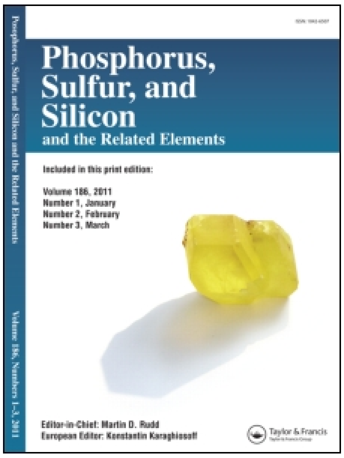

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A Convenient Synthesis of 2,5-Thienylene Oligomers; Some of Their Spectroscopic and Electrochemical Properties

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A CONVENIENT SYNTHESIS OF 2,5-THIENYLENE OLIGOMERS; SOME OF THEIR SPECTROSCOPIC AND ELECTROCHEMICAL PROPERTIES

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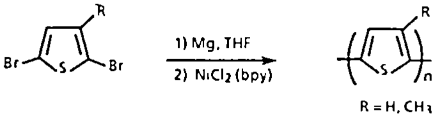
Key words: 2,5-Thienylene oligomers, UV spectra, oxidation potentials, cyclic voltammetry.

A convenient synthesis of a number of oligomeric thiophenes and oligomeric methyl-, and ethyl-substituted thiophenes as building blocks for novel conducting polymers is reported. The synthesis is based on a $NiCl_2(dppp)$ ($dppp = Ph_2PCH_2CH_2CH_2PPh_2$) catalyzed coupling reaction between appropriately substituted bromothiophenes and Grignard compounds derived of them. The λ_{max} of the UV spectra of the unsubstituted oligomeric thiophenes increases, as expected, with the number of thiophene units in the oligomers. Also, as expected, the oxidation potential E_{ox} of these compounds decreases with increasing the number of thiophene units. In the series of the methyl- or ethyl-substituted oligomeric thiophenes such a clear cut relationship is not observed. This behavior is discussed on the basis of diminishing coplanarity due to steric hindrances by the alkyl groups in the 3,3′-positions, which results in a blue shift of the λ_{max} of the UV spectra and a decreased stability of the radical cation formed upon electrooxidation, manifesting itself by a higher oxidation potential.

INTRODUCTION

Poly(2,5-thienylene), and poly(3-methyl-2,5-thienylene) were recently obtained by Yamamoto *et al.* via a transition metal promoted polymerization of the Grignard compounds derived from the 3-substituted 2,5-dibromothiophenes.[1]



Due to their high electrical conductivity,[1,2a] and to possibly further increase their electrochemical properties it became important to synthesize oligomeric 2,5-thienylenes as building blocks for novel, and hopefully, better organic conductors. The interest in these compounds stems from our findings that poly(3-substituted-2,5-thienylene)s prepared by a $CuCl_2$-promoted polymerization of 3-methyl-2,5-dilithiothiophene[2a] as well as a number of different 3-substituted-2,5-dilithiothiophenes can be "doped" with water to give unusually stable materials with excellent conductivity and electrochemical properties.[2b]

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† Taken in part from M.S. Thesis of A. Burkhardt, University of Cincinnati, 1987.
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In this report the synthesis and the UV spectra of a representative number of oligo-2,5-thienylenes ($n = 2, 3, 4, 5$) as well as oligomers of 3-methyl- or 3-ethyl-substituted thienylenes will be discussed. We will also, though only briefly, discuss their oxidation potentials. Detailed electrochemical results obtained with most of these compounds have been reported recently.[3]

It is also interesting to note that a number of 2,5-thienylene oligomers recently were found to show important biological properties,[4] including nematicidal[4b] and insecticidal[4c] activities, thus explaining a renewed interest in the synthetic methodology of this class of compounds. Various methods for their synthesis have been reported. More than fifty years ago Steinkopf and coworkers obtained oligomers with 2 to 7 thiophene units by heating 2-iodothiophene with copper bronze or through copper promoted coupling of 2,5-diiodothiophene with 2-iodothiophene.[5,6] However, these methods gave a mixture of oligomeric species which were difficult to obtain in a pure state. 2,2′:5′,2″-Terthienyl has been prepared via a sodium sulfide promoted cyclization of 1,4-dithienyl-1,3-butadiyne[7a,b] or by a similar reaction of 1,4-di(2′-thienyl)-1,4-butadione.[8,9] Recently Kagan and Arora reported the synthesis of 2,5-thienylene oligomers via an organoborane compound[10] or by oxidative coupling of 2-lithiothiophenes with $CuCl_2$.[11] Neither method could be reproduced by us to come even close to the reported yields. In a recent review article[12] all of these methods for the preparation of oligomeric thienylenes were reported and discussed in some detail. We wish to report here an efficient and general synthesis of 2,5-thienylene, and 3- and/or 4-alkyl-2,5-thienylene oligomers.

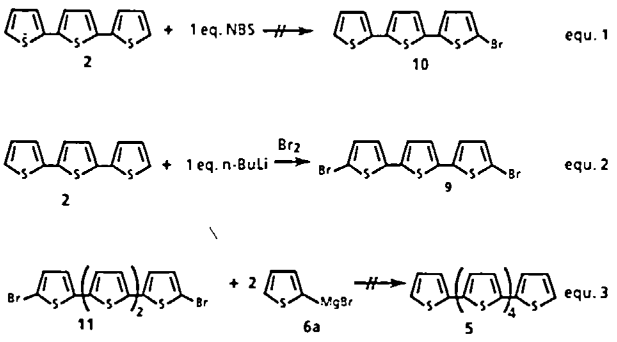
RESULTS

We found that unsubstituted, methyl-, and ethyl-substituted thiophene oligomers could conveniently be prepared by a procedure developed by Kumada *et al.*[13] for cross-coupling of Grignard reagents with *n*-alkyl or arylbromo compounds. This coupling takes place in the presence of nickel(II)[1,3-bis(diphenylphosphino)-propane]chloride,$NiCl_2$(dppp).[14]

$$\mathrm{Ar-Br + Ar'MgBr \xrightarrow[\text{Ether}]{NiCl_2(dppp)} Ar-Ar'}$$

This method was successfully applied by us[15] and others[16] for the synthesis of 3-alkylthiophenes. In the present work we utilized this procedure for the preparation of the following oligomers: 2,2′-bithienyl **1**, 2,2′:5′,2″-terthienyl **2**, and 2,2′:5′,2″:5″,2‴-quaterthienyl **3**. Thus, 2-bromothiophene **6**, 2,5-dibromothiophene **7**, 5,5′-dibromo-2,2′-bithienyl **8**, and 5,5″-dibromo-2,2′:5′:2″-terthienyl **9** were treated under these mild conditions with the appropriate molar amounts of 2-thienylmagnesium bromide **6a** to give the cross-coupling products **1**, **2**, **3**, and 2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethienyl **4** in excellent yields.

