Linearly Extended Tetrathiafulvalene Analogues with Dithienyl and Difuryl Polyenes π-Conjugated Spacers

Amina Benahmed-Gasmi,[†,‡] Pierre Frère,*[,†] El Hadj Elandaloussi,[†]
Jean Roncali,*[,†] Jesus Orduna,[§] Javier Garin,[§] Michel Jubault,[†]
Amédée Riou,[†] and Alain Gorgues[†]

Ingénierie Moléculaire et Matériaux Organiques, CNRS, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France; Laboratoire de Chimie Organique, Université d'Oran, ES-SENIA, 31000, Algeria; and Laboratorio de Quimica Organica, Universidad de Zaragoza, Zaragoza, Spain

Received January 19, 1996. Revised Manuscript Received May 7, 1996[⊗]

The synthesis of new classes of extended hybrid tetrathiafulvalene analogues built around difuryl and dithienyl polyenic π-conjugated spacers containing $n = 1$, 2, or 3 conjugated double bonds and bearing CO_2Me, SMe, and *n*-propyl substituents (R) at the 1,3-dithiole ring is described. The electronic absorption spectra of these compounds show that the wavelength of the absorption maximum and the HOMO−LUMO energy gap depend on the nature of the heterocycle, the length of the π-conjugated spacer and the electronic effects of R. Cyclic voltammetry shows that except for $n = 1$ and $R = CO_2Me$, all compounds are directly oxidized into their dicationic state through a single-step two-electron transfer. The combined effects of the various structural parameters allow oxidation potentials lying among the lowest reported to date for TTF analogues to be reached.

Introduction

Hybrid tetrathiafulvalenes analogues (HTTFs) built by insertion of a linearly π-conjugated systems between two 1,3-dithiole units have recently become a focus of keen attention.[1] While in the past few years this interest was mainly motivated by the increased dimensionality and hence better charge-transport properties anticipated for the corresponding cation-radical salts,[1b] more recent works have shown that these hybrid systems are also potentially interesting materials for the design of small bandgap molecular semiconductors[2] or for quadratic and cubic nonlinear optics.[3] In this regard, it has been shown theoretically that whereas second-harmonic generation with push−pull molecules does not require extensively conjugated systems, push−push compounds should exhibit increasing cubic nonlinear efficiency as a function of conjugation length.[4]

An important parameter for the design of HTTFs is of course the selection of an appropriate π-conjugated spacer group. Such a spacer must allow extensive charge delocalization associated with good environmental stability. Numerous studies on materials for quadratic nonlinear optics have shown that while olefinic spacers incorporated in push−pull molecules exhibit efficient electron transmission and high second-order nonlinearities, they suffer from a lack of thermal stability.[3,5] On the other extreme case, the more stable oligophenylenes are poorly efficient due to their twisted structure and to the strong aromatic character of their ground state.[3,6] However, it has been shown that replacing the phenyl ring by heterocyclic-based π-conjugated systems that lose less aromatic resonance energy upon charge separation could represent a good compromise between nonlinear efficiency and stability.[3,5,6]

While previous works have shown that the insertion of conjugated oligothiophene spacers allows a significant improvement of π-donor ability compared to both constitutive building blocks,[7] further investigations have revealed that interannular rotational disorder increases rapidly with the number of thiophene rings almost resulting in saturation of effective conjugation already for a terthienyl spacer.[8]

[†] Université d'Angers.

[‡] Université d'Oran.

[§] Universidad de Zaragoza.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) (a) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439. (b) A superconducting state has recently been observed in a conjugated TTF analogue: Misaki, Y.; Higuchi, N.; Fujiwara, H.; Yamabe, T.; Mori, T.; Mori, H., Tanaka, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1222.

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

(3) Schöbert, U.; Salbeck, J.; Daub, J. *Adv. Mater.* **1992**, *4*, 41. Jen, K.-Y.; Rao, V. P.; Drost, K. J.; Wong, K. Y.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2057. Jen, K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. Sylla, M.; Zaremba, J.; Chevalier, R.; Rivoire, G.; Khanous, A.; Gorgues, A. *Synth. Met.* **1993**, *59*, 111. Nguyen, T. T.; Sallé, M.; Sahraoui, B.; Sylla, M.; Bourdin, J. P.; Rivoire, G.; Zaremba J. *J. Mod. Opt.* **1995**, *42*, 2095.

(4) Meyers, F.; Brédas, J. L. *Organic Materials for Nonlinear Optics III*; Ashwell, G., Bloor, D., Eds.; Royal Society of Chemistry: Cambridge, 1993.

(5) Gilmour, S.; Montgomery, R. A.; Marder, S. R.; Cheng, L.-T.; Jen, K.-Y.; Cai, Y.; Perry, J. W.; Dalton, L. R. *Chem. Mater.* **1994**, *6*, 1603.

(6) Gorman, C. B.; Marder, S. R., *Proc. Natl. Acad. Sci.* **1993**, *90*, 11297. Dirk, C. W.; Katz, H. E.; Schilling, M. I.; King, L. A., *Chem. Mater.*, **1990**, *2*, 700.

(7) (a) Benahmed-Gasmi, A.; Frère, P.; Garrigues, B.; Gorgues, A.; Jubault, M.; Carlier, R.; Texier, F. *Tetrahedron Lett.* **1992**, *33*, 6457. (b) Hansen, T. K.; Lakshmikantam, M. V.; Cava, M. P.; Niziurski-Mann, R. E.; Jensen, F.; Becher, J. *J. Am. Chem. Soc.* **1992**, *114*, 5035. (c) Roncali, J.; Giffard, M.; Frère, P.; Jubault, M.; Gorgues, A. *J. Chem. Soc., Chem. Commun.* **1993**, 689. (d) Takahashi, K.; Nihira, T.; Yoshifuji, M.; Tomitani, K. *Bull. Chem. Soc. Jpn.* **1994**, *66*, 2330.

(8) 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.

