Synthesis of Conjugated *F*-Polyenes Containing Thienyl Ring Systems

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Received December 11, 1996[⊗]

Novel 1-substituted *F*-1,3-butadienes ThioAr−CF=CFCF=CF_2, ThioAr = 2-thienyl and 2-benzo[*b*]thienyl, and symmetrically 1,4-disubstituted *F*-1,3-butadienes ThioAr-CF=CFCF=CF−ThioAr, ThioAr = 5-R′-2-thienyl (R′ = Me, $SiMe_3$, CF=CFCl), 3-thienyl, and 4-dibenzo[*b,d*]thienyl, inclusive of the above-named substituents, were prepared by the reaction of organolithium derivatives with *F*-1,3-butadiene (PFBD). Monothioaryl-substituted *F*-1,3-butadienes were used as intermediates in subsequent reactions with other (thioaryl)organolithium derivatives for the synthesis of a new series of unsymmetrically substituted α,ω-bis(thioaryl)-*F*-polyenes ThioAr−$(CF=CF)_n$−ThioAr′, where $n = 2$, ThioAr, ThioAr′ = 4-RC_6H_4 (R = H, Me, OC_6H_{11}, NMe_2), 2-thienyl, 5-methyl-2-thienyl, 2-benzo[*b*]thienyl, 4-dibenzo[*b,d*]thienyl, and for $n = 3$, ThioAr = 2-thienyl, ThioAr′ = 5-methyl-2-thienyl. The reaction of 2,5-dilithiothiophene with 1-(2-thienyl)-*F*-1,3-butadiene affords 2,5-bis[4-(2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadienyl]thiophene (**5**). 2,5-Thienylene-*F*-polyenylene polymers were prepared by the reaction of 2,5-dilithio- and 2,5-bis(bromomagnesio)thiophene derivatives with PFBD and *F*-ethylene. The oligomers **5** and 2,5-bis[2-(2-thienyl)-1,2-difluoroethylenyl]thiophene (**16**) were found to possess liquid crystalline properties. The reaction of 1,4-bis(2-thienyl)-*F*-1,3-butadiene with nitric acid led to substitution in one or in both thienyl rings at position 5. NMR, electronic spectra, and structural aspects of the title compounds are discussed.

Introduction

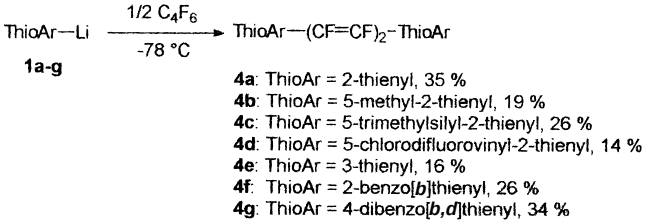
Conjugated polythiophenes[1] and systems with aromatic or heteroaromatic and conjugated aliphatic units[2] are attractive materials, possessing interesting electrical and NLO properties useful from a practical point of view. Following our research interest in conjugated fluoropolyenes,[3] we have attempted to develop new fluoropolyene systems containing thienyl rings. We were encouraged by the fact that many symmetrical and unsymmetrical α,ω-diaryl-*F*-polyenes were found as thermally stable compounds with a relatively wide range of mesophase transition temperatures[3,4] and materials displaying transmission of electronic effects comparable to hydrocarbon polyethylene and polyacetylene systems.[5]

Our synthetic approach to novel thienyl-, 2-benzo[*b*]thienyl-, and 4-dibenzo[*b,d*]thienyl-substituted *F*-polyenes consists of reactions of the corresponding thienyllithiums **1a**−**g** with easily available *F*-1,3-butadiene (**2**, PFBD).[6]

