J. Org. Chem. **1995**, *60*, 2443–2447

Electrochemical Synthesis of Extended TTF

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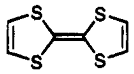
Received October 18, 1994®

An efficient electrochemical synthesis of new extended TTFs (tetrathiafulvalenes) starting from 1,4-dithiafulvenes is presented, and the mechanism is discussed. Single crystal X-ray structure of the neutral extended TTF **7d** is reported. These novel π-electron donor molecules show one two-electron reversible oxidation wave in cyclic voltammetry.

Introduction

Among the organic donors, much work has been done on tetrathiafulvalenes (TTF) **1** in the race for new organic conductors.[1] Modifications of the basic TTF framework leading to new functionalized π donors have been intensively studied.[2] A wide variety of extended TTF where the two dithiole rings are separated by cyclic or aliphatic conjugated spacer moieties have been prepared and studied.[3] An interesting type of extended TTF is TTF vinylogue **2** involving an ethanediylidene unit in the central conjugation. The addition of one vinyl spacer group between the dithiole rings has the effect of lowering the oxidation potential and decreasing the difference between the two oxidation potentials, due to reduced coulombic repulsion in the dication species. The synthesis of such extended TTFs reported in the literature is mainly based on the Wittig reaction of a (1,3-dithiole)phosphonium salt with an appropriate aldehyde.[4] On the other hand, oxidative dimerization of substituted 1,4-dithiafulvenes **3** has been known for some time to afford the dimeric dication **4**.[5] It is interesting to note that the neutral dimers have never been characterized. We decided to investigate this route to synthesize new TTF vinylogues. All the compounds reported in this paper are obtained in one pot by a two-step electrochemical synthesis: first an oxidation and then a reduction. Furthermore, we also report our investigations on the mechanism of dimer formation.



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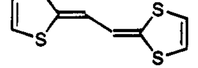

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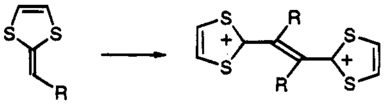
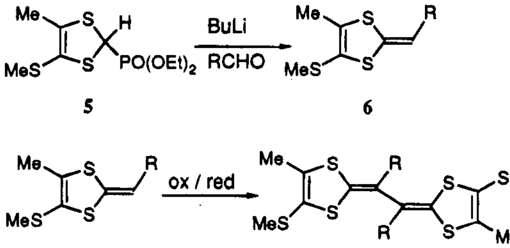


3 **4**

Scheme 1



Results and Discussion

The starting materials, 1,4-dithiafulvenes **6**, were prepared according to a Wittig–Horner-type reaction of a (1,3-dithiole)phosphonate **5** in basic medium and different aldehydes (Scheme 1).[6]

Electroanalytical investigations were carried out at a platinum disk electrode (A = 1 mm ^{2}) in a 10^{-3} M solution of **6** in acetonitrile, containing 1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The cyclic voltammogram of compound **6c**, recorded at 0.1 V s^{-1}, is reported in Figure 1; very similar results were obtained for the other dithiafulvenes, except for **6e** (vide infra). As can be seen in Figure 1 on the first anodic scan, an irreversible oxidation peak (a) is observed. The peak current is proportional to the square root of the scanning rate v, but the peak potential moves toward more anodic potentials when v is increased. On the reverse scan a cathodic peak (b) appears at less positive potentials. Then on the second anodic scan, a new oxidation peak (c) is observed, forming with (b) a

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® Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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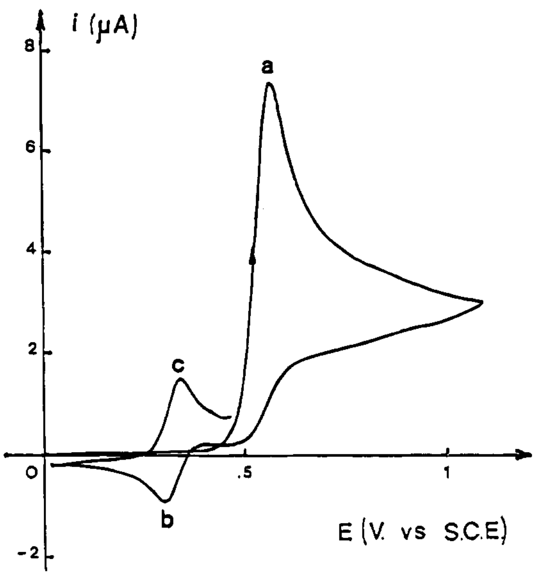

Figure 1. Cyclic voltammogram of 1,4-dithiafulvene **6c** in CH_3CN at a scan speed of 100 mV s^{-1}.