S0897-4756(96)00035-X CCC: $12.00

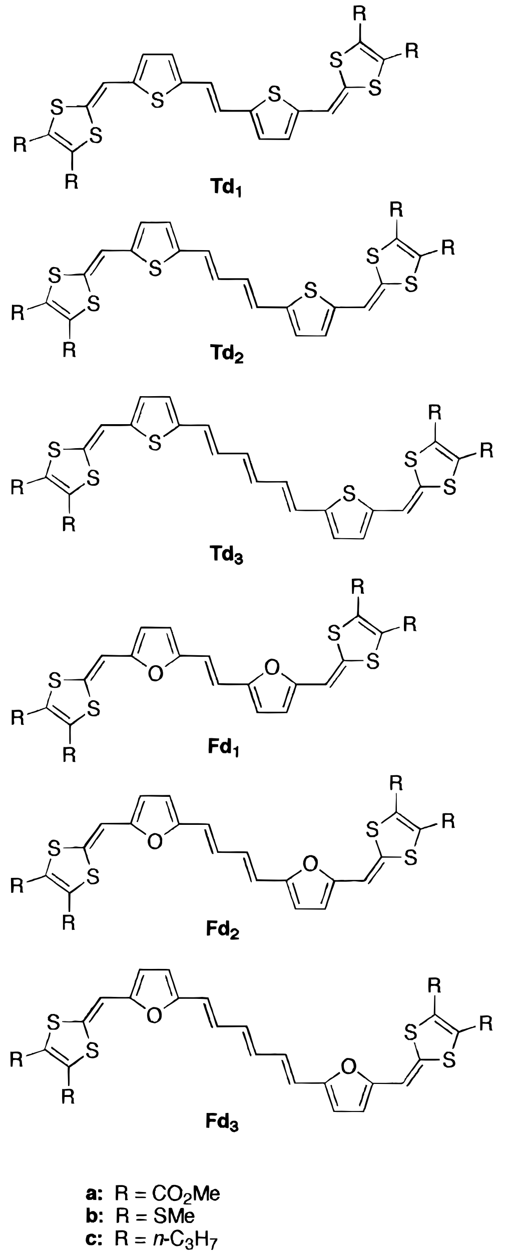
A first answer to this problem consists in the synthesis of ladder-type π-conjugated systems in which the bridging of the thiophene rings prevents inter-ring rotation and leads to considerable reduction of the bandgap.[2,9] We have shown recently that the use of thienylenevinylene oligomers as spacer group represents an interesting alternative strategy which combines a limitation of rotational disorder with a decrease of the overall aromatic character of the spacer.[10] A further step in this direction could involve the insertion of more than a single double bond between the two heterocycles of the spacer. Such an approach would take advantage of the superior electron transmission properties of polyolefinic bridging groups while allowing a further decrease of the overall aromatic character of the conjugated spacer. This strategy was recently exemplified with the synthesis of several dithienyl polyenes showing interesting third order nonlinearities in their bipolaronic state.[11]

We report here the synthesis of new classes of linearly extended HTTFs in which the π-conjugated spacer consists in two thiophene or furan rings separated by one, two or three double bonds **Td$_1$–3a–c** and **Fd$_1$–3a–c** (Chart 1). In the used short-hand notation the capital letter refers to the heterocycle (**T** = thiophene, **F** = furan) and **d$_n$** to the number of double bonds between the two heterocycles. The various R substituents on the 1,3-dithiole ring (**a**–**c**) were selected for solubility reasons (especially in the case of the SMe and *n*-propyl groups) and also in order to gain some first information on the influence of the electronic effects of R on the electrochemical and optical properties of the hybrid π-conjugated system. The analysis of the optical and electrochemical properties of these compounds shows that they exhibit moderate HOMO–LUMO energy gaps which decrease with the length of the spacer without any evidence of saturation. On the other hand, cyclic voltammetry shows that except for $n = 1$, all compounds are directly oxidized into stable dications through a single-step two-electron transfer.

Results and Discussion

The synthesis of **Td$_1$** compounds has already been described.[10] **Fd$_1$ a–c** were obtained from difurylethylene using the same procedure.[12] The new diheteroarylpolyene-based π-donors **Td$_{2-3}$**, and **Fd$_{2-3}$ a–c** were prepared according to the synthetic strategy depicted in Scheme 1. Dimethyl-2-furyl(thienyl)methylphosphonates **5** and **6** were obtained in 68 and 64% yield, respectively, from the corresponding alcohols **1** and **2** via the bromomethyl derivatives **3** and **4**. Aldol condensation of 2-thiophene carboxaldehyde with acetaldehyde afforded *trans*-3-(2-thienyl)acrolein (**8**) in 37% yield. Difurylbutadiene (**10**) and dithienylbutadiene (**11**) were obtained in high yields (96 and 94%, respectively) by Wittig–Horner olefination of **8** and **9** with appropriate phosphonates **6** and **5**. Difurylhexatriene **12** and dithienylhexatriene **13** were obtained in respectively 33 and 57% yield by McMurry coupling of the corresponding aldehydes **9** and **8**.

Chart 1



a: R = CO_2Me
b: R = SMe
c: R = n-C_3H_7

Dicarboxaldehydes **14–17** were prepared by reaction of DMF with the dilithiated derivatives of compounds **10–13**. Lithiation of the difuryl compounds was performed in the presence of TMEDA, but formylation yields were noticeably lower than in the case of dithienyl compounds. The trans configuration of **14–17** is confirmed by the 11 and 15 Hz ^3J couplings in the ^{1}H NMR signal of the ethylenic protons. Moreover, X-ray structure determination of compound **17** clearly reveals the all-trans configuration of the ethylenic spacer and shows the planar conformation adopted by the molecule (Figure 1). The target compounds **Td$_2$** and **Td$_3$a–c** and **Fd$_2$** and **Fd$_3$a–c** were then obtained by Wittig or Wittig–Horner olefination of dialdehydes **14–17** using Akiba's reagents.[13]

Table 1 lists the main electronic absorption data of **Td$_n$** and **Fd$_n$** compounds in CH_2Cl_2. For each n value

---

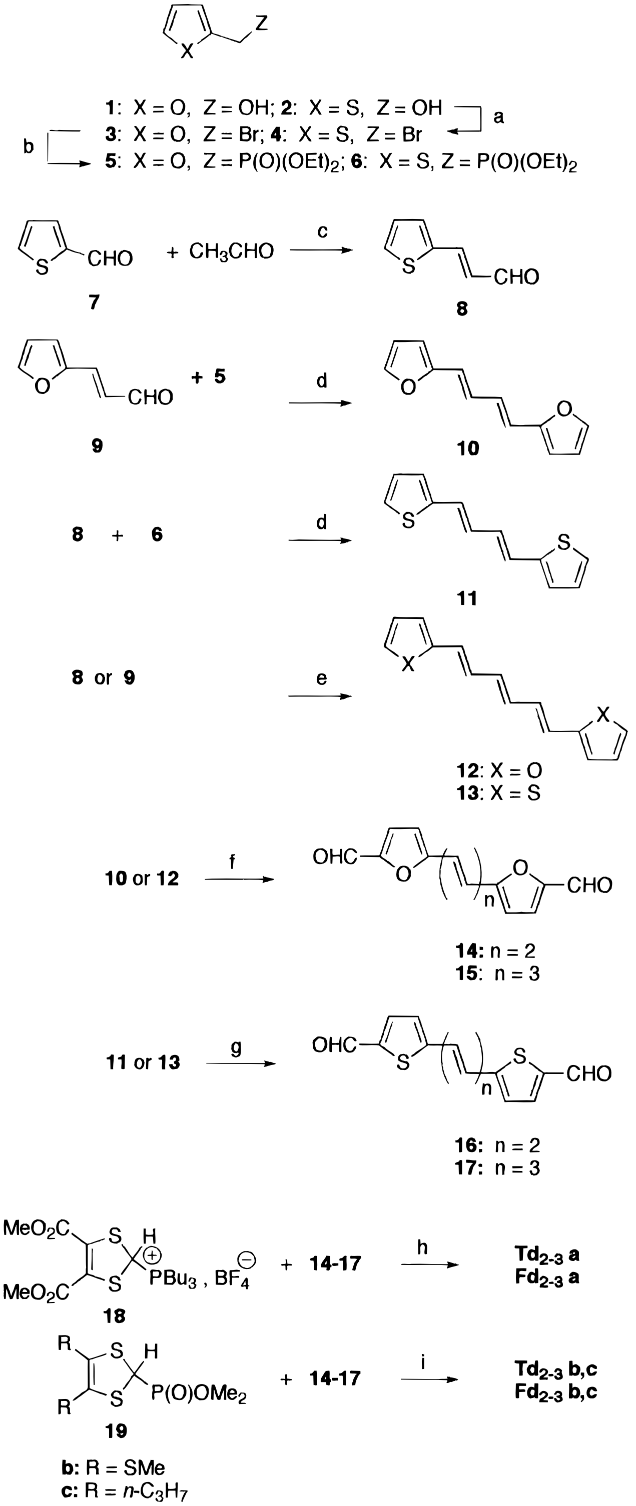
(9) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846. Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E.; Frère, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2249.