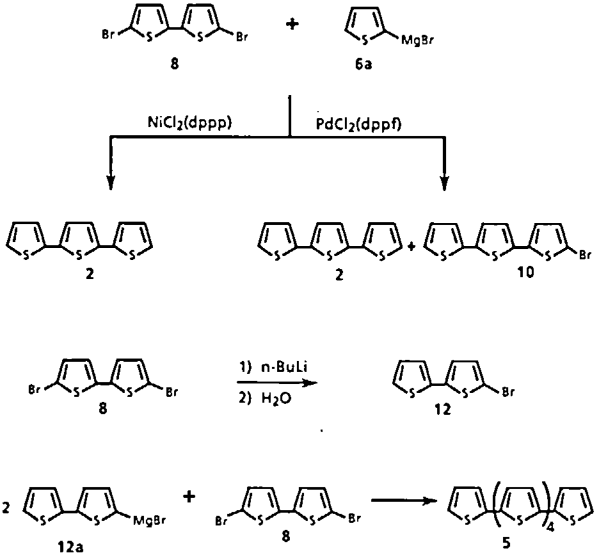
The synthesis of the 2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithienyl **5** proved to be more elusive than anticipated. The most straightforward attempt towards its synthesis, namely the coupling of 5-bromo-2,2′:5′,2″-terthienyl **10** with its Grignard compound **10a** could not be carried out because **10** could not be



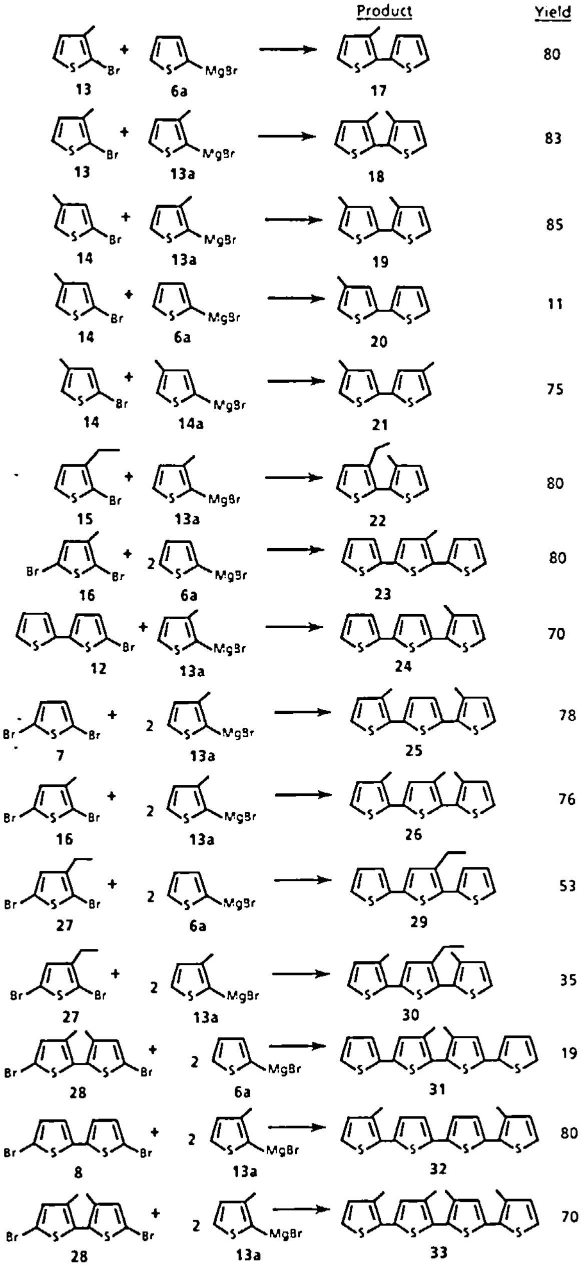
SCHEME 1

obtained. Attempts to prepare **10** by reacting the terthienyl **2** with one equivalent of NBS[17] (Scheme 1, Equation 1) or with one equivalent of *n*-butyllithium followed by a bromine metal exchange reaction using elemental bromine[7a] gave only the dibromo compound 5,5″-dibromo-2,2′:5′,2″-terthienyl **9** (Scheme 1, Equation 2). The insolubility of 5,5‴-dibromo-2,2′:5′,2″:5″,2‴-quaterthienyl **11** in ether and THF precluded the preparation of **5** according to Equation 3 (Scheme 1).

Using cross-coupling procedures for the synthesis of the desired compound **10** also showed little success. Thus, when **8** was reacted with one equivalent of 2-thienylmagnesium bromide **6a** in the presence of $PdCl_2$(dppf)[7b] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) only a mixture of the desired compound **10** together with **2** resulted. This mixture, however, could not be separated satisfactorily. Using $NiCl_2$(dppp) as catalyst for the same reaction yielded only **2**. The elusive 5-bromo-2,2′-bithienyl **12** eventually was obtained in a yield of 70%



SCHEME 2


Product
Yield
Br
MgBr
13 + 6a → 17 80
13 + 13a → 18 83
14 + 13a → 19 85
14 + 6a → 20 11
14 + 14a → 21 75
15 + 13a → 22 80
16 + 2 6a → 23 80
12 + 13a → 24 70
7 + 2 13a → 25 78
16 + 2 13a → 26 76
27 + 2 6a → 29 53
27 + 2 13a → 30 35
28 + 2 6a → 31 19
8 + 2 13a → 32 80
28 + 2 13a → 33 70

SCHEME 3

by reacting **8** with one equivalent *n*-butyllithium at −70°C and subsequent aqueous work-up. Finally, the Grignard reagent **12a** (2 equivalents) derived from **12** underwent cross coupling with **8** to give the desired sexithienyl **5**. These reactions are compiled in Scheme 2.