Results and Discussion

Symmetrical 1,4-Bis(thienyl)-*F*-1,3-butadienes. 2-Lithiothiophenes **1a**−**c**, 2-lithiobenzo[*b*]thiophene[7] (**1f**), and 4-lithiodibenzo[*b,d*]thiophene[8] (**1g**) were prepared by the metalation reaction of thiophene (**3a**) and its 2-methyl- (**3b**) and 2-(trimethylsilyl)- (**3c**) derivatives, benzo[*b*]thiophene (**3f**), and dibenzo[*b,d*]thiophene (**3g**) with butyllithium according to the known procedures. 3-Thienyllithium (**1e**) was prepared by Br/Li exchange reaction of 3-bromothiophene (**3e**) with BuLi at −78 °C.[9] Further reactions of lithio derivatives **1a**−**g** with 0.5 equiv of **2** in THF at −78 °C produced symmetrically substituted 1,4-bis(thioaryl)-*F*-1,3-butadiene derivatives **4a**−**g** containing various thienyl ring systems (Scheme 1).

Scheme 1



The resulting *F*-1,3-butadiene derivatives **4a**−**g** were separated as yellowish crystalline substances in moderate (14−55%) yields, and their *E,E* configuration was proved by ^{19}F NMR. The *E,Z* isomers were detected in the crude reaction mixture and the mother liquor in a rather smaller portion.

Additionally, an interesting derivative **5** containing three thienyl rings connected with two *F*-1,3-butadienylene units was obtained as a minor product of the reaction, 2,5-dilithiothiophene arising from the partial dilithiation of thiophene occurring if polar conditions (Et_2O) are used.[10]

1-(2-Thienyl)- and 1-(2-Benzo[*b*]thienyl)-*F*-1,3-butadienes. The addition of thienyllithiums **1a** and **1f**

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) (a) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. (b) Garnier, F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 513. (c) Effenberger, F.; Wurthner, F.; Steybe, F. J. *Org. Chem.* **1995**, *60*, 2082. (d) Xu, B.; Fichou, D.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1991**, *3*, 150. (e) Garnier, F.; Horowitz, G.; Peng, X.; Fihou, D. *Adv. Mater.* **1990**, *1*, 592.

(2) (a) *Handbook, of conducting polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; p 384. (b) Rao, V.; Jen, A. K. Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118.

(3) Shtarev, A. B.; Kremlev, M. M.; Chvatal, Z. *J. Org. Chem.* **1997**, *62*, 3040.

(4) Yurchenko, V. M.; Yegorov, Yu. P.; Khranovskii, V. A. *Ukr. Phys. Zh.* **1978**, *23*, 337.

(5) Kremlev, M. M.; Moklyachuk, L. I.; Fialkov, Yu. A.; Ignatiev, V. V.; Yagupolskii L. M. *Zh. Org. Khim.* **1985**, *21*, 769−774 and references therein.

(6) Dědek, V.; Chvátal, Z. *J. Fluorine Chem.* **1986**, *31*, 363. **Caution!** Perfluoro-1,3-butadiene is flammable gas (bp 6−7 °C), and it is believed to be toxic.

(7) (a) Iddon, B.; Scrowston, R. M. *Adv. Heterocycl. Chem.* **1970**, *11*, 178. (b) Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664.

(8) Gilman, H.; Gray, S. *J. Org. Chem.* **1958**, *23*, 1476.

(9) Moses, P.; Gronowitz, S. *Ark. Kemi* **1962**, *18*, 119.

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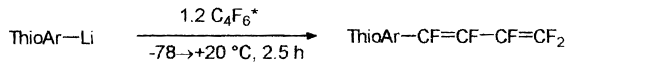
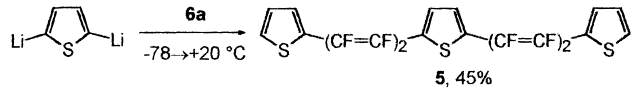
Scheme 2



1a: ThioAr = 2-thienyl
1f: ThioAr = 2-benzo[b]thienyl
6a: ThioAr = 2-thienyl, 35%, *E*/*Z* = 96/4
6b: ThioAr = 2-benzo[b]thienyl, 35%, *(E)*

*solution of C_4F_6 was treated with organometallic

Scheme 3



5, 45%

Scheme 4

6a: ThioAr = 2-thienyl
6a: ThioAr = 2-thienyl
6a: ThioAr = 2-thienyl
10b: ThioAr = *p*-tolyl
10e: ThioAr = *p*-$C_6H_4NMe_2$
10a: ThioAr = Ph
10d: ThioAr = *p*-$C_6H_4OC_6H_{11}$