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

(11) Spangler, C. W.; Liu, P. K.; Dembek, A. A.; Havelka, K. O. *J. Chem. Soc., Perkin Trans. 1* **1991**, 799. Spangler, C. W.; He, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 715.

(12) Elandaloussi, E.; Frère, P.; Roncali, J., submitted to *J. Mater. Chem.*

Scheme 1. Reagents and Solvents: (a) Br_2−PPh_3/Et_2O; (b) NaH−$(EtO)_2P(O)H$/THF; (c) NaOH/H_2O; (d) *t*-BuOK/THF; (e) $TiCl_4$−Zn/THF; (f) *n*-BuLi−TMEDA−DMF/Hexan-THF; (g) *n*-BuLi/DMF; (h) Et_3N/CH_3CN; (i) *n*-BuLi/THF



and for a given R substituent, thiophene-based compounds absorb at longer wavelengths than their furan analogues; however, the increase of *n* tends to minimize this difference, and for example **Td$_{3c}$** and **Fd$_{3c}$** exhibit the same absorption maximum (λ_{max}) at 512 nm. As expected, for both series of compounds the increase of the number of conjugated double bonds leads to a bathochromic shift of λ_{max} with a concomitant reduction of the HOMO−LUMO gap (ΔE, estimated from the low-energy absorption edge).

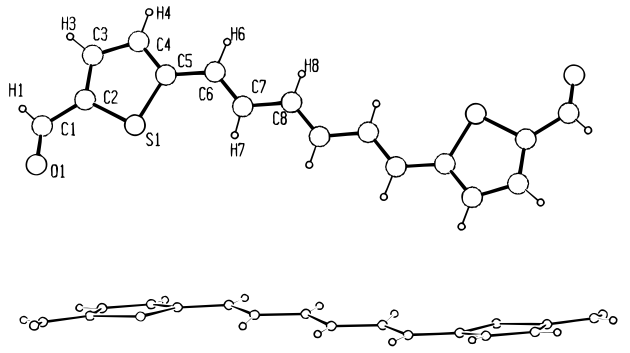


Figure 1. X-ray structure of **17**.

Table 1. Electronic Absorption Data for Td and Fd1−3,a−c 5 × 10^{-5} M in CH_2Cl_2

compd	λ_{max} (nm)	ΔE (eV)	compd	λ_{max} (nm)	ΔE (eV)
Td1a	468	2.34	**Fd1a**	460	2.36
Td1b	484	2.25	**Fd1b**	475	2.30
Td1c	493	2.17	**Fd1c**	477	2.25
Td2a	476	2.27	**Fd2a**	475	2.25
Td2b	489	2.20	**Fd2b**	489	2.19
Td2c	502	2.14	**Fd2c**	499	2.16
Td3a	486	2.24	**Fd3a**	485	2.24
Td3b	501	2.16	**Fd3b**	503	2.13
Td3c	512	2.09	**Fd3c**	512	2.09

For each *n* value both λ_{max} and ΔE exhibit a marked dependence on the nature of R. Thus replacing the electron-withdrawing CO_2Me group by electron-releasing ones such as SMe and especially *n*-propyl, leads for each series to a red-shift of λ_{max} and to a narrowing of ΔE. A closer examination of the data in Table 1 shows that the magnitude of the effects of R is roughly independent of the nature of the heterocycle and of the length of the conjugated spacer. Thus, for each series of compounds, replacing CO_2Me by SMe produces a 0.08−0.09 eV decrease of ΔE while substituting the SMe group by *n*-propyl induces a further 0.06−0.07 eV reduction of ΔE.

Finally a comparison of the data of **Td** and **Fd** compounds shows that the decrease of ΔE is of slightly larger magnitude in the **Fd** series. Thus for R = *n*-propyl, ΔE decreases from 2.17 to 2.09 eV for **Td** compounds and from 2.25 to 2.09 eV in the **Fd** series. These differences could reflect a better electron delocalization over the whole π-conjugated system allowed by the lower aromatic resonance energy of the furan ring.

Figures 2 and 3 show as representative examples the electronic absorption spectra of **Td$_3$** and **Fd$_3$** **a** and **c**. As observed for **Td$_1$a**−**c**,[10] the spectrum of **Td$_3$a** shows a well-resolved fine structure involving a main absorption band with a maximum at 486 nm, an additional low-energy band at 520 nm and a shoulder at 450 nm. This spectrum is consistent with a vibronic structure with a 0−0 transition at 520 nm and vibronic sidebands at 484 and 450 nm as already observed for other

---

(13) Akiba, K.; Ishikawa, K.; Inasoto, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2674. Hansen, T. K.; Lakshmikantham, M. V.; Cava, M. P.; Metzger, R. M.; Becher, J. *J. Org. Chem.* **1991**, *56*, 2720. Moore, A. J.; Bryce, M. R.; Ando, D. T.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1991**, 320.

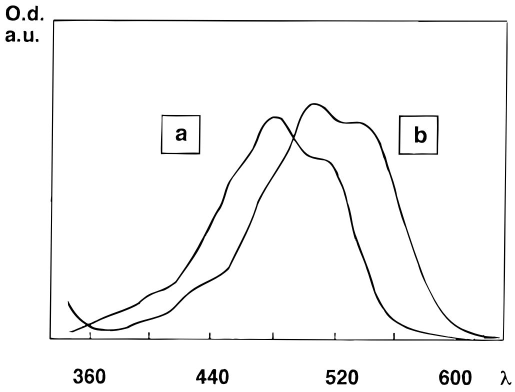


Figure 2. UV–visible absorption spectra of **Td$_3$a** (a) and **Td$_3$c** (b) in CH_2Cl_2.

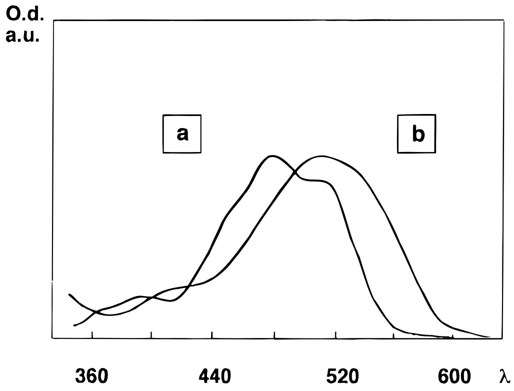


Figure 3. UV–visible absorption spectra of **Fd$_3$a** (a) and **Fd$_3$c** (b) in CH_2Cl_2.

conjugated poly- and oligothiophenes.[14] The energy difference between two consecutive maxima lies in the range 0.17–0.19 eV which is consistent with a C=C stretching mode of the thiophene ring strongly coupled to the electronic structure.[14a] Finally, it should be pointed out that occurrence of this vibrational fine structure is characteristic of all-trans compounds,[15] which confirms the stereoselectivity of the coupling reactions. As appears in Figure 2, except for a slight increase of the oscillator strength in the low-energy region of the spectrum, the resolution of the vibronic fine structure is not affected by the nature R. A similar behavior was observed in the spectra of **Td$_1$** and **Td$_2$** compounds (not shown) suggesting that substitution of the 1,3-dithiole ring has little influence on the rigidity of the π-conjugated system of **Td** compounds.