Table 1. Cyclic Voltammetry Data of the Monomers and Dimers, *E* in V vs SCE, Pt Working Electrode with 0.1 M n-Bu_4NPF_6 100 mV/s in CH_3CN

R	*E* monomers **6**	E_0 dimers **7**
a, C_6H_4-*p*-NO_2	0.74	0.48
b, C_6H_4-*p*-CN	0.69	0.44
c, C_6H_5	0.56	0.34
d, C_6H_4-*p*-OMe	0.47	0.32
e, C_6H_4-*p*-NMe_2	0.28	0.23
f, thiophene	0.5	0.35
g, $(CH_2)_2CH_3$	0.58	0.32
unsymmetrical		
ad, NO_2OMe		0.38
bd, CNOMe		0.35
	E_{ox}^1	E_{ox}^2
DMDMT-TTF	0.38	0.77

reversible electrochemical system. The new redox (b/c) system is associated with the redox behavior of dimer **7** formed in the solution. Upon successive scans the intensity of the anodic peak (a) decreases while the reversible redox system (b/c) increases. This voltammogram shape indicates an ECE process: the first electrochemical oxidation (E), corresponding to the oxidation of 1,4-dithiafulvene **6** to the cation radical $\mathbf{6}^{\bullet+}$, is followed by a chemical reaction (C) leading to **7**, which is further oxidized (E) at less positive potentials. The fact that peak b is less than half of peak a indicates a rather slow dimerization reaction (a slight reversibility of peak a can be observed at a higher scan rate). This can also explain the cross-over in the cyclic voltammogram of Figure 1. Electroanalytical investigations gave preliminary insight into the dimerization process which occurs here, and the 1,4-dithiafulvene **6** oxidation potentials are listed in Table 1.

Macroscale electrolyses were performed in a divided cell, the working electrode being a platinum grid. In a typical experiment, 50 mL of an acetonitrile solution containing 2 mmol of the 1,4-dithiafulvene **6** and 1 M of tetrabutylammonium hexafluorophosphate is introduced in the working compartment. The solution is then oxidized under controlled potential (0.6−0.8 V vs aqueous SCE, depending on R). Coulometric measurements show that 2 mol of electron per mol of substrate are required for complete oxidation. The highly colored solution is then, without any treatment, reduced at −0.2 V SCE. Complete reduction is achieved after consumption of 1 mol of electron per mol of substrate. Workup of the solution leads to neutral dimer **7** (Scheme 1).

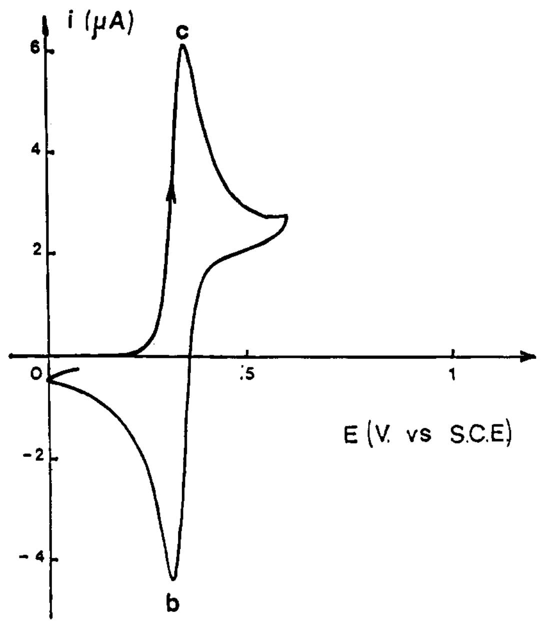

Figure 2. Cyclic voltammogram of dimer **7c** in CH_3CN at a scan speed of 100 mV s^{-1}.