ThioAr´ = Bu
ThioAr´ = *p*-tolyl
1b: ThioAr´ = 5-methyl-2-thienyl
1f: ThioAr´ = 2-benzo[*b*]thienyl
1f: ThioAr´ = 2-benzo[*b*]thienyl
1g: ThioAr´ = 4-dibenzo[*b,d*]thienyl
1g: ThioAr´ = 4-dibenzo[*b,d*]thienyl

ThioAr—$(CF=CF)_2$—ThioAr´

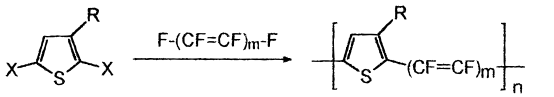
7: 37 %
8: 23 %
9: 28 %
11a: 47 %
11b: 25 %
12a: 51 %
12b: 30 %

to 1.2 equiv of a solution of PFBD (Scheme 2) made it possible to prepare mono-2-thienyl- and 2-benzo[*b*]thienyl-substituted *F*-1,3-butadienes **6a**,**b**. The 35% yields of **6a**,**b** derivatives are much higher than those obtained in the similar reaction of PFBD with (4-bromophenyl)-lithium,[3] when mostly the 1,4-disubstituted derivative was formed. It could indicate a difference in chemical behavior of aryl- and thienyllithium reagents. Compounds **6a**,**b** were found as pure *E* isomer (**6b**) or with a low content (3−8%) of *Z* isomer (**6a**). Compounds **6a**,**b** are relatively stable; only after a longer storage at ambient temperature do they partly undergo isomerization, dimerization, and polymerization reactions.[11] The availability of compound **6a** made it possible to prepare compound **5** independently (Scheme 3).

Unsymmetrically 1,4-Substituted *F*-1,3-Butadienes. The synthetic availability and a high sensitivity of the terminal *F*-vinyl group in 1-(2-thienyl)- and 1-aryl-*F*-1,3-butadienes toward C-nucleophiles were explored for the novel preparation of various unsymmetrical derivatives containing alkyl, aryl, and thienyl substituents in the terminal positions of the *F*-1,3-butadienylene moiety (Scheme 4).

Thus, the reaction of **6a** with BuLi, *p*-tolyllithium, and (5-methyl-2-thienyl)lithium (**1b**) gave the product **7**, **8**, and **9**. Analogously, 1-aryl-*F*-butadienes **10a**,**b**,**d**,**e**, which we prepared recently,[3] afforded 1-(2-benzo[*b*]thienyl)-4-aryl-*F*-1,3-butadienes **11a**,**b** and 1-(4-dibenzo[*b,d*]thienyl)-4-aryl-*F*-1,3-butadienes **12a**,**b** in the reaction with thienyllithiums **1f** and **1g**. In the crude reaction product, various possible isomers were determined by ^{19}F NMR in the ratios reported in Table 3 (Supporting Information). The *E*,*E* isomers, being the main reaction products, were obtained in pure form by crystallisation.

Scheme 5



14, m = 2, R = Me, 88%, (56/44),* X = Li
15a, m = 2, R = H, 75%, (33/67),* X = Li
15b, m = 2, R = H, 13%, X = MgBr
16, m = 1, R = H, 73%, (7/93),* X = Li

* Ratio of soluble/insoluble in ether polymers

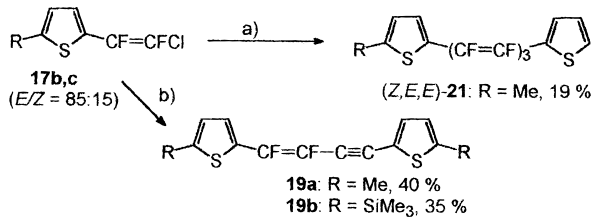
2,5-Thienylene-*F*-polyenylene polymers. Different polymers of this type were prepared by the reaction of 2,5-dilithio- and 2,5-bis(bromomagnesio)thiophenes with PFBD and *F*-ethylene (**13**) (Scheme 5).