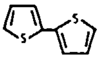
Methyl- and Ethylthienylene Oligomers

These compounds were all synthesized by the same cross-coupling reactions as outlined for the unsubstituted oligomeric 2,5-thienylenes. Thus, cross-coupling of 2-bromo-3-methylthiophene **13**, 2-bromo-4-methylthiophene **14**, and 2-bromo-3-ethylthiophene **15** with the Grignard reagents derived from **6**, **13**, and **14** afforded the bithienyls 3-methyl-2,2′-bithienyl **17**, 3,3′-dimethyl-2,2′-bithienyl **18**, 3,4-dimethyl-2,2′-bithienyl **19**, 4-methyl-2,2′-bithienyl **20**, 4,4′-dimethyl-2,2′-bithienyl **21**, and 3-methyl-3′-ethyl-2,2′-bithienyl **22**. Similarly 3′-methyl-2,2′:5′,2″-terthienyl **23**, 3-methyl-2,2′:5′:2″-terthienyl **24**, 3,3″-dimethyl-2,2′:5′,2″-terthienyl **25**, 3,3′3″-trimethyl-2,2′:5′,2″-terthienyl **26**, 3′-ethyl-2,2′:5′,2″-terthienyl **29** and 3,3″-dimethyl-3′-ethyl-2,2′:5′,2″-terthienyl **30** were obtained. The reactions of 5,5′-dibromobithienyl derivatives with 2 equivalents of Grignard reagents **6a** or **13a** gave rise to the formation of the quaterthienyls **31**, **32**, and **33**. In most of these reactions satisfactory yields in the range between 70–85% were obtained (Scheme 3).

UV Absorption Spectra

The electronic absorption spectra of 2,2′-bithienyl **1**, and a number of its derivatives have been intensively studied.[18,19,20] Molecular orbital calculations[21,22] favor a nearly planar structure. The planar conformer of **1** may exist in either the *s*-cis (a) or the *s*-trans (b) conformation

a



b

Many physical studies concerned with the determination of the preferred conformation of **1** have been reported. The planar *s*-trans-conformer is favored in the solid state.[23] However, in the gaseous state,[24] and in solution[25] the molecule is somewhat twisted about the 2,2′-bond. The angle of twist about the central C—C bond in the *s*-cis-conformer varies between 34°–85°C. However, a molecular orbital study[22] has shown that there is no distinct energy minima on varying the angle of twist from 0°–180°C in compound **1**.

The electronic absorption spectra of the 2,5-thienylene oligomers in chloroform show two absorption maxima. The strong absorption band at higher wavelength is assigned to the characteristic $\pi\rightarrow\pi^*$ electron transfer of the entire chromophore,[26] while the less intense band may be due to the $\pi\rightarrow\pi^*$ local excitation transition of the heteronucleus (Table I).[27]

As expected, the long wavelength absorption shifts to red and its absorption coefficients increases with increasing numbers of thiophene units, while the position of the local excitation absorption band remains virtually unchanged.

TABLE I

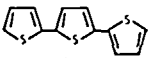
UV spectra of unsubstituted oligomeric 2,5-thienylenes

Compound	λ_{max}(nm)	λ_{max}(nm)	Δ	ε^1	ε^2
	(local excit.)	($CHCl_3$)		(M^{-1} cm^{-1})	
	243	243			1560
 1	243	302	59	10910	12470
 2	245	355	53	12580	25050
 3	248	390	45	20450	45500
 4	245	416	26	9700	55200
 5	243	432	16	4800	~60000

Similar to the para-poly(phenylene) series[28] the increment of the red shift of λ_{max} decreases with each added thiophene unit while the height of extinction coefficient after reaching a maximum with compound **3** also decreases with lengthening of the oligomer chain. This phenomena most probably is due to increasing thermal motion, and thus diminishing coplanarity of the oligomers, with the extension of the length of the chain.

Figure 1 gives a correlation between the two absorption maxima and the number of thienylene units. For the terthienyl **2**, there are three possible planar conformers, all cis (a), cis-trans (b), and all trans (c).

a



b

c

The latter form (c) has the lowest dipole moment,[22] consequently, it should be least affected by solvent polarity and no shift of λ_{max} with solvent polarity is expected, and this is precisely what was found. This is a good indication that the all *s*-trans (c) form is the predominant conformer in solution (Figure 2).

The UV absorption spectra of the mono-, and dibromo-substituted oligomers **12**, **8**, **9**, and **11** show a red shift when compared with their unsubstituted oligomers. The bathochromic effect of the bromo substitutent decreases with each additional thiophene unit (Table II).

Table III gives the λ_{max} values of the long wavelength absorption of the methyl-, and ethyl-substituted 2,5-thienylene oligomers.

A significant blue shift of 32 nm was observed for **18** when compared with the

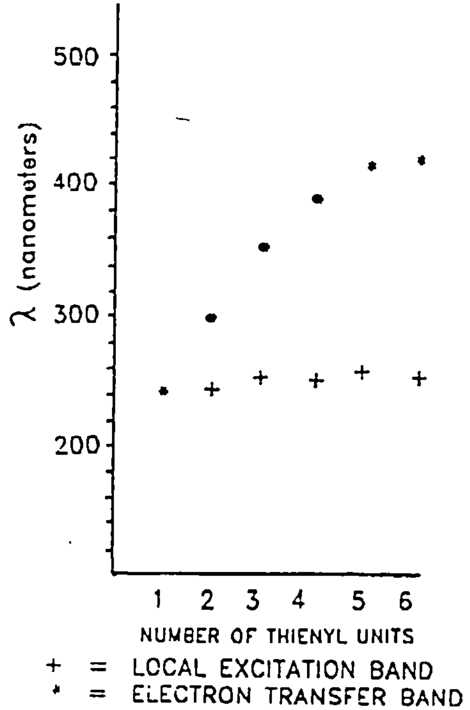


FIGURE 1 UV spectra of oligomers in dependency of number of thienyl units.