In the same experimental conditions as previously described for monomers **6**, dimers **7** display a reversible electrochemical system in cyclic voltammetry (Figure 2), corresponding to peaks b and c of Figure 1. Moreover, the process is a two-electron transfer ($\Delta E_p = 0.03$ V), which indicates that stretching the TTF stabilizes the dication state owing to reduction of on-site Coulombic repulsion. This is an unusual feature for TTF vinylogues (R = H), as they are known in the literature to present two monoelectronic waves.[4] Conjugation inhibition associated with the two R groups could reasonably explain that behavior by considering that conformation changes drastically when oxidation occurs. The molecular structure of the extended TTF **7d** determined by single-crystal X-ray analysis is shown in Figure 3.[7] In contrast with planar TTF vinylogues (R = H),[4c] the neutral extended TTF **7d** is nonplanar. The cyclic voltammetry data of monomers **6** and dimers **7** are collected in Table 1 together with the oxidation potentials of dimethyl dimethylthio-TTF (DMDMT-TTF) for comparison. These data clearly indicate that vinyloguous TTFs are easier to oxidize than the corresponding DMDMT-TTF.

Electrochemical Behavior of Compound 6e. This compound displays peculiar voltammetric behavior (Figure 4a): three oxidation peaks are observed during the anodic scan and three reduction peaks on the cathodic scan. Peaks b and d correspond to a reversible system, and peak e appears only when oxidation is carried out up to peak c. By comparison with other compounds, peaks b and c correspond to the oxidation of the (dimethylamino)aryl substituent. When oxidation is limited to +0.75 V, only peaks a and f appear looking like a partially reversible system (Figure 4b). As this is not in agreement with our previous results, we decided to look

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(7) Crystal data: monoclinic, $P2_1/n$, $a = 10.514(2)$ Å, $b = 23.917(7)$ Å, $c = 11.63(2)$ Å, $\beta = 111.33(7)°$, $V = 2730(5)$ Å^3. Full X-ray crystal structure details will be reported elsewhere.

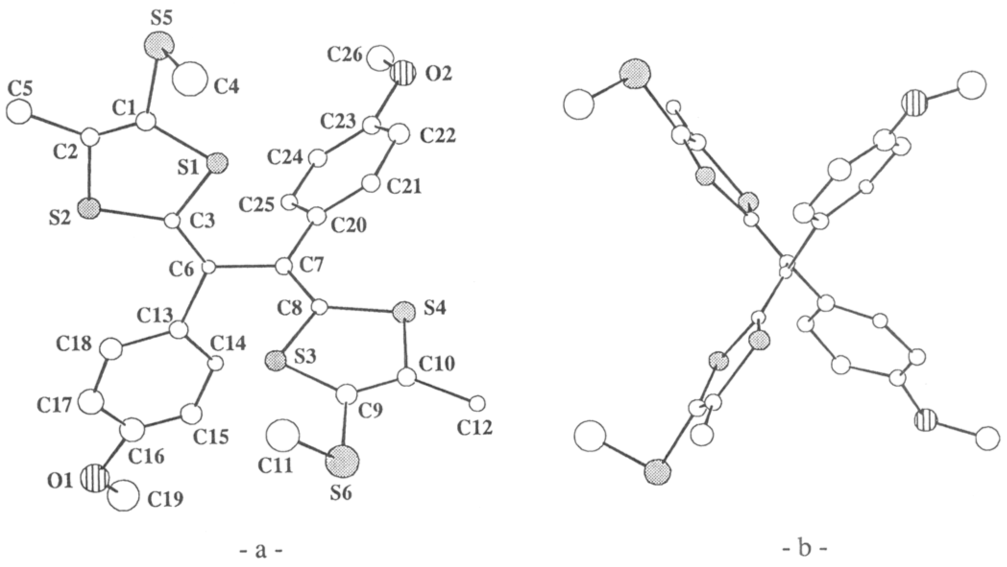

Figure 3. Crystal structure of compound **7d**. (a) General view of the molecular structure. (b) Evidence of the nonplanarity of the compound.

at the Hammett correlation for the oxidation potentials of monomers and dimers (Figure 5).

The two values get closer when the electron-donor ability of the substituent of the aryl group increases. For the dimethylamino substituent, oxidation of the monomer and the dimer occur roughly at the same value. The shape of the voltammogram in Figure 4b is then fortuitous, with peak f corresponding again to the reduction leading to the neutral dimer. This is confirmed by macroscale electrolyses: oxidation at +0.6 V followed by reduction at −0.2 V lead to dimer **7e**. In acetonitrile, this dimer shows two reversible bielectronic transfers in cyclic voltammetry (Figure 6a). Peaks b and d are identical to those observed on Figure 4a and correspond to the reversible oxidation of the *p*-(dimethylamino)aryl group (Scheme 2). Consequently, peak c is associated with the oxidation of the same group linked to the monomer radical cation. When the same study is carried out in dichloromethane, two close monoelectronic reversible waves are observed instead of peaks g and f (Figure 6b).