2,5-Dilithiothiophenes gave higher yields of polymers if compared with 2,5-bis(bromomagnesio)thiophenes. The solubility of oligomers in ether, important for processability, decreases in the following order: 3-methyl-2,5-thienylene-*F*-1,3-butadienylene (**14**) > 2,5-thienylene-*F*-1,3-butadienylene (**15a**) > 2,5-thienylene-*F*-ethylene (**16**). All *F*-1,3-butadienylene oligomers, soluble in ether, were found by ^{19}F NMR mostly as *E*,*E* isomers, when (*E*,*E*): (*E*,*Z*) ≥ 3. The λ_{max} are shifted to lower frequencies in the following order: 2,5-thienylene-*F*-ethenylene (**16**, 463 and 436 nm, $\epsilon = 1.6 \times 10^4$ and 2.0×10^4) > 2,5-thienylene-*F*-1,3-butadienylene (**5**, 398 nm, **15a**, 389 nm) > 3-methyl-2,5-thienylene-*F*-1,3-butadienylene (**14**, 372 nm) oligomers.

2-(2-Chloro-1,2-difluorovinyl)thiophenes and 1,4-Bis(2-thienyl)-*F*-1,3-hexatrienes. The successful lithiation of β-chloro-α,β-difluorovinylstyrenes by chlorine/lithium exchange and their addition−elimination reaction with *F*-ethylene and *F*-1,3-butadiene made it possible to lengthen the *F*-polyene chain and prepare diaryl-*F*-1,3,5-hexatrienes[3] and diaryl-*F*-1,3,5,7-octatetraenes.[12] We wondered if this synthetic approach would be applicable for the preparation of dithienyl-*F*-polyene homologs, if the reaction of [2-(2-thienyl)-1,2-difluorovinyl]lithiums with *F*-butadiene derivatives would be applied. The starting 2-(2-chloro-1,2-difluorovinyl)thiophenes **17a**,[13] **17b**, and **17c**[14] were prepared as a mixture of *E* and *Z* isomers, where *E* isomer predominated (79−85%), by the reaction of corresponding (2-thienyl)lithiums, **1a**−**c** with chlorotrifluoroethylene (**18**). It is in contrast to (2-chloro-1,2-difluorovinyl)benzenes, prepared by the reaction of Grignard reagents, where *Z* isomer predominated (76−80%).[15] The reaction of [5-(trimethylsilyl)-2-thienyl]-magnesium bromide with **18** and further hydrolysis gave mostly 2-(trimethylsilyl)thiophene (**3c**) and only 13% of **17c** (78% of *Z* isomer).[16] The lithiation of 2-(2-chloro-1,2-difluorovinyl)thiophene (**17a**) at −70 to −65 °C and further reaction with PFBD gave 1,4-dithienyl-*F*-1,3-butadiene **4d**, though in low yield (Scheme 1). This is a result of the preferable metalation of the thiophene ring

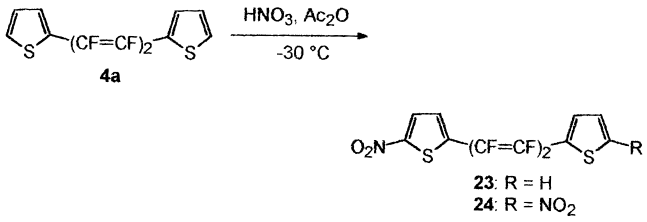
(10) Chadwick, D. J.; Willbe, C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 887.
(11) Shtarev, A. B.; Chvátal, Z. Manuscript in preparation.
(12) Yagupolskii, L. M.; Kremlev, M. M.; Fialkov, Yu. A.; Khranovskii, V. A.; Yurchenko, V. M. *Zh. Org. Khim.* **1977**, *13*, 1561.
(13) Dixon, S. *J. Org. Chem.* **1956**, *21*, 400.
(14) Starostina, T. A.; Rybakova, L. F.; Shifrina, R. R. *Zh. Org. Khim.* **1980**, *16*, 1968−1973.
(15) Yagupolskii, L. M.; Kremlev, M. M.; Khranovskii, V. A.; Fialkov, Yu. A. *Zh. Org. Khim.* **1976**, *12*, 1372.
(16) A solution of 2-bromo-5-(trimethylsilyl)thiophene in THF was refluxed over Mg for 3 h. The Grignard reagent was cooled to −70 °C and evacuated, and gaseous **18** was condensed into the reagent. After being stirred for 1 h at −20 °C, the mixture was stirred at room temperature overnight and worked up by the usual procedure. The fractional distillation in vacuum gave **3c** (yield 60%) and the fraction containing 65% of 2-bromo-5-(trimethylsilyl)thiophene and 30% of **17c** (yield 13%, *E*:*Z* = 22:78).