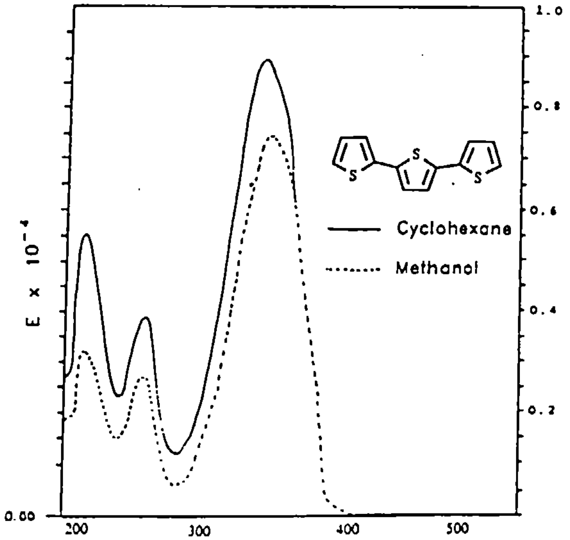
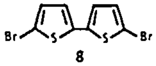
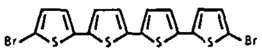


FIGURE 2 UV spectrum of 2,2′:5′,2″-terthienyl in dependency of solvent.

TABLE II

UV spectra of selected bromothienylenes

Compound	λ_{max}(nm) (CHCl$_3$)	ε (M^{-1}cm^{-1})	$\Delta\lambda^{*}_{max}$
 **12**	309	14540	+7
 **8**	321	17970	+19
 **9**	365	24330	+10
 **11**	396	31480	+6

* $\Delta\lambda_{max}$ refers to unsubstituted oligomers (see Table I).

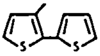
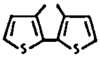
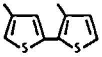
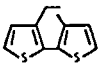
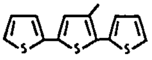
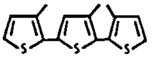
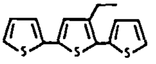
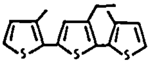
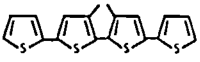
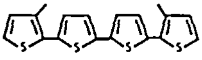
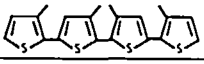
unsubstituted bithienyl **1**. The extinction coefficient ($\varepsilon = 7460$) of the long wavelength band is lower than the one of the local excitation band ($\varepsilon = 10\,940$) which is an indication of steric hindrance between the methyl groups in the 3,3′-positions in the *s*-cis conformer. Steric hindrance also could be used as an argument for these observations if one assumes that due to hyperconjugation the partially occupied *d*-orbital of the sulfur atom and one methyl group of the *s*-trans-conformer interfer with coplanarity of the rings as indicated in Figure 3. It also shows that in the *s*-trans-conformer interference between the methyl groups and *d*-electrons of the sulfur atoms of the thiophene rings force the rings out of coplanarity. A more detailed study of this hypothesis, namely steric hindrance due to *d*-orbital involvement, is in progress and will be published shortly.

Substitution of a methyl group in the 3-position of **17** causes a slight blue shift which also is due to a steric effect. The slight red shift of 3 nm of **19** when compared with **17** is most likely due to the inductive effect of the methyl group in the 4′-position of **19**. On the other hand, introduction of one methyl group in the 4-position as in **20** or two methyl groups in the 4-, and 4′-positions as in **21** produces a red shift in the order of 7 and 10 nm, respectively, when compared to the unsubstituted bithienyl **1**. In the alkyl substituted terthienyls **23**, **24**, **25**, **26**, **29**, **30**, and quaterthienyls **31**, **32**, **33**, a blue shift is observed when compared with the unsubstituted oligomers **2** and **3**. Again, this phenomenon can be explained by steric and electronic factors caused by the alkyl groups. Interestingly, however, we found that **24** has a higher λ_{max} than **23**, though the degree of steric hindrance due to the methyl group should be the same for both compounds. This fact might be explained by assuming that the electrons of the methyl group as situated in **24** are delocalized by hyperconjugation through all three rings as depicted in Figure 4. Thus, a higher degree of coplanarity is achieved and a concomitant red shift is observed.

As was the case with the unsubstituted 2,2′-biphenyls, bromination also causes a red shift as shown in Figure 5 for 5,5′-dibromo-3,3′-dimethyl-2,2′-bithienylene

TABLE III

Values of λ_{max} of the long wavelength absorption of the methyl-, and ethyl-substituted thiophene oligomers

	Compound	λ_{max} (nm)	ε
17		299	12300
18		270	7460
19		302	12870
20		309	10018
21		312	10600
22		280	5317
23		336	15980
24		352	18860
25		344	17340
26		324	29732
29		345	13061
30		321	11212
31		348	15069
32		380	16960
33		342	29800

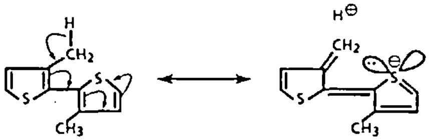


FIGURE 3 Hyperconjugative effects in 3-methyl-2,2'-bithienyl.

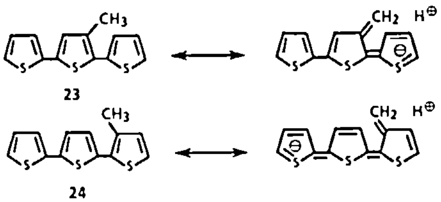
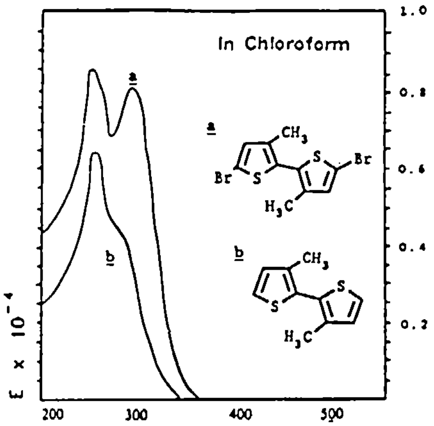


FIGURE 4 Comparison of hyperconjugative effects between 3'-methyl-2,2':5',2"-terthienyl and 3-methyl-2,2':5',2"-terthienyl.



	λ Maximum E
a	286
b	270

FIGURE 5 Comparison of λ_{max} between 3,3'-dimethyl-2,2'-trithienyl and 5,5'-dibromo-3,3'-dimethyl-2,2'-trithienyl.

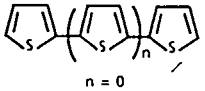
28 ($\Delta\lambda_{max} = 16\,\text{nm}$). This shift is nearly identical with the one observed for the corresponding unsubstituted compounds **8** and **1**, respectively (Figure 5).