As shown in Figure 3, **Fd$_n$** compounds exhibit a quite different behavior since in addition to changes in λ_{max} and ΔE, the nature of R has a marked influence on the resolution of the vibronic fine structure. Thus, replacement of CO_2Me by more electron-donating groups produces a decrease of the resolution of the fine structure which almost vanishes for R = *n*-propyl. This phenomenon is independent of the number of double bonds and a similar behavior was observed for **Fd$_1$** and **Fd$_2$** compounds.

Table 2. Cyclic Voltammetric Data for Td and Fd1–3,a–c 10^{-4} M in 0.1 M Bu_4NPF_6/CH_2Cl_2 (Scan Rate 200 mV s^{-1}; s, Shoulder)

compd	E_{pa1}, E_{pa2} (V/SCE)	compd	E_{pa1}, E_{pa2} (V/SCE)
Td1a	0.59 s, 0.66	**Fd1a**	0.48 s, 0.57
Td1b	0.43	**Fd1b**	0.32
Td1c	0.29	**Fd1c**	0.18
Td2a	0.58	**Fd2a**	0.48
Td2b	0.37	**Fd2b**	0.31
Td2c	0.26	**Fd2c**	0.17
Td3a	0.54	**Fd3a**	0.45
Td3b	0.40	**Fd3b**	0.31
Td3c	0.24	**Fd3c**	0.16

The contrasting behaviors of thiophene- and furan-based compounds show that the nature of R exerts a significant influence on the rigidity of the π-conjugated system in **Fd$_n$** compounds. Previous X-ray studies of hybrid TTF analogues with oligothiophene π-conjugated spacers have shown that these compounds have a syn conformation stabilized by strong intramolecular interactions between the sulfur atoms of the 1,3-dithiole and thiophene rings, the intramolecular S···S distance being smaller than the sum of the van der Walls radii.[8] Such intramolecular interactions have also been observed between the sulfur atom of the 1,3-dithiole ring and the oxygen of an adjacent furan ring.[16] Interestingly, in this case, the length of the intramolecular nonbonded S···O contact was shown to decrease when replacing the SMe substituents on the dithiole ring by more electron-withdrawing groups.[16] On the basis of these observations, the loss of resolution of the vibrational fine structure observed in **Fd** compounds bearing the most electron-releasing R substituents could reflect a decrease of the rigidity of the π-conjugated backbone caused by the weakening of the intramolecular S···O interactions. X-ray studies in progress in our laboratory should permit to definitively confirm this hypothesis.

Cyclic Voltammetry. The cyclic voltammetric data of the various compounds (Table 2) show that, as for the optical features, the electrochemical properties depend on the nature of the heteroatom, the length of the π-conjugated bridge, and the nature of R. The CV of **Fd$_1$a** (Figure 4) exhibits a first anodic shoulder at 0.48 V (Epa1) followed by a main reversible oxidation wave peaking at 0.57 V (Epa2) corresponding to the successive generation of the cation radical and dication. Compared to the parent compound built around a single furan ring,[7a] the potential difference Epa2–Epa1 decreases from 200 to 90 mV, indicating a considerable reduction of the Coulombic repulsion between positive charges in the dication.

As shown in Table 2, except **Fd$_1$a** and **Td$_1$a** for which the two successive oxidation steps can be observed, all other compounds are directly oxidized to their dicationic state through a reversible two-electron process as indicated by the separation between the oxidation and the reduction peak potentials Epa1–Epc1 close to the expected 30 mV (Figure 5). This behavior is in marked contrast with that of the parent compounds built around oligothiophene spacers for which two successive one-electron oxidation steps were still observed even with a terthienyl spacer.[8] These contrasting behaviors confirm, in agreement with previous results,[10] that the

---

(14) (a) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci.* **1987**, *25*, 1071. (b) Roncali, J.; Korri Youssoufi, H.; Garreau, R.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1990**, 414. (c) Li, H. S.; Garnier, F.; Roncali, J. *Solid State Commun.* **1991**, *77*, 811. (c) Yassar, A.; Horowitz, G.; Valat, P.; Wintgens, V.; Hmyene, M.; Deloffre, F.; Srivastava, P.; Lang, P.; Garnier, F. *J. Phys. Chem.* **1995**, *99*, 9155.

(15) Zechmeister, L. *Chem. Rev.* **1944**, *34*, 267.

(16) Hansen, T. K.; Bryce, M. R.; Howard, J. A. K.; Yufit, D. S. *J. Org. Chem.* **1994**, *59*, 5324.

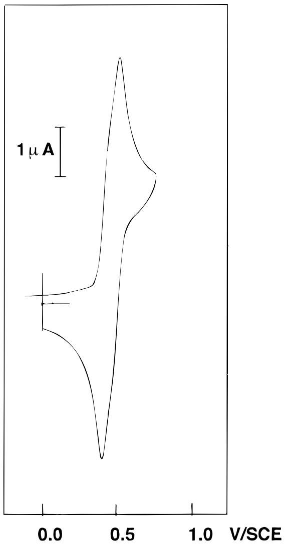


Figure 4. Cyclic voltammogram of **Fd$_1$a** (10^{-4} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2 scan rate 100 mV s^{-1}.

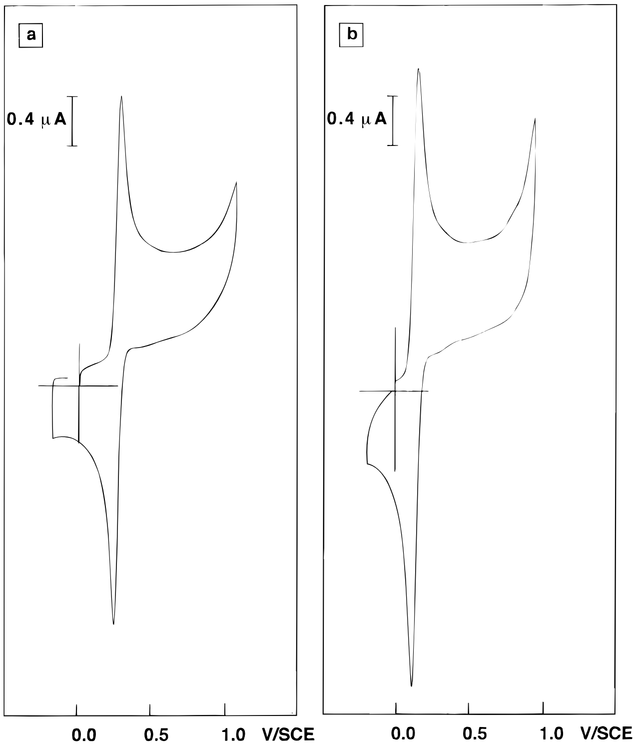


Figure 5. Cyclic voltammogram of (a) **Td$_3$c** (5×10^{-5} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2 scan rate 100 mV s^{-1}. (b) **Fd$_3$c** same conditions.

insertion of olefinic bridges between the heterocycles allows a significant decrease of the charge localization related to the resonance energy of fully polyaromatic spacers.