Mechanism of Dimer Formation. It was interesting to investigate the mechanism of dimerization. Globally, the two electrochemical reactions can be summarized as in Scheme 3. But the formation of dication $\mathbf{7}^{2+}$, according to an ECE mechanism, involves three steps: (i) oxidation of **6** into a radical-cation $\mathbf{6}^{\bullet+}$ (E), (ii) formation by dimerization of neutral dimer **7** (C), and (iii) oxidation of the latter into $\mathbf{7}^{2+}$ (E). Nevertheless, a question remains[8] about the chemical reaction: does it take place from the coupling of two radical-cations $\mathbf{6}^{\bullet+}$ or from the condensation of $\mathbf{6}^{\bullet+}$ on the substrate?

In order to solve this problem, we tried cross-coupling oxidation of a mixture of two 1,4-dithiafulvenes (**6a**, **6d** or **6b**, **6d**) at different potentials. When the oxidation of the mixture is performed at a potential allowing only the formation of the radical cation of **6d** as shown in Scheme 4 one dimer is obtained. Obtention of unsymmetrical dimers **7ad** and **7bd** (20% yield), in addition to symmetrical dimers, only occurs when oxidation is carried out at sufficiently positive potential to allow the formation of the two cation-radicals. This is in favor of the coupling of two cation radicals. Moreover, it is worth noting that the oxidation potentials of the two unsymmetrical dimers (cf. Table 1) take place on the Hammett correlation line if the half-sum of the two corresponding σp coefficients is put in abcissa.

Conclusion

In summary, several new vinylogous TTFs have been electrochemically synthesized and characterized. Furthermore, we have shown that this reaction results from the dimerization of two cation radicals. These nonplanar extended TTFs appear to be easily oxidized into the dication species. The scope of this electrochemical strategy to build other extended TTFs is currently in progress, as well as the possibility of forming new conducting charge transfer salts with these compounds.

Experimental Section

^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on Bruker AM 300 spectrometer with tetramethylsilane as internal reference. IR were obtained on a Nicolet 205 FT-IR spectrometer. Mass spectra were determined with a Varian Mat 311 Spectrometer (Centre de Mesures Physiques de l'Ouest). Melting points were measured using a Kofler hot stage apparatus. Elemental analysis results were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon).

General Experimental Details for 1,4-Dithiafulvenes 6. All the molecules synthesized and described below are present as two isomers (*Z*/*E*) in solution which were observed by ^{1}H NMR but not separated. The melting points measured below correspond to the single higher-melting point isomer.[9] Phosphonates were prepared using literature procedures.[6]

Phosphonate (5 mmol) was dissolved in dry THF in a three-necked flask, and BuLi in hexane (5.5 mmol from a 1.6 M solution) was added at −78 °C under nitrogen atmosphere. The aldehyde (5 mmol) is then added to the solution. After 10 min at low temperature the mixture was allowed to reach room temperature and stirred for 2 h. THF was removed in vacuo, the reaction mixture was extracted with methylene chloride, and the extract was washed with water, dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel column with ether to give the corresponding 1,4-