Electrochemical Investigations

So far only monomeric thiophene species and a few dimers were electrooxidized to obtain conducting polymers.[1,2] For this investigation we decided to use a number of oligomeric 2,5-thienylenes as monomer units for subsequent polymerizations. Therefore, we were interested in measuring the oxidation potentials of the oligomers. The oxidation process consists of the removal of one electron from the oligomer under the cyclic voltammetric conditions employed. The resulting radical cation should be more stable the more electron delocalization possibilities exist. Thus, with extension of the conjugated system, the magnitude of the oxidation potentials should become less positive because for the removal of the electron less energy is necessary. Also, besides coplanarity of the conjugated system—which is partially impaired by steric hindrance caused by the alkyl groups—electron releasing power of these methyl groups will influence the oxidation potential. Since the same factors also contribute to the position of the

TABLE IV

Differential pulse voltammetry of unsubstituted oligomeric thienylenes

Compound*	Peak potential in volts vs. $Ag^+/AgCl$
	
n = 0	1.28
n = 1	1.05
n = 2	0.97
n = 3	0.70
n = 4	0.46†

* For comparison the value of thiophene was found to be 1.94

† Because of the very low solubility of this oligomer, we cannot be sure that the very small oxidation peak current observed is truly that of the oxidation of this oligomer or that of some impurity in the system. The large magnitude of the potential shift from the $n = 3$ to the $n = 4$ oligomers makes us very suspicious of what is being oxidized in the later case.

λ_{max} values of the UV spectra of these species, we expected that the trend in position of the λ_{max} values and the magnitude of the oxidation potentials should parallel each other. This is what actually was found. The data are compiled in Table IV. As becomes evident from these data, and as expected, there is a monotonous decline of the oxidation potentials in the series of unsubstituted 2,5-thienylenes with an increasing number of 2,5-thienylene units. However, there is no such clear cut relationship in the alkyl substituted oligomers (Table V). The oxidation potentials for the methyl substituted oligomeric species can be explained to some extent on the basis of steric hindrance and the electron releasing power of the methyl groups. Thus, explaining the differences of the oxidation potentials among the methyl- or ethyl-substituted oligomers is not possible at this time because it is difficult to estimate, even in a qualitative way,

TABLE V

Differential pulse voltammetry of substituted oligometric thienylenes

Compound	Peak potential in volts vs. $Ag^+/AgCl$
17	1.22
18	1.58
19	1.07
20	1.67
21	1.16
23	1.11
24	1.13
25	1.09
26	0.98
33	0.90

the electronic influence of the methyl or ethyl groups in different positions on the magnitude of the oxidation potential.

There is a further complication in the correlation of oxidation current peak potentials with structure which does not enter into the optical adsorption wavelength structure correlation. The oxidation current peak potential is a combination of the thermodynamic redox potential of the oligomer plus the kinetics of the electron transfer reaction and any subsequent chemical reactions of the polymerization reaction(s). The fact that the shift in the electrochemical peak potentials parallel the changes in optical adsorption maxima, suggests that the kinetic rates involved in the various oligomers probably are similar and, hence, independent of structure and composition of the oligomers. However, this is only inferred and in no way proves that the electrochemical kinetics are the same for each oligomer.

EXPERIMENTAL

Melting points were determined with a Mel Temp apparatus and are uncorrected, as are the boiling points. IR spectra were recorded by using a Perkin–Elmer Model 599 spectrometer calibrated against the 1601 cm^{-1} band of poly(styrene) and/or Fourier-transform IR spectrometer. The ^{1}H NMR spectra were recorded on a Varian T-60 and/or an IBM 80 (80 mHz) spectrometer. Chemical shifts are expressed in δ relative to tetramethylsilane as internal standard. MS data were obtained on a gas chromatograph/mass spectrometer HP 5995. UV-Vis spectra were recorded on Perkin–Elmer Lambda 5, UV-Vis spectrometer. Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona. All reactions were performed under a blanket of argon. The reported yields refer to pure isolated materials.

Materials. 2-Bromothiophene, 2,5-dibromothiophene, and 3-methylthiophene were purchased from Fairfield Chemical Co., Inc. All solvents used were reagent grade. Tetrahydrofuran (THF) was purified by continuous distillation under argon from benzophenone-potassium. Nickel(II)[1,3-bis(diphenylphosphino)propane] chloride, $NiCl_2$(dppp), was prepared as reported earlier.[14]

2,2'-Bithienyl **1**: To a solution of 16.3 g (0.1 mol) of 2-bromothiophene and 60 mg of $NiCl_2$(dppp) in 100 ml of ether was added dropwise an ether solution of 0.1 mol of 2-thienylmagnesium bromide. The resulting black brownish solution was refluxed for 20 hrs, hydrolyzed with ice cold 1 N HCl and then extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated. The residue was distilled in vacuum and 13.4 g (81%) of **1** were obtained; bp. 96°C/1.5 mm Hg; it solidified at room temperature; mp. 33°C; (lit. 33°C[16]). ^{1}H NMR ($CDCl_3$) δ 7.0–7.6 (m).

2,2':5',2"-Terthienyl **2**: It was obtained as described above from 9.76 g (0.04 mol) of 2,5-dibromothiophene, 60 mg of $NiCl_2$(dppp) and 0.1 mol of 2-thienylmagnesium bromide in 100 ml of ether. The mixture was refluxed for 16 hrs. After usual workup the obtained solid was recrystallized from hexane and gave 8.5 g (86%) of slightly yellow green crystals; mp. 94–95°C; (lit. 95°C[17]).

5,5'-Dibromo-2,2'-bithienyl **8**: To a suspension of 8 g (0.048 mol) of **1** and 4.4 g (0.041 mol) of sodium bicarbonate in 100 ml of chloroform was added 5.1 ml (0.1 mol) of bromine dissolved in 20 ml of the same solvent. After stirring for 1 hr at room temperature the mixture was filtered and the solvent evaporated. The resulting solid was recrystallized from methanol/THF to give 12 g (77%) of **8** (colorless prism); mp. 142°C (lit. 143°C[17]). ^{1}H NMR ($CDCl_3$) δ 6.82 (d, $J = 3.9$ Hz, 2H) 6.94 (d, $J = 3.9$ Hz, 2H).

