukazawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 4576.

(366) Takahashi, K.; Sakai, T. *Chem. Lett.* **1993**, 157.

(367) Tamura, R.; Nagata, Y.; Shimizu, H.; Matsumoto, A.; Ono, N.; Kamimura, A.; Hori, K. *Adv. Mater.* **1993**, *5*, 719.

(368) Elandaloussi, E.; Frère, P.; Roncali, J.; Richomme, P.; Jubault, M.; Gorgues, A. *Adv. Mater.* **1995**, *7*, 390.

(369) Elandaloussi, E.; Frère, P.; Roncali, J. *Tetrahedron Lett.* **1996,** *37*, 6121.

(370) Benahmed-Gasmi, A.; Frère, P.; Elandaloussi, E.; Roncali, J.; Orduna, J.; Garin, J.; Jubault, M.; Riou, A.; Gorgues, A. *Chem. Mater.* **1996**, *8*, 2291.

(371) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *9*, 1487.

(372) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846.

(373) Brisset, H.; Thobie-Gautier, C.; Jubault, M.; Gorgues, A.; Roncali, J. *J. Chem. Soc. Chem. Commun.* **1994**, 1765.

(374) Büchner, W.; Garreau, R.; Lemaire, M.; Roncali, J. *J. Electroanal. Chem.* **1990**, *277*, 335.

(375) Büchner, W.; Garreau.R.; Roncali, J.; Lemaire, M. *J. Fluorine Chem.* **1992**, *59*, 301.

(376) Thobie-Gautier, C.; Guy, A.; Gorgues, A.; Jubault, M.; Roncali, J. *Adv. Mater.* **1993**, *5*, 637.

(377) Bryce, M. R.; Chissel, A. D.; Gol, J.; Kathirgamanathan, P.; Parker, D. *Synth. Met.* **1991**, *39*, 397.

(378) Sundholm, F.; Sundholm, G.; Törrönen, M. *Synth. Met.* **1992**, *53*, 109.

(379) Thobie-Gautier, C.; Bouligand, Y.; Gorgues, A.; Jubaul, M.; Roncali, J. *Adv. Mater.* **1994**, *6*, 138.

(380) Thobie-Gautier, Gorgues, A.; Jubault M.; Roncali, J. *Macromolecules* **1993**, *26*, 4094.

(381) Kaufman, F. B.; Shroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1980**, 102, 483.

(382) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 1869.

(383) Roncali, J.; Thobie-Gautier, C.; Brisset, H.; Favard, J. F.; Guy, A. *J. Electronanal. Chem* **1995**, *381*, 257.

(384) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

(385) Jérome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, 95.

(386) Saito, G.; Enoki, T.; Torium, K.; Inokuchi, H. *Solid-State Commun.* **1982**, *42*, 557.

(387) Blanchard, P.; Boubekeur, K.; Sallé, M.; Duguay, G.; Jubault, M.; Gorgues, A.; Martin, J. D.; Canadell, E.; Auban-Senzier, P.; Jérome, D.; Batail, P. *Adv. Mater.* **1992**, *4*, 579.

(388) Seki, K.; Tang, T.; Mori, T.; Wu, P.; Saito, G.; Inokuchi, H. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1067.

(389) Wang, P.; Enoki, T.; Imaeda, K.; Iwasaka, N.; Yamochi, H.; Urayama, H.; Saito, G., Inokuchi, H. *J. Phys. Chem.* **1989**, *93*, 5947.

(390) Inokuchi, H. *Int. Rev. Phys. Chem.* **1989**, *8*, 95.

(391) Yassar, A.; Horowitz, G.; Valat, P.; Wintgens, V.; Hmyene, M.; Deloffre, F.; Srivastava, P.; Lang, P.; Garnier, F. *J. Phys. Chem.* **1995**, *99*, 9155.

(392) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.*, **1951,** *73*, 5691.

(393) Cram, D. J.; Allinger, N. L.; Steinberg, H. *J. Am. Chem. Soc.* **1954**, *76*, 6132.

(394) Dewhirst, K. C.; Cram, D. J. *J. Am. Chem. Soc.* **1958**, *80*, 3115.

(395) Mizogami, S.; Yoshimura, S. *J. Chem. Soc., Chem. Commun.* **1985**, 427.

(396) Grimme, W.; Kämmerling, H. T.; Lex, J.; Gleiter, R.; Heinze, J.; Dietrich, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 205.

(397) Roncali, J.; Garnier, F. *J. Phys. Chem.* **1988**, *92*, 833 and references cited therein.

(398) Bidan, G. *J. Chim. Phys.* **1989**, *86*, 45.

(399) Corriu, R. J.; Moreau, J. J. E.; Thepot, P.; Wong Chi Man, M.; Chorro, C.; Lère-Porte, J. P.; Sauvajol, J. L. *Chem. Mater.* **1994**, *6*, 640.

(400) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431.

(401) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(402) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413.

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