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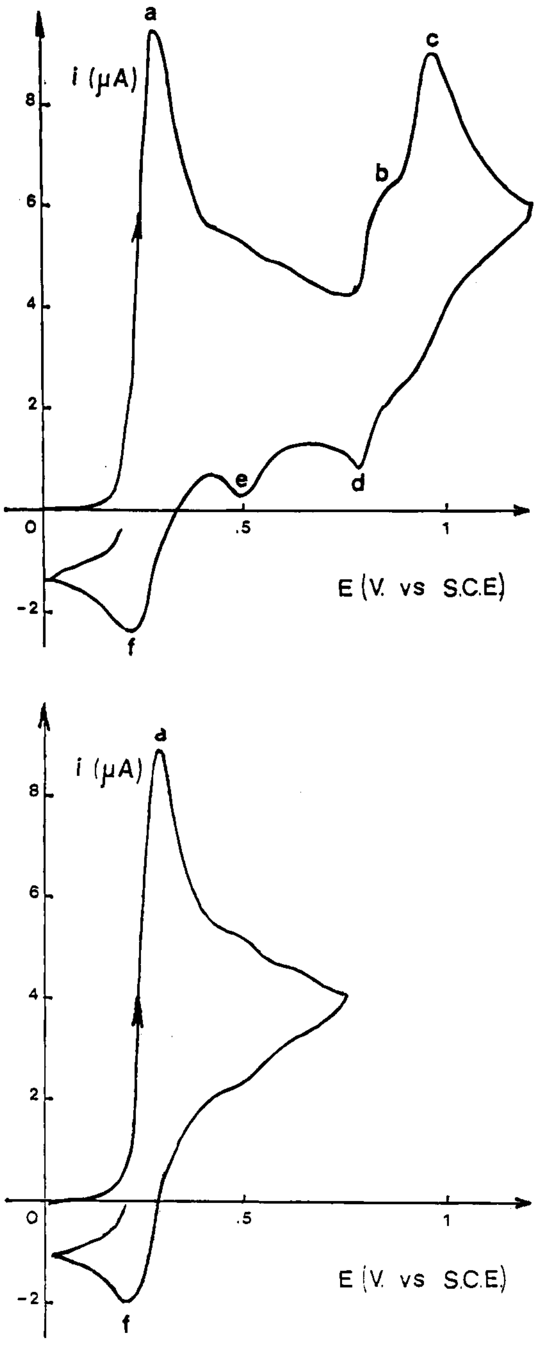


Figure 4. Cyclic voltammogram of 1,4-dithiafulvene **6e** in CH$_3$CN at a scan speed of 100 mV s^{-1}. (Top) oxidation up to 1.2 V. (Bottom) Oxidation limited at 0.75 V.

dithiafulvene. These compounds are not stable as they slowly decompose. **6 a,b** can be recrystallized in methanol, but for **6c–g** they are used in the next step within a few hours without further purification.

6a: red powder; yield 45%; mp 111–113 °C; ^{1}H NMR (CDCl$_3$) δ 2.18 (s, 3H), 2.35 (s, 3H), 6.49 (s 1H), 7.27 (d, 2H, J = 8.9 Hz), 8.17 (d, 2H, J = 8.9 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.33, 19.19, 110.58, 120.32, 124.14, 126.35, 133.93, 141.07, 142.80, 144.05. Anal. Calcd for C$_{12}$H$_{11}$NO$_2$S$_3$: C, 48.45; H, 3.72; N, 4.71; S, 32.34. Found: C, 48.50; H, 3.70; N, 4.64; S, 32.06.

6b: yield 75%; yellow crystals; mp 94–96 °C; ^{1}H NMR (CDCl$_3$) δ 2.17 (s, 3H), 2.35 (s, 3H), 6.43 (s, 1H), 7.25 (d, 2H, J = 8.5 Hz), 7.58 (d, 2H, J = 8.5 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.33, 19.36, 107.58, 110.97, 119.38, 119.88, 126.55, 132.27, 133.58, 139.14, 140.77; IR (KBr) ν (CN) 2220 cm^{-1}. Anal. Calcd for C$_{13}$H$_{11}$NS$_3$: C, 56.27; H, 3.99; N, 5.04; S, 34.67. Found: C, 56.05; H, 4.13; N, 4.97; S, 34.83.

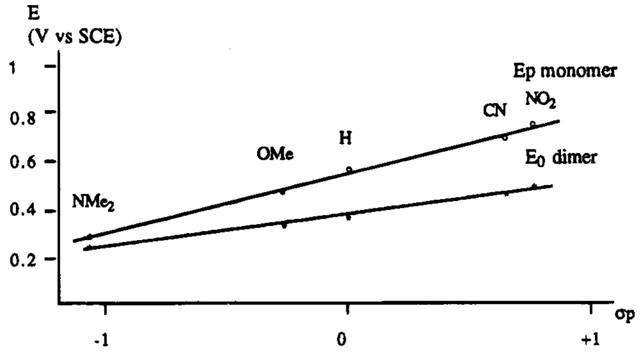


Figure 5. Correlation between the oxidation peak potential (monomers) or E_0 (dimers) and Hammet parameter σ_p.