2,2':5',2":5",2'"-Quaterthienyl **3**: Oligomer **3** was prepared as described for **1** from 4 g (12.3 mmol) of **8**, 60 mg of $NiCl_2$(dppp), and 30 mmol of 2-thienylmagnesium bromide. The resulting intense yellow suspension was refluxed for 30 min and cooled to room temperature. The obtained precipitate was filtered off and recrystallized from ethanol/dioxane and gave 3.6 g (89%) of yellow crystals; mp. 210°C (lit. 210–211°C[17]). MS, *m/e* 330 ($M^{+\cdot}$).

5,5"-Dibromoterthienyl **9**: It was obtained as described for **8** from 2.23 g (9 mmol) of **2**, 0.84 g (10 mmol) of sodium bicarbonate and 0.95 ml (18 mmol) of bromine in chloroform. Recrystallization from methanol/THF gave 2.9 g (80%) of gold yellow crystals; mp. 154–155°C, (lit. 155°C[17]). MS, *m/e* 408 ($M^{+\cdot}+2$), 406 ($M^{+\cdot}$), 404 ($M^{+\cdot}-2$), 326, 328 ($M^{+\cdot}-Br$) 246 ($M^{+\cdot}-2Br$).

2,2′:5′,2″:5″,2‴:5‴,2⁗-Quinquethienyl **4**: It was obtained as described for **1** from 0.378 g (0.93 mol) of **9**, 60 mg $NiCl_2$(dppp), and 3.3 mmol of 2-thienylmagnesium bromide in ether. After refluxing for 30 min the precipitate was filtered, washed with 1 N HCl, ether and hexane. It was recrystallized from dioxane/water and gave 0.35 g (91%) of **4** as an orange powder; mp. 253°C; (lit. 253°C[17]).

5-Bromo-2,2′-bithienyl **12**: To a solution of 3.24 g (0.01 mol) of **8** in 30 ml of THF were added at −70°C 6.13 ml of a 1.6 N *n*-butyllithium in n-hexane. After stirring for 30 min at this temperature the reaction mixture was hydrolyzed and the organic layer was dried over $MgSO_4$ and evaporated. Since TLC-analysis indicated the presence of **12** the colorless solid product was purified by column chromatography (silica gel/hexanes), 70% yield (1.7 g); mp. 31°C (lit. 30–33°C[29]). ^1H NMR ($CDCl_3$) δ 6.8–7.3 (m). MS, *m/e* 246 ($M^{+\cdot}+2$), 244($M^{+\cdot}$), 166, 165($M^{+\cdot}-Br$).

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-Sexithienyl **5**: It was obtained as described for **1** from 0.324 g (1 mmol) of **8**, 40 mg $NiCl_2$(dppp), and 2.5 mmol of 5-(2,2′-bithienyl) magnesium bromide (prepared from **12** and magnesium). The dark red mixture was refluxed for 2 hrs and hydrolyzed with 1 N HCl. The red precipitate was filtered under suction. Sublimation of the isolated solid at 330°C gave bright red crystals of **5** in 56% yield; mp. 303°C; (lit. 304°C[17]). MS, *m/e* 493, 495 ($M^{+\cdot}$) Anal. Calcd. for $C_{24}H_{14}S_6$: C, 58.26; H, 2.86. Found: C, 58.21; H, 2.86.

3-Methyl-2,2′-bithienyl **17**: This compound was prepared according to the same procedure used for the synthesis of **1** from 8.85 g (0.05 mol) of 2-bromo-3-methylthiophene,[30] 60 mg of $NiCl_2$(dppp) and 2-thienylmagnesium bromide in ether and refluxed for 2 hrs. After usual work-up an oil was obtained which was distilled to give 6.5 g (72%) of **17**; bp. 107°C/2.2 mm. ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H); 6.82–7.36 (m, 5H) Anal. Calcd. for $C_9H_8S_2$; C, 59.96; H, 4.47. Found: C, 59.81; H, 4.36.

3,3′-Dimethyl-2,2′-bithienyl **18**: This compound was obtained as described for **1** from 17.7 g (0.1 mol) of 2-bromo-3-methylthiophene, 60 mg of $NiCl_2$(dppp), and 0.1 mol of 3-methyl-2-thienylmagnesium bromide in 100 ml ether. The red brown mixture was refluxed for 16 hrs. After usual work-up distillation of the resulting oil gave 16.7 g of **18** (86%); bp. 112°C/2.3 mm Hg; (lit. 131°C/11 mm, Hg[31]). ^1H NMR ($CDCl_3$) δ 2.16 (s, 6H); 6.90 (d, $J = 5.6$ Hz, 2H); 7.23 (d, $J = 5.6$ Hz, 2H).

3,4′-Dimethyl-2,2′-bithienyl **19**: It was obtained as described for **1** from 0.7 g (0.4 mmol) of 2-bromo-4-methylthiophene,[32] 40 mg $NiCl_2$(dppp) and 0.4 mol of 3-methyl-2-thienylmagnesium bromide in ether. The product was purified by column chromatography (silica gel/hexanes) giving 0.66 g (85%) of a colorless liquid. ^1H NMR ($CDCl_3$) δ 2.25 (s, 3H); 2.38(s, 3H) 6.8–7.35 (m, 4H). Anal. Calcd. for $C_{10}H_{10}S_2$: C, 61.81; H, 5.18. Found: C, 62.08; H, 5.40.

4-Methyl-2,2′-bithienyl **20**: To a suspension of 0.48 g (20 mmol) of magnesium in 10 ml dry ether was added dropwise 3.54 g (20 mmol) of 4-methylthiophene. After all the magnesium has been reacted, the Grignard reagent was transferred to another flask containing 3.26 g (20 mmol) of 2-bromothiophene and 150 mg $NiCl_2$(dppp) in 50 ml dry ether. The addition was performed at room temperature, where the color of the reaction mixture changed to deep red. The reaction mixture was refluxed for 20 hrs and worked-up as usual to give after purification using a silica gel column 0.4 g (11%) of the title compound as an oil. ^1H NMR ($CDCl_3$) δ 2.25 (s, 3H, $\underline{CH_3}$); 7.75 (s, 1H), 6.9–7.1 (m, 2H), 7.1–7.3 (m, 2H). Anal. Calcd. for $C_9H_8S_2$: C, 59.96; H, 4.47. Found: C, 60.08; H, 4.44.