For a given R substituent, **Fd$_n$** compounds show Epa1 values ca. 100 mV less positive for their **Td$_n$** analogues. This difference could be related to the lower aromatic resonance energy of the furan ring which results in a smaller energy cost for oxidation. For both series of compounds the increase of the number of double bonds leads a steady negative shift of Epa1. Although the magnitude of this shift is rather limited (40 mV between **Td$_1$c** and **Td$_3$c** and 20 mV between **Fd$_1$c** and **Fd$_3$c**), it is worth noting that this behavior contrasts with that of other series of HTTFs built around olefinic,[17] oligothiophene,[8] or oligothienylenevinylene[10] spacers for which the increase of the length of the conjugated bridge led to saturation or even to a reincrease of Epa1. The comparison of the shifts of Epa1 with the corresponding optical data in Table 1 shows that in each case the decrease of ΔE is much larger than the corresponding negative shift of Epa1. Thus whereas ΔE decreases by 0.08 eV between **Td$_1$c** and **Td$_3$c** the negative shift of Epa1 is only of 0.04 V. Similarly ΔE decreases by 0.14 eV between **Fd$_1$c** and **Fd$_3$c** while Epa1 shifts only 0.02 V. These differences suggest, in agreement with previous conclusions, that in extended HTTFs the length of the conjugated spacer affects essentially the energy of the LUMO while the major contribution to the HOMO level arises from the 1,3-dithiole ring.[10,17] This latter point is supported by the strong impact of the electronic effects of R on Epa1. Thus, for each series, replacing CO_2Me by SMe produces a 150−180 mV negative shift of Epa1 while a further 140−150 mV shift occurs for R = *n*-propyl. Although thioalkyl groups are generally considered as stronger electron donors than alkyl groups, the reverse effects are observed in the TTF series.[7,8,10,17]

As for the optical data, the effects of R on Epa1 are roughly independent of the nature of the heterocycle and of the length of the conjugated spacer. This brings a further support to the conclusion that R exerts a major influence on the HOMO level. Owing to the combined effects of the various structural parameters, oxidation potentials as low as 0.16 V/SCE have been reached in the case of **Fd$_n$** compounds. These values are among the lowest reported to date in the TTF series, surpassed only by some two-dimensionally extended TTF analogues.[18]

Conclusion

New series of extensively π-conjugated TTF analogues built around dithienyl- and difurylpolyenes conjugated spacers have been synthesized. While the HOMO−LUMO gap shows only a moderate decrease as the length of the spacer increases, it exhibits a strong dependence on the electronic effects of the substituents attached at the 1,3-dithiole ring. This result suggests, in agreement with previous works, that the energy level of the HOMO is essentially controlled by this part of the molecule.

Except for compounds with only one double bond in the conjugated spacer and bearing electron-withdrawing R substituents, all compounds can be directly converted into stable dications at very low positive potentials,. These results, which confirm the excellent π-donor ability of these new compounds, suggest that they could represent interesting models for the study of stable bipolarons.

Experimental Section

The synthesis of **Td$_1$** compounds has already been reported.[10] **Fd$_1$** compounds were obtained by the same procedure.[12] Dithiolium salts **18** and **19** were prepared using known methods.[13]

---

[17] Sugimoto, T.; Awaji, H.; Sugimoto, I.; Misaki, Y.; Kawase, T.; Yoneda, S.; Yoshida, Z. *Chem. Mater.* **1989**, *1*, 535.

[18] (a) Belyasmine, A.; Frère, P.; Gorgues, A.; Jubault, M.; Duguay, G.; Hudhomme, P. *Tetrahedron Lett.* **1993**, *34*, 4008. (b) Sallé, M.; Jubault, M.; Gorgues, A.; Boubekeur, K.; Fourmigué, M.; Batail, P.; Canadell, E. *Chem. Mater.* **1993**, *5*, 1196. (c) Frère, P.; Gorgues, A.; Jubault, M.; Texier, F.; Cousseau, J.; Duguay, G. *Synth. Met.* **1993**, *55−57*, 1803.

2-(Bromomethyl)furan (3). Bromine (16 g, 0.1 mol) is added dropwise at 0 °C to 26.23 g (0.1 mol) of triphenylphosphine dissolved in 160 mL of ether. 2-Furfuryl (9.81 g, 0.1 mol) alcohol (**1**, Aldrich) is added dropwise causing an exothermic reaction. After 1 h of stirring, evaporation of the ether (**caution**: risk of explosion!) yields 16.25 g of a yellow oil, which darkens rapidly and much be used immediately for the next step.

Diethylfuran-2-Phosphonate (5).[19] To 7.2 g of NaH (80% in oil) rinsed twice with dry THF and 250 mL of dry THF cooled to −20 °C is added dropwise 30 mL of diethyl phosphite in 30 mL of THF. After 30 min of stirring at −20 °C, 16.25 g of 2-bromomethylfuran in 40 mL of THF is added dropwise, and the mixture is refluxed for 1 h. The mixture is then cast on ice and extracted with ether. The organic phase is dried over $MgSO_4$, evaporated, and distilled, giving 14.82 g (68%) of pale yellow oil (bp 96−97 °C/0.19 Torr). ^1H NMR ($CDCl_3$, ppm) 7.26 (br, 1H), 6.25 (br) 1H), 6.16, (br 1H), 4.04−3.93 (m, 4H), 3.19−3.12 (2s, 2H), 1.23−1.17 (m, 6H).

Diethyl-2-(thienylmethyl)phosphonate (6).[20] This compound is obtained using the same procedure from 100 mmol of 2-thiophenemethanol (Aldrich, **2**). Distillation yields 64% of colorless oil (bp 126−127 °C/0.14 Torr). ^1H NMR ($CDCl_3$, ppm) 7.22−7.20 (m, 2H), 7.15 (br) 1H), 4.06−3.95 (m, 4H), 3.34−3.27 (2s, 2H), 1.32−1.21 (m, 6H).

3-(2-thienyl)prop-2-enal (8).[21] To 30 mL of acetaldehyde and 800 mL of H_2O cooled to 0 °C are added dropwise 27.5 mL of 2-thiophenecarboxaldehyde (Aldrich) and 50 mL of 7 M aqueous NaOH. After 6 h of stirring at 0 °C the mixture is extracted with ether. The organic phase is dried over $MgSO_4$, evaporated, and distilled, yielding 10.18 g (37%) of yellow oil (bp 90.5−91 °C/0.13 Torr). MS calcd for C_7H_6OS: 138. Found 138. ^1H NMR ($CDCl_3$, ppm) 9.60 (d, 1H, $^3J = 7.5$ Hz), 7.54 (d, 1H, $^3J = 15.5$ Hz), 7.49 (d, 1H, $^3J = 5.16$ Hz), 7.35 (d, 1H, $^3J = 3.76$ Hz), 7.12 (dd, 1H, $^3J = 3.76$ Hz, $^3J = 5.16$ Hz), 6.54−6.46 (dd, 1H, $^3J = 7.5$ Hz, $^3J = 15.5$ Hz).