Scheme 6[a]



[a] Key: (a) (i) BuLi, THF/Et_2O/hexane, −100 to 95 °C, (ii) **6**a, −95 → −65 °C; (b) BuLi, −78 °C.

Scheme 7



in position 5, rather than the Cl/Li exchange in the 2-chloro-1,2-difluorovinyl group.[14] The configuration of the prevailing *E*,*E*,*E*,*E* **4d** isomer (85%) was determined by ^{19}F NMR, although there is no distinction in the ^{19}F NMR signals between the other present *Z*,*E*,*E*,*Z* and *E*,*E*,*E*,*Z* isomers. The yields of **4d**,**e** obviously dropped because of undesirable polymer formation.

The reaction of 2-(2-chloro-1,2-difluorovinyl)thiophenes **17b** and **17c**, containing CH_3 and $Si(CH_3)_3$ substituents in position 5 of the thiophene ring, with BuLi at −78 °C gave 1,4-(2,5-dithienyl)-1,2-difluorobut-1-en-3-ynes **19a**,**b** as mixture of *E* and *Z* isomers (Scheme 6).

This is explainable by the decomposition of (thienyldifluorovinyl)lithiums **20a,b** through LiF elimination giving 1-fluoro-2-thienylacetylene intermediates that react further with **20a**,**b** to give **19a**,**b**. This was also observed earlier for aryl-substituted analogues.[17] However, if a lower temperature (−100 °C) is used for lithiation of **17c**, [2-(5-methyl-2-thienyl)-1,2-difluorovinyl]lithium reacts next with 1-(2-thienyl)-*F*-1,3-butadiene (**6a**) to give (*Z*,*E*,*E*)-*F*-1,3,5-hexatriene derivative **21**. For the preparation of (*E*,*Z*,*E*)-1,6-bis(2-thienyl)-*F*-1,3,5-hexatriene (**22**), the reaction of (*Z*)-*F*-1,3,5-hexatriene[6,18] with (2-thienyl)lithium (**1a**) was used.

Direct Functionalization of (*E*,*E*)-1,4-Bis(2-thienyl)-*F*-1,3-butadiene (4a). In the contents of reactivity studies, the butadiene **4a** was treated with nitric acid at −30 °C to afford 5-nitro-2-thienyl **23** and bis(5-nitro-2-thienyl) **24** derivatives (Scheme 7).

These derivatives were present in the crude product as a mixture, where *E*,*E* isomers predominated. However, some isomerization processes occurred during the reaction and the column chromatography separation of the products.

Physical Properties. The majority of disubstituted *F*-butadienes containing thienyl ring systems are yellow crystals that do not possess liquid−crystalline properties opposite to diaryl analogues.[3] Only compounds **5** and **16** containing a longer chain exhibit mesogen properties with a reversible nematic phase, and they are the first examples of thermally stable, rodlike liquid−crystalline materials built from thienyl-*F*-butadienyl units. Most of the 5-methyl-2-thienyl-substituted derivatives, such as **9**, **21**, **17b**, and **19a**, are unstable substances that easily turn to a dark resinous material at ambient conditions.