4,4′-Dimethyl-2,2′-bithienyl **21**: It was obtained as described for **1** from 4.36 g (25 mmol) of 2-bromo-4-methylthiophene, 60 mg of $NiCl_2$(dppp) and 25 mmol of 4-methyl-2-thienylmagnesium bromide in ether. The mixture was refluxed for 1 day. After usual work-up the crude product was purified by column chromatography (silica gel/hexanes) to give 3.6 g (75%) of **21** as colorless crystals, mp. 64°C. ^1H NMR ($CDCl_3$) δ 2.21 (s, 6H); 6.80 (s, 2H) 7.00 (s, 2H). Anal. Calcd. for $C_{10}H_{10}S_2$: C, 61.81; H, 5.18. Found: C, 61.48; H, 4.98.

3-Ethyl-3′-methyl-2,2′-bithienyl **22**: It was prepared as **1** from 5.2 g (0.027 mol) of 2-bromo-3-ethylthiophene,[33] 150 mg of $NiCl_2$(dppp), and the Grignard reagent derived from 9.62 g (0.054 mol) of 2-bromo-3-methylthiophene in anhydrous diethyl ether and then the reaction mixture was refluxed for 16 hrs. After normal work-up, the brownish residue was distilled under vacuum using a Vigreux column to give 4.5 g (30%) of **22** (bp. 120°C/2 torr) as a colorless liquid. ^1H NMR ($CDCl_3$) δ (ppm)

1.15 (t, 3H) with $J = 7$ Hz; 2.12 (s, 3H) 2.52 (q, 2H) with $J = 7$ Hz, 7.05(m, 4H). UV spectrum: $\lambda_{max} = 280$ nm ($\Sigma = 5317$). MS (m/e, %) 210 ($M^{+\cdot} + 2$, 7.88), 209 ($M^{+\cdot} + 1$, 8.58), 208 ($M^{+\cdot}$, 58.92), 195 ($M^{+\cdot} - CH_3 + 2$, 10.30), 194 ($M^{+\cdot} - CH_3 + 1$, 9.75), 193 ($M^{+\cdot} - CH_3$, 100). Anal. Calcd. for $C_{11}H_{12}S_2$: C, 63.41; H, 5.80. Found: C, 63.60; H, 5.90.

3′-Methyl-2,2′:5′,2″-terthienyl **23**: It was prepared similar to **1** from 10.24 g (0.04 mol) 2,5-dibromo-3-methylthiophene,[34] 60 mg of $NiCl_2$(dppp), and 0.1 mol of 2-thienylmagnesium bromide. The tan reaction mixture was refluxed for 16 hrs. Purification by chromatography on a column silica gel with hexanes as eluant gave 8.5 g (80%) of **23** as light yellow oil. It solidified under refrigeration; mp. 31–32°C. ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H); 6.8–7.35 (m, 7H). MS, *m/e* 262 ($M^{+\cdot}$). Anal. Calcd. for $C_{13}H_{10}S_3$: C, 59.50; H, 2.84. Found: C, 59.64; H, 4.14.

3-Methyl-2,2′:5′,2″-terthienyl **24**: It was obtained analogously from 0.950 g (3.8 mmol) of **12**, 60 mg of $NiCl_2$(dppp), and 4 mmol of 3-methyl-2-thienylmagnesium bromide by refluxing for 16 hrs. Purification was accomplished by column chromatography (silica gel/hexanes) to yield 0.7 g (70%) of **24** as a yellow oil, which slowly solidified by keeping it refrigerated; mp. 40°C (yellow green powder). MS, m/e 262 ($M^{+\cdot}$). ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H); 6.7–7.3 (m, 7H). Anal. Calcd. for $C_{13}H_{10}S_3$: C, 59.50; H, 3.84. Found: C, 59.82; H, 4.12.

3,3″-Dimethyl-2,2′:5′,2″-terthienyl **25**: It was prepared similar to **1** from 3.63 g (0.015 mol) of 2,5-dibromothiophene, 60 mg of $NiCl_2$(dppp), and 0.0355 mol of 3-methyl-2-thienylmagnesium bromide. After refluxing for 16 hrs the crude product was purified by column chromatography (silica gel/hexanes) to give 3.23 g (78%) of **25** as a light yellow oil, which solidified under refrigeration; mp. 50–51°C, light yellow powder. ^1H NMR ($CDCl_3$) δ 2.40 (s, 6H); 6.87 (d, $J = 5.6$ Hz; 2H); 7.12 (d, $J = 5.6$, 2H); 7.05 (s, 2H). MS, *m/e* 276 ($M^{+\cdot}$). Anal. Calcd. for $C_{14}H_{12}S_3$: C, 60.83; H, 4.37. Found: C, 60.88; H, 4.47.

3,3′,3″-Trimethyl-2,2′:5′,2″-terthienyl **26**: It was prepared analogously from 6.4 g (0.025 mol) of 3-methyl-2,5-dibromothiophene, 60 mg of $NiCl_2$(dppp), and 0.05 mol of 3-methyl-2-thienylmagnesium bromide and refluxed for 16 hrs. The crude product was purified by column chromatography (silica gel, hexanes) to afford 5.5 g (76%) of **26** as pale yellow crystals, mp. 39°C. ^1H NMR ($CDCl_3$) δ 2.17 (s, 3H); 2.22 (s, 3H); 2.40 (s, 3H); 6.90 (d, $J = 5.6$ Hz, 1H); 7.0 (s, 1H), 7.18 (d, $J = 5.6$ Hz, 1H); 7.35 (d, $J = 5.6$ Hz, 1H) 6.98 (d, $J = 5.6$ Hz, 1H). Anal. Calcd. for $C_{15}H_{14}S_3$: C, 62.02; H, 4.86. Found: C, 61.88; H, 4.64.

5,5′-Dibromo-3,3′-dimethyl-2,2′-bithienyl **28**: To a solution of 8.5 g (43.8 mmol) of **18** in 100 ml of glacial acetic acid were added dropwise 4.98 ml (97.2 mol) of bromine in 20 ml of glacial acetic acid. After stirring for 1 hr the resulting colorless suspension was diluted with 100 ml water and exhaustively extracted with ether. The organic layer was dried over $MgSO_4$, and evaporated to give 12.3 g (80%) of **28** as colorless crystals; mp. 58°C (methanol/THF). ^1H NMR ($CDCl_3$) δ 2.10 (s, 6H); 6.86 (s, 2H) MS, *m/e* 352 ($M^{+\cdot}$); 354 ($M^{+\cdot} + 2$); 350 ($M^{+\cdot} - 2$); 273 ($M^{+\cdot} - Br$); 192 ($M^{+\cdot} - Br_2$). Anal. Calcd. for $C_{10}H_8S_2Br_2$: C, 34.11; H, 2.29; Br, 45.38. Found: C, 33.92; H, 2.42; Br, 45.57.