1,4-Bis(2-furyl)buta-1,3-diene (10). Potassium terbutylate (1.683 g, 15 mmol) is added portionwise under nitrogen to 1.22 g (10 mmol) of *trans*-3-(2-furyl)acroleine (Aldrich, **9**) and 2.62 g (12 mmol) of phosphonate **5** dissolved in 200 mL of dry THF. After 1 h of stirring at ambient temperature and evaporation of the solvent, the mixture is extracted with CH_2Cl_2. The organic phase is dried over $MgSO_4$ and evaporated, giving an orange oil which crystallizes. Column chromatography (silica gel/CH_2Cl_2) gives 3.09 g (96%) of orange crystals, mp 95 °C; MS calcd for $C_{12}H_{10}O_2$: 186. Found: 186. ^1H NMR ($CDCl_3$, ppm) 7.32 (d, 2H, $^3J = 1.7$ Hz), 6.76−6.70 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 15.0$ Hz), 6.40−6.35 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 15.0$ Hz), 6.34 (dd, 2H, $^3J = 1.7$ Hz, $^3J = 3.0$ Hz), 6.22 (d, 2H, $^3J = 3.0$ Hz); UV−vis (CH_2Cl_2) 365, 347.

1,4-Bis(2-thienyl)buta-1,3-diene (11).[22] This compound is prepared using the same procedure from 0.76 g (5.5 mmol) of aldehyde **8** and 1.562 g (6.6 mmol) of phosphonate **6**. Yield 94%, yellow crystals, mp 170 °C (lit. 173 °C[22]). MS calcd for $C_{12}H_{10}S_2$: 218. Found 218. Anal. Calcd: C 65.93 (66.05), H 4.58 (4.58). ^1H NMR ($CDCl_3$, ppm) 7.20−7.17 (dd, 2H, $^3J = 2.1$ Hz, $^3J = 4.2$ Hz), 7.01−6.97 (m, 4H), 6.82−6.66 (m, 4H); UV−vis (CH_2Cl_2) 380, 361 nm.

1,6-Bis(2-furyl)hexa-1,3,5-triene (12). Zn (6.5 g, 100 mmol) is added portionwise to a mixture of 5.41 mL (50 mmol) of $TiCl_4$ and 400 mL of dry THF at 0 °C under nitrogen. After 1 h of reflux the mixture is cooled to 0 °C, and a solution of 5 g (40 mmol) of 2-furylethenal and 4 mL of pyridine in 100 mL of THF is added. The mixture is refluxed for 2 h cooled, and extracted with CH_2Cl_2. After drying on $MgSO_4$ and removal of the solvent, the crude product is purified by column chromatography on silica gel (2:1 petroleum ether/CH_2Cl_2.) yielding 4.33 g (43%) of the title compound, mp 149 °C. MS calcd for $C_{14}H_{12}O_2$: 212. Found: 212. ^1H NMR ($CDCl_3$, ppm) 7.38 (d, 2H, $^3J = 1.1$ Hz), 6.83−6.74 (m, 4H, $^4J = 3.2$ Hz, $^3J = 7.3$ Hz, $^3J = 15.3$ Hz), 6.48−6.35 (m, 6H), 6.18 (d, 2H, $^3J = 3.3$ Hz); UV−vis (CH_2Cl_2) 391, 370 nm.

1,6-Bis(2-thienyl)hexa-1,3,5-triene (13).[22] This compound is obtained according to the same procedure from 6.24 g (45 mmol) of 2-thienylethenenal, yellow powder, yield 57%, mp 213 °C (lit. 199 °C[22]). MS calcd for $C_{14}H_{12}S_2$: 244. Found: 244. ^1H NMR ($CDCl_3$, ppm) 7.19−7.17 (m, 2H), 6.99−6.96 (m, 4H), 6.71−6.68 (m, 4H), 6.45−6.41 (m, 4H). UV−vis (CH_2Cl_2) 404, 382 nm.

1,4-Bis(5-formyl-2-furyl)buta-1,3-diene (14). To a solution of 0.744 g (4 mmol) of **10** in 50 mL of THF is added 1.2 mL (8 mmol) of TMEDA under nitrogen. After cooling to 0 °C 7 mL (11 mmol) of *n*-butyllithium (1.6 M in hexane) is added dropwise. The mixture is then refluxed for 30 min and cooled again to 0 °C, and 5 mL (65 mmol) of DMF is added dropwise. After 1 h stirring at 0 °C, the mixture is allowed to warm to ambient temperature, hydrolyzed with 3 N aqueous NH_4Cl, and extracted with CH_2Cl_2; the organic phase is washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/ethylacetate 10:1) to provide 0.426 g (44%) of a brown solid, mp 187 °C. MS calcd for $C_{14}H_{10}O_4$: 242. Found: 242. Anal. (calcd) C 69.30 (69.42), H 4.20, (4.13). ^1H NMR ($CDCl_3$, ppm) 9.61 (s, 2H), 7.25 (d, $^3J = 3.8$ Hz), 7.19−7.13 (dd, 2H, $^3J = 11.5$ Hz, $^4J = 3.0$ Hz), 6.63−6.57 (dd, 2H, $^3J = 11.5$ Hz, $^4J = 3.0$ Hz), 6.55 (d, 2H, $^3J = 3.8$ Hz); IR (KBr) 1697 cm^{-1} (CHO); UV−vis (CH_2Cl_2) 422, 398 nm.

1,6-Bis(5-formyl-2-furyl)hexa-1,3,5-triene (15). The same procedure applied to 0.160 g of **12** afforded the title compound as a red solid in 37% yield, mp 212 °C. MS calcd for $C_{16}H_{12}O_4$: 268. Found: 268. Anal. (calcd) C 71.99 (71.64), H 4.87 (4.48). ^1H NMR ($CDCl_3$, ppm) 9.59 (s, 2H), 7.25 (d, 2H, $^3J = 3.8$ Hz), 7.18−7.08 (m, 2H, $^3J = 15.3$ Hz, $^3J = 7.3$ Hz, $^4J = 3.0$ Hz), 6.61−6.57 (dd, 2H, $^3J = 7.3$ Hz, $^4J = 3.0$ Hz), 6.50 (d, 2H, $^3J = 3.8$ Hz), 6.49 (d, 2H, $^3J = 15.3$ Hz); IR (KBr) 1668 cm^{-1} (CHO); UV−vis (CH_2Cl_2) 442, 416 nm.