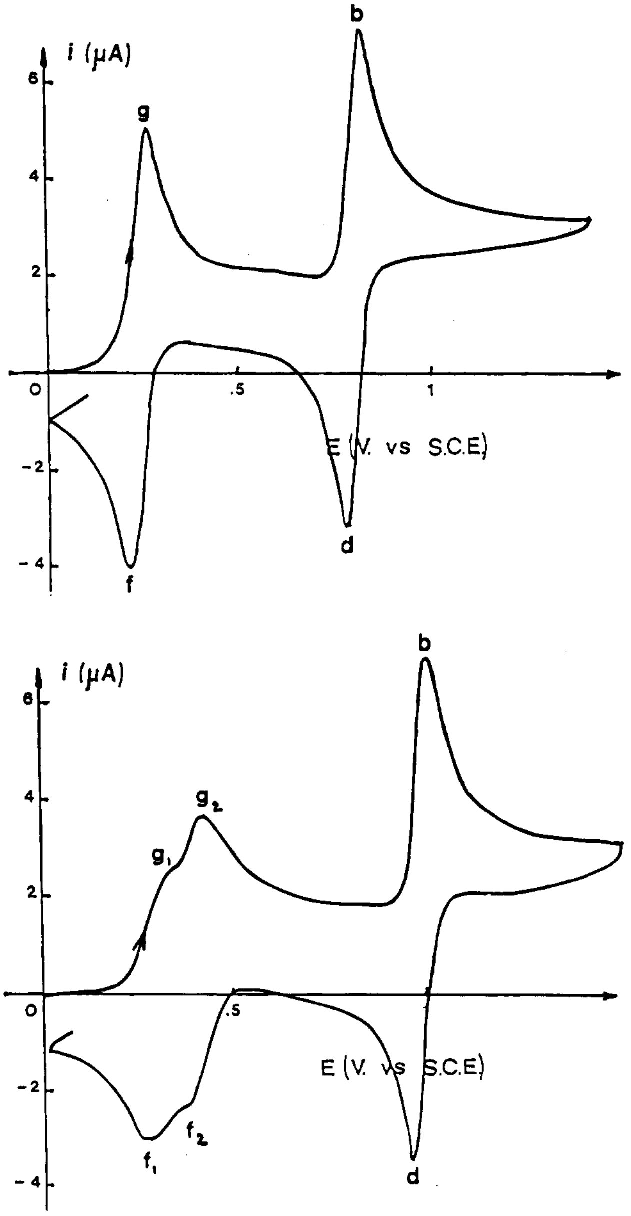
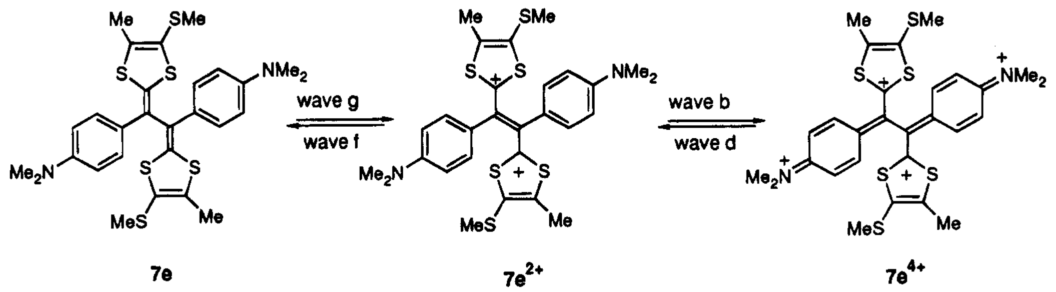


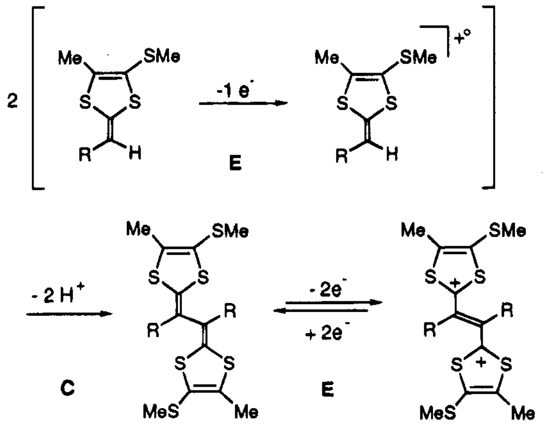
Figure 6. Cyclic voltammogram of dimer **7e** at a scan speed of 100 mV s^{-1} (top) in CH$_3$CN and (bottom) in CH$_2$Cl$_2$.

6c: yield 80%; slighty yellow oil; ^{1}H NMR (CDCl$_3$) δ 2.04 (s, 3H), 2.22 (s, 3H), 6.36 (s, 1H), 7.12 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.43, 19.22, 113.33, 118.63, 125.58, 127.59, 128.53, 131.74, 132.75, 136.68; HRMS calcd for C$_{12}$H$_{12}$S$_3$ 252.0101, found 252.0095.