3′-Ethyl-2,2′:5′,2″-terthienyl **29**: It was prepared similarly from 3 g (0.011 mol) 2,5-dibromo-3-ethylthiophene,[30] 160 mg of $NiCl_2$(dppp), and 2-bromothienyl-magnesium bromide derived from 5.7 g (0.035 mol) 2-bromothiophene. The reaction mixture was held under gentle reflux for 24 hrs and worked-up in the usual way and purified on silica gel column using hexanes as eluent to give 1.6 g (53%) of the title compound as dark yellow oil. ^1H NMR δ (ppm) 1.23 (t, 3H); 2.73 (q, 2H); 7.08 m, 7H). UV spectrum: $\lambda_{max} = 347$ nm ($\Sigma = 13000$). MS (*m/e, %*): 278 ($M^{+\cdot} + 2$, 14.42); 277 ($M^{+\cdot} + 1$, 16.20); 276 ($M^{+\cdot}$, 87.10), 263 ($M^{+\cdot} - CH_3 + 2$, 10.89); 262 ($M^{+\cdot} - CH_3 + 1$, 12.39), 261 ($M^{+\cdot} - CH_3$, 62.32); 127 ($C_4H_3S - C{\equiv}S^+$, 100). Anal. Calcd. for $C_{14}H_{12}S_3$: C, 60.82; H, 4.38. Found: C, 60.84; H, 4.48.

3′-Ethyl-3,3″-dimethyl-2,2′:5′,2″-terthienyl **30**: Prepared from 2,5-dibromo-3-ethylthiophene (0.02 mol), 200 mg $NiCl_2$(dppp), and 0.055 mol of 3-methyl-2-thienylmagnesium bromide to give after refluxing 22 hrs 2.1 g (35%) of **30** as yellow oil. ^1H NMR δ (ppm): 1.17 (t, 3H); 2.20 (s, 3H); 2.39 (s, 3H) 2.54 (q, 2H), 6.81–7.27 (m, 5H). UV spectra: $\lambda_{max} = 321$ nm ($\Sigma = 11700$). MS (*m/e, %*): 306 ($M^{+\cdot} + 2$, 17.50); 305 ($M + ^{+\cdot} + 1$, 20.01); 304 ($M^{+\cdot}$, 100), 289 ($M^{+\cdot} - CH_3$, 34.36); 274 ($M^{+\cdot} - 2CH_3$, 28.97). Anal. Calcd. for $C_{16}H_{16}S_3$: C, 63.11; H, 5.30. Found: C, 62.95; H, 5.42.

4′,3″-Dimethyl-2,2′:5′,2″:5″,2‴-tetrathienyl **31**: It was obtained by reacting 3.92 g (0.012 mol) of **28**, 100 mg of $NiCl_2$(dppp), and 4.56 g (0.028 mol) of 2-bromothienylmagnesium bromide in anhydrous diethyl ether. After 24 hrs of gently refluxing and the usual work-up, the residue was purified on a silica gel column to give 0.75 g (19%) of bright yellow crystals. ^{1}H NMR δ (ppm) 2.20 (s, 6H); 6.90–7.25 (m, 8H). UV spectra: $\lambda_{max} = 348$ nm ($\Sigma_{max} = 22340$). MS (*m/e*, %): 361 ($M^{+\cdot} + 3$, 4); 360 ($M^{+\cdot} + 2$, 18.1); 359 ($M^{+\cdot} + 1$, 22.3); 358 ($M^{+\cdot}$, 100). Anal. Calcd. for $C_{18}H_{14}S_4$: C, 60.30; H, 3.94. Found: C, 59.37; H, 4.14.

3,3‴-Dimethyl-2,2′:5′,2″:5″,2‴-tetrathienyl **32**: It was prepared by adding the Grignard reagent prepared from 0.025 mol of 2-bromo-3-methylthiophene to a mixture of **8** (0.01 mol) and 100 mg of $NiCl_2$(dppp) in anhydrous diethyl ether. Immediately a deep orange precipitate was formed which, after 6 hrs of reaction time, was filtered off, dried under reduced pressure and recrystallized from 100 ml of a 1:1 mixture of ethanol and dioxane. The resulting orange powder was dried for 30 hrs under reduced pressure to give 2.87 g (80.2%) of the title compound; m.p. 112°C. ^{1}H NMR δ (ppm) 2.42 (s, 6H); 7.05 (m, 8H) ($CHCl_3$) UV spectra: $\lambda_{max} = 382$ nm ($\Sigma = 17000$). MS (*m/e*, %): 361 ($M^{+\cdot} + 3$, 3); 360 ($M^{+\cdot} + 2$, 18); 359 ($M^{+\cdot} + 1$, 20) 358 (M^{+}, 100). Anal. Calcd. for $C_{18}H_{14}S_4$: C, 60.30; H, 3.94. Found: C, 60.72; H, 4.06.

3,4′,3″,3‴-Tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene **33**: The procedure described for 1 was employed by using 2 g (5.6 mmol) of **28**, 60 mg of $NiCl_2$(dppp), and 1.7 mmol of 3-methyl-2-thienylmagnesium bromide in 100 ml of ether. The crude product was purified by chromatography (silica gel/hexanes) to yield 1.5 g (69%) of **33** as a yellow amorphous powder, mp. 73°C. ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 6H); 2.41 (s, 6H); 6.85 (d, $J = 5.2$ Hz, 2H); 7.0 (s, 2H); 7.15 (d, $J = 5.2$ Hz, 2H). MS, *m/e* 332 ($M^{+\cdot}$). Anal. Calcd. for $C_{20}H_{18}S_4$: C, 62.13; H, 4.69. Found: C, 62.14; H, 4.62.

Oxidation Potential Measurements. Concentrations varied depending on solubility. Typically 1 mM or less in argon deaerated acetonitrile as solvent and TBAFB (tetrabutylammonium tetrafluoroborate) supporting electrolyte. Reference electrode AG^+/AgCl was 26 mV lower than a SCE. Differential Pulse Voltammetry: sweep rate 4 mV/sec, pulse amplitude 30 mV, pulse width 50 msec, pulse period 1000 msec.

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