1,4-Bis(5-formyl-2-thienyl)buta-1,3-diene (16). To a solution of 0.634 g (2.9 mmol) of **11** in 100 mL of Et_2O + 50 mL of THF are added dropwise 10 mL (16 mmol) of *n*-butyllithium (1.6 M in hexane) at 0 °C under nitrogen. The mixture is stirred at 0 °C for 2 h, and 7 mL (90 mmol) of DMF is added dropwise. After 2 h of stirring at ambient temperature and hydrolysis with 3 N aqueous NH_4Cl, the mixture is extracted with CH_2Cl_2, the organic phase is washed with water, dried over $MgSO_4$, and evaporated. Column chromatography of the residue (silica gel, CH_2Cl_2/ethyl acetate 10:1) gives 0.424 g (56%) of a red solid, mp 200 °C. MS calcd for $C_{14}H_{10}S_2O_2$: 274. Found: 274. Anal. (calcd): C 61.36 (61.31), H 3.78 (3.65). ^1H NMR ($CDCl_3$, ppm) 9.86 (s, 2H), 7.65 (d, 2H, $^3J = 4$ Hz), 7.14 (d, 2H, $^3J = 4$ Hz), 6.86 (m, 4H); IR (KBr) 1644 cm^{-1} (CHO). UV−vis (CH_2Cl_2) 436, 412 nm.

1,6-Bis(5-formyl-2-thienyl)hexa-1,3,5-triene (17). This compound was obtained by the same method from 0.732 g (3 mmol) of **13**, yield 0.643 g (71%), mp 206 °C. MS calcd for $C_{16}H_{12}S_2O_2$: 300. Found: 300. Anal. (calcd) C 63.41 (63.97), H 4.21 (4.03). ^1H NMR ($CDCl_3$, ppm) 9.85 (s, 2H), 7.65 (d, 2H, $^3J = 4$ Hz), 7.11 (d, 2H, $^3J = 4$ Hz), 6.95−6.86 (m, 2H, $^3J = 15.3$ Hz, $^3J = 6.8$ Hz, $^4J = 3$ Hz), 6.80−6.75 (d, 2H, $^3J = 15.3$ Hz), 6.58−6.55 (dd, 2H, $^3J = 6.8$ Hz, $^4J = 3$ Hz); IR (KBr) 1644 cm^{-1} (CHO); UV−vis (CH_2Cl_2) 457, 431 nm.

1,4-Bis[5-(1,4-dithia-2,3-dimethylcarboxylatefulven-6-yl)-2-furyl]buta-1,3-diene (Fd_2a). Dialdehyde **14** (0.121 g, 0.5 mmol) and 0.508 g (1 mmol) of dithiolium salt **18** are dissolved in 40 mL of 1:1 acetonitrile/THF under nitrogen at ambient temperature. Upon addition of 1 mL of Et_3N, the solution turns red and a red precipitate forms. The mixture is stirred for 2 h, and 2 mmol of **18** and 2 mL of Et_3N are added. After stirring overnight, MeOH is added and the precipitate is filtered, washed with MeOH, and dried giving 0.226 g (70%) of purple powder, mp 195 °C. MS calcd for $C_{28}H_{22}S_4O_{10}$: 646. Found: 646 (FAB). Anal. (calcd) C 52.20 (52.01), H 3.49 (3.43). IR (KBr) 1739 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) ppm 6.87−6.82 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 11.3$ Hz), 6.48−6.43 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 11.3$ Hz), 6.34 (d, 2H, $^3J = 3.5$ Hz), 6.32 (s, 2H), 6.19 (d, 2H, $^3J = 3.5$ Hz), 3.88−3.92 (2s, 12H).

---

(19) Seeboth, H.; Andreae, S. *Z. Chem.* **1977**, *16*, 399.

(20) Kellog, R. M.; Groen, M. B.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 3093.

(21) Rao, C. S.; Chandrasekharam, M.; Patro, B.; Ila, H.; Junjappa, H. *Tetrahedron* **1992**, *50*, 5783.

(22) Miller, R. E.; Nord, F. F. *J. Org. Chem.* **1951**, *16*, 1380.

The same procedure was used for the preparation of other compounds bearing CO_2Me substituents.

1,6-Bis[5-(1,4-dithia-2,3-dimethylcarboxylatefulven-6-yl)-2-furyl]hexa-1,3,5-triene (Fd$_3$a). Purification by column chromatography (silica gel, CH_2Cl_2/ethyl acetate, 50:1). Yield 77%, mp 234 °C. MS calcd for $C_{30}H_{24}S_4O_{10}$: 672. Found: 672 (FAB). Anal. (calcd) C 53.44 (53.57), H 3.53 (3.57). ^{1}H NMR ($CDCl_3$, ppm) 6.86−6.77 (m, 2H, $^4J = 3.0$ Hz, $^3J = 7.5$ Hz, $^3J = 15.0$ Hz), 6.52−6.48 (dd, 2H, $^4J = 3.0$ Hz; $^3J = 7.5$ Hz), 6.36 (d, 2H, $^3J = 15$ Hz), 6.33−6.30 (m, 4H), 6.18 (d, 2H, $^3J = 3.5$ Hz), 3.92−3.87 (2s, 12H); IR (KBr) 1730 cm^{-1} (C═O).

1,4-Bis[5-(1,4-dithia-2,3-dimethylcarboxylatefulven-6-yl)-2-thienyl]buta-1,3-diene (Td$_2$a). Yield 84%, orange powder, mp 270 °C. MS calcd for $C_{28}H_{22}S_6O_8$: 678. Found: 678 (FAB). Anal. (calcd) C 49.32 (49.53), H 3.22 (3.26). IR (KBr) 1717 cm^{-1} (C═O). The solubility was too low to obtain correct NMR spectra.

1,6-Bis[5-(1,4-dithia-2,3-dimethylcarboxylatefulven-6-yl)-2-thienyl]hexa-1,3,5-triene (Td$_3$a). Yield 57%, mp 244 °C. MS (FAB) calcd for $C_{30}H_{24}S_6O_8$: 704. Found: 704. Anal. (calcd) C 50.96 (51.12), H 3.41 (3.43). ^{1}H NMR ($CDCl_3$, ppm) 6.95−6.90 (m, 2H), 6.78−6.71 (m, 3H), 6.69−6.67 (br, 4H), 6.64−6.62 (m, 2H), 6.46−6.42 (br, 1H), 3.88 (2s, 12 H); IR (KBr) 1714 (C═O), 1556 cm^{-1} (C═C).

1,4-Bis[5-(1,4-dithia-2,3-dithiomethylfulven-6-yl)-2-thienyl]buta-1,3-diene (Td$_2$b). A mixture of phosphonate **19b** (4 mmol) and 0.166 g (0.55 mmol) of dialdehyde **17** in 10 mL of THF is cooled to 0 °C, and 3 mL (4 mmol) of *n*-butyllithium (1.6 M in hexane) is added dropwise. After 2 h of stirring at 0 °C a red solid precipitates which is filtrated, washed with methanol and ether, and dried, giving 0.273 g (87%) of the title compound as a dark red powder, mp 202 °C. MS calcd for $C_{24}H_{22}S_{10}$: 630. Found: 630 (FAB). Anal. (calcd) C 44.51 (45.71), H 3.43 (3.49). ^{1}H NMR ($CDCl_3$, ppm) 6.91 (d, 2H, $^4J = 4.0$ Hz), 6.74−6.70 (m, 6H), 6.65 (s, 2H), 2.46−2.43 (2s, 12H).

The same procedure was used for the preparation of the following compounds.