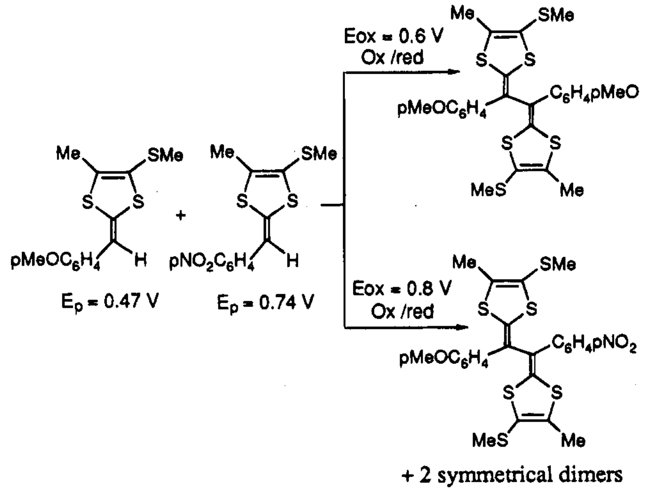
Scheme 2



Scheme 3



Scheme 4



6d: yield 90%; yellow oil; ^{1}H NMR (CDCl$_3$) δ 2.09 (s, 3H), 2.24 (s, 3H), 3.71 (s, 3H), 6.31 (s, 1H), 6.78 (d, 2H, J = 6.7 Hz), 7.08 (d, 2H, J = 6.7 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 15.16, 19.19, 55.31, 113.23, 113.96, 118.20, 127.99, 129.51, 129.7, 131.41, 157.48; HRMS calcd for $C_{13}H_{14}OS_3$ 282.0206, found 282.0164.

6e: yield 85%; yellow oil; ^{1}H NMR (CDCl$_3$) δ 2.14 (s, 3H), 2.29 (s, 3H), 2.93 (s, 6H), 6.35 (s, 1H), 6.70 (d, 2H, J = 8.8 Hz), 7.12 (d, 2H, J = 8.8 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.48, 19.18, 40.59, 112.47, 114.13, 118.5, 125.61, 126.53, 127.87, 131.53, 148.38; HRMS calcd for $C_{14}H_{17}NS_3$ 295.0523, found 295.0560.

6f: yield 81%; yellow oil; ^{1}H NMR (CDCl$_3$) δ 2.06 (s, 3H), 2.24 (s, 3H), 6.59 (s, 1H), 6.8 (m, 1H), 6.97 (m, 1H), 7.15 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 15.04, 19.07, 106.72, 119.24, 123.15, 123.22, 127.16, 131.03, 133.18, 140.64; HRMS calcd for $C_{10}H_{10}S_4$ 257.9665, found 257.9647.

6g: yield 65%; orange oil; ^{1}H NMR (CDCl$_3$) δ 0.94 (t, 3H) 1.43 (m, 2H) 2.09 (s, 3H) 2.24 (s, 3H) 2.37 (m, 2H) 5.32 (t, 1H); HRMS calcd for $C_9H_{14}S_3$ 218.0257, found 218.0240.

General Experimental Details for Vinylogous TTF 7. After the macroscale electrolyses the solvent was removed in vacuo, and toluene (50 mL) was added to the residue. Tetrabutylammonium hexafluorophosphate precipitated and was filtered off. The organic phase was evaporated, and the residue was chromatographied on silica gel column using methylene chloride/petroleum ether (1:1) as eluent. The vinylogous TTF **7** crystallized in methylene chloride/methanol.

7a: red powder; yield 68%; mp > 270 °C; ^{1}H NMR (CDCl$_3$) δ 2.13 (s,3H), 2.17 (s, 3H), 2.28 (s, 3H), 2.39 (s, 3H), 7.52 (d, 4H, J = 8.8 Hz), 8.17 (d, 4H, J = 8.8 Hz); HRMS calcd for $C_{24}H_{20}N_2O_4S_6$ 591.9747, found 591.9753. Anal. Calcd for $C_{24}H_{20}N_2O_4S_6$: C, 48.62; H, 3.4; N, 4.72; S, 32.45. Found: C, 48.59; H, 3.51; N, 4.81; S, 31.88.