Table 1. UV Absorption Maxima of 5-R-2-thienyl and 4-R-phenyl 1,4-Disubstituted (*E*,*E*)-*F*-1,3-Butadienes

R−Ar−CF=CF−CF=CF−Ar′−R′

		λ_{max} (nm), ($\epsilon \times 10^4$)		
R	R′	Ar = Ar′ = (C_4H_2S)	Ar = C_6H_4, Ar′ = (C_4H_2S)	Ar = Ar′ = C_6H_4
Me	H	**9**, 343 (3.45)	**8**, 324 (1.3)	296 (3.4)[3]
Me	Me	**4b**, 348 (3.9)		304 (2.19)[3]
NO_2	H	**23**, 376 (1.18)		330 (2.4)[19]

Table 2. UV Absorption Maxima of (*E*,*E*)-1,4-Bis(thioaryl)-*F*-1,3-butadienes

ThioAr−CF=CF−CF=CF−ThioAr

	ThioAr	λ_{max} (nm)	($\epsilon \times 10^{-4}$)
	Ph[19]	300	3.2
4a	2-thienyl	337	2.5
4e	3-thienyl	308	3.2
4f	2-benzo[*b*]thienyl	372	5.0
		358	5.3
4g	4-dibenzo[*b*,*d*]thienyl	350	1.2
		294	1.9

In the series of the symmetrical bis(2-thienyl) **4a** and **4b**, as well as the unsymmetrical 2-thienyl/tolyl **8**, or dithienyl **9** and **23** derivatives, the 2-thienyl group causes the 28−46.5 nm bathochromic shift of λ_{max} compared to the similarly substituted 1,4-diphenyl-*F*-1,3-butadienes (Tables 1 and 2).[3,19] This shift is greater than that caused by 3-thienyl group in **4e**.

This effect confirms that for *F*-1,3-butadiene, as well as for many other chromophores,[20] a replacement of phenyl for 2-thienyl group causes bathochromic shift, as a result of the superior electron-releasing power of the 2-thienyl group. An even more pronounces bathochromic shift was observed for 1,4-disubstituted *F*-1,3-butadienes with two, (*E*,*E*)-**4f** (Table 2), or one, **11a** (λ_{max} = 336.6 nm, $\epsilon = 4.41 \times 10^4$), benzo[2]thienyl groups.

When the ^{19}F NMR data for symmetrically substituted *F*-1,3-butadienes **4a**−**c** and **24** were analyzed, the substituents in the 5-position of the thienyl ring were found to affect the chemical shifts of all fluorines of the *F*-1,3-butadiene chain. We assume that δ could correlate with σ_p^+,[20] similarly as for *p*-substituted 1-phenyl-*F*-1,3-butadienes where the correlation with σ_p constants was found.[3] The characteristic δ values found for symmetrically substituted *F*-1,3-butadienes **4a**,**b**, **24**, and **4f**,**g** were then used for the signal assignment in the obtained unsymmetrically disubstituted *F*-1,3-butadienes. The relatively large long-range coupling constants ($^5J_{F(1)F(4)}$ = 29.7−32.6 Hz) of all (*E*,*E*)-bis(thioaryl)-*F*-1,3-butadienes indicate the unplanar s-cisoid conformation of *F*-1,3-butadiene chain similar to diaryl-substituted analogues.[21] The values of $^3J_{FF}$ *trans* coupling constants in *E*,*E* isomers are in the range from −124 to −128 Hz for a difluorovinylene group close to

(17) Yarmolenko, S. N.; Fialkov, Yu. A.; Kremlev, M. M.; Yagupolskii, L. M. *Zh. Org. Khim*. **1988**, *24*, 2584−2590.
(18) Hrabal, R.; Chvátal, Z.; Dědek, V. *J. Fluorine Chem*. **1993**, *63*, 185.
(19) Fialkov, Yu. A.; Sevastiyan, A. P.; Khranovski, V. A.; Yagupolskii, L. M. *Zh. Org. Khim*. **1978**, *4*, 1005.
(20) Gronowitz, S. *Thiophene and its derivatives*; John Wiley & Sons: New York, 1991; Part 4, p 157.
(21) Yurchenko, V. M.; Kremlev, M. M.; Fialkov, Yu. A.; Sass, V. P.; Khranovskii, V. A.; Egorov, Yu. P.; Yagupolskii L. M. *Teor. Eksp. Khim*. **1982**, *18*, 745.