1,4-Bis[5-(1,4-dithia-2,3-dipropylfulven-6-yl)-2-thienyl]-buta-1,3-diene (Td$_2$c). Column chromatography on silica gel (CH_2Cl_2), yield 67%, mp 146 °C. MS calcd for $C_{32}H_{38}S_6$: 614. Found: 614. Anal. (calcd) C 62.55 (62.54), H 6.22 (6.19). ^{1}H NMR ($CDCl_3$, ppm) 6.88 (d, 2H, $^3J = 4.0$ Hz), 6.70−6.68 (br, 6H), 6.64 (s, 2H), 2.45−2.34 (m, 8H), 1.65−1.52 (m, 8H), 1.02−0.94 (m, 12H).

1,6-Bis[5-(1,4-dithia-2,3-dithiomethylfulven-6-yl)-2-thienyl]hexa-1,3,5-triene (Td$_3$b). Red powder, yield 90%, mp 216 °C. MS calcd for $C_{34}H_{24}S_{10}$: 656. Found: 656. Anal. (calcd) C 45.94 (47.56), H 3.57 (3.66). ^{1}H NMR ($CDCl_3$, ppm) 6.90 (d, 2H, $J = 3.7$ Hz), 6.73 (d, 2H, $J = 3.7$ Hz), 6.68−6.65 (m, 6H), 6.44−6.39 (m, 2H), 2.47 (2s, 12H).

1,6-Bis[5-(1,4-dithia-2,3-dipropylfulven-6-yl)-2-thienyl]-hexa-1,3,5-triene (Td$_3$c). Red powder, yield 77%, mp 168 °C. MS calcd for $C_{34}H_{40}S_6$: 640. Found: 640. Anal. (calcd) C 63.62 (63.70), H 6.33 (6.28). ^{1}H NMR ($CDCl_3$, ppm) 6.88 (d, 2H $^3J = 4.0$ Hz), 6.70 (d, 2H, $^3J = 4.0$ Hz), 6.66−6.64 (m, 6H), 6.43−6.41 (m, 2H), 2.45−2.34 (m, 8H), 1.68−1.52 (m, 8H), 1.02−0.94 (m, 12H).

1,4-Bis[5-(1,4-dithia-2,3-dithiomethylfulven-6-yl)-2-furyl]buta-1,3-diene (Fd$_2$b). Yield 58%, mp 74 °C. MS calcd for $C_{24}H_{22}S_8O_2$: 598. Found: 598. Anal. (calcd) C 48.17 (48.12), H 3.75 (3.70). ^{1}H NMR ($CDCl_3$, ppm) 6.87−6.82 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 11.3$ Hz), 6.46−6.41 (dd, 2H, ^4J =3.0 Hz, $^4J = 11.3$ Hz), 6.41−6.33 (m, 4H), 6.15 (d, 2H, $^3J = 3.7$ Hz), 2.52 (2s, 12H).

1,4-Bis[5-(1,4-dithia-2,3-dipropylfulven-6-yl)-2-furyl]-buta-1,3-diene (Fd$_2$c). Viscous red oil, yield 51%. MS calcd for $C_{32}H_{38}S_4O_2$: 582. found: 582 (FAB). Anal. (calcd) C 63.70 (65.98), H 6.80 (6.53). ^{1}H NMR ($CDCl_3$, ppm) 6.85−6.80 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 11.5$ Hz), 6.42−6.37 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 11.5$ Hz), 6.34 (s, 2H), 6.32 (d, 2H), $^3J = 3.5$ Hz), 6.11 (d, 2H, $^3J = 3.5$ Hz), 2.45−2.32 (m, 8H), 1.68−1.50 (m, 8H), 1.02−0.90 (m, 12H).

1,6-Bis[5-(1,4-dithia-2,3-dithiomethylfulven-6-yl)-2-furyl]hexa-1,3,5-triene (Fd$_3$b). Yield 60%, mp 104 °C. MS calcd for $C_{26}H_{24}S_8O_2$: 624. Found: 624 (FAB). Anal. (calcd) C 51.10 (49.96), H 4.00 (3.87). ^{1}H NMR ($CDCl_3$, ppm) 6.86−6.77 (m, 2H, $^3J = 15.0$ Hz, $^3J = 7.5$ Hz, $^4J = 3.0$ Hz), 6.51−6.47 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 7.5$ Hz), 6.40−6.31 (m, 6H), 6.15 (d, 2H), $^3J = 3.5$ Hz), 2.46 (2s, 12H).

1,6-Bis[5-(1,4-dithia-2,3-dipropylfulven-6-yl)-2-furyl]-hexa-1,3,5-triene (Fd$_3$c). Column chromatography on silica gel (CH_2Cl_2), yield 54%, mp 152 °C. MS calcd for $C_{34}H_{40}S_4O_2$ 608. Found: 608 (FAB). Anal. (calcd) C 66.66 (67.06), H 6.59 (6.62). ^{1}H NMR ($CDCl_3$, ppm) 6.84−6.75 (m, 2H, $^4J = 3.0$ Hz, $^3J = 7.5$ Hz, $^3J = 15.0$ Hz), 6.48−6.44 (dd, 2H, $^4J = 3.0$ Hz, $^3J = 7.5$ Hz), 6.37−6.31 (m, 6H), 6.11 (d, 2H, $^3J = 3.5$ Hz), 2.45−2.35 (m, 8H), 1.65−1.51 (m, 8H), 1.04−0.96 (m, 12H).

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

X-ray Diffraction Studies. Red single crystals of **17** were obtained from $CHCl_3$ solution.

Crystal (0.5mm × 0.5 mm × 0.04 mm) was mounted on an Enraf-Nonius MACH3 diffractometer with graphite monochromator and Mo Kα radiation at $T = 294$ K. Unit-cell parameters were refined from a least-squares analysis of 25 reflections.

Crystal data: $C_{16}H_{12}S_2O_2$, MW = 300.4, monoclinic, $P2_1/c$, $a = 9.720$ (3) Å, $b = 6.291$ (2) Å, $c = 12.615$ (8) Å, $\beta = 108.27$ (3)°, $V = 732.6$ (6) Å^3, $D_c = 1.358$ g cm^{-3}, $Z = 2$, $F(000) = 312$, $\mu = 3.442$ cm^{-1}, $\lambda = 0.710\ 69$ Å.

Data collection: the data collection by zig-zag $\omega/2\theta$ scan technique, $2.24 \leq \theta \leq 30$, $t_{\max} = 40$ s, range *hkl* (*h* 0.13; *k* 0.8; *l* −17.17), intensity controls without appreciable decay (0.2%) gives 2414 reflections from which 1037 were independent with $I > 3\sigma(I)$.

Structure refinement: After Lorenz and polarization corrections, the structure was solved with direct methods (SIR) which reveal all the non-hydrogen atoms. After anisotropic refinement, the hydrogen atoms are found with a Fourier difference (between 0.39 and 0.19 e Å^{-3}). The whole structure was refined by the full-matrix least-squares techniques (use of F magnitude; x, y, z, U_{ij} for S, C, and O atoms and x, y, z for H atoms; 115 variables and 1037 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting $R = 0.057$, $R\omega = 0.065$.

CM960035R