7b: yellow crystals; yield 78%; mp 267 °C; ^{1}H NMR (CDCl$_3$) δ 2.11 (s,3H), 2.18 (s, 3H), 2.27 (s, 3H), 2.36 (s, 3H), 7.52 (m, 8H); IR (KBr) ν (CN) 2222 cm^{-1}; ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.47, 15.29, 19.26, 19.39, 108.82, 108.96, 119.15, 120.26, 126.14, 126.36, 132.57, 133.17, 135.09, 135.17, 140.82, 140.96, 143.49, 143.65; HRMS calcd for $C_{26}H_{20}N_2S_6$ 551.9950, found 551.9945. Anal. Calcd for $C_{26}H_{20}N_2S_6$: C, 56.48; H, 3.64; N, 5.06; S, 34.80. Found: C, 56.50; H, 3.50; N, 5.13; S, 34.87.

7c: colorless crystals; yield 70%; mp 163 °C; ^{1}H NMR (CDCl$_3$) δ 2.07 (s, 3H), 2.10 (s, 3H), 2.27 (s, 3H), 2.31 (s, 3H), 7.29 (m, 10H). Anal. Calcd for $C_{24}H_{22}S_6$: C, 57.33; H, 4.41; S, 38.25. Found: C, 57.14; H, 4.47; S, 38.31.

7d: yellow crystals; yield 71%; mp 164 °C; ^{1}H NMR (CDCl$_3$) δ 2.08 (s, 3H), 2.10 (s, 3H), 2.28 (s, 3H), 2.31 (s, 3H), 3.76 (s, 3H), 3.77 (s, 3H), 7.15 (m, 8H); HRMS calcd for $C_{26}H_{26}O_2S_6$ 562.0257, found 562.0285. Anal. Calcd for $C_{26}H_{26}O_2S_6$: C, 55.47; H, 4.65; S, 34.17. found: C, 55.36; H, 4.54; S, 34.36.

7e: yellow orange powder; yield 73%; mp 168–170 °C; ^{1}H NMR (CDCl$_3$) δ 1.95 (s,3H), 1.98 (s, 3H), 2.15 (s, 3H), 2.19 (s, 3H), 2.79 (s, 12H), 6.86 (m, 8H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.48, 15.36, 19.08, 19.20, 40.50, 40.52, 112.18, 112.24, 117.91, 118.05, 124.81, 124.86, 125.61, 125.76, 127.54, 127.67, 131.80, 131.76, 134.24, 134.34, 148.79, 148.85. Anal. Calcd for $C_{28}H_{32}N_2S_6$: C, 57.09; H, 5.47; N, 4.75; S, 32.66. Found: C, 56.87; H, 5.44; N, 4.5; S, 32.17.

7f: orange powder; yield 66%; mp 177–180 °C; ^{1}H NMR (CDCl$_3$) δ 2.03 (s,3H), 2.14 (s, 3H), 2.21 (s, 3H), 2.31 (s, 3H), 6.85 (m, 2H), 6.93 (m, 2H), 7.12 (m, 2H); HRMS calcd for $C_{20}H_{18}S_8$ 513.9174, found 513.9147.

7g: orange oil; yield 65%; ^{1}H NMR (CDCl$_3$) δ 0.95 (t, 6H) 1.45 (m, 4H) 2.07 (s, 6H) 2.35 (s, 6H) 2.4 (m, 4H); HRMS calcd for $C_{18}H_{26}S_6$ 434.0358, found 434.0360.

7bd: yellow powder; yield 20%; mp 128–130 °C; ^{1}H NMR (CDCl$_3$) 2.05 (s, 3H), 2.08 (s, 3H), 2.19 (s, 3H), 2.28 (s, 3H), 3.71 (s, 3H), 6.91 (m, 4H), 7.31 (m, 4H); IR (KBr) ν (CN) 2223 cm^{-1}; HRMS calcd for $C_{26}H_{23}NOS_6$ 557.0103 found 557.0145.

7ad: red powder; yield 18%; mp 139 °C. ^{1}H NMR (CDCl$_3$) 2.10 (s, 3H), 2.13 (s, 3H), 2.29 (s, 3H), 2.34 (s, 3H), 3.71 (s, 3H), 6.97 (m, 4H), 7.82 (m, 4H); HRMS calcd for $C_{25}H_{23}NO_3S_6$ 577.0002 found 577.0033.

Supplementary Material Available: ^{1}H NMR spectra for compounds **6c–f** and **7b,d,f,g,ad,bd** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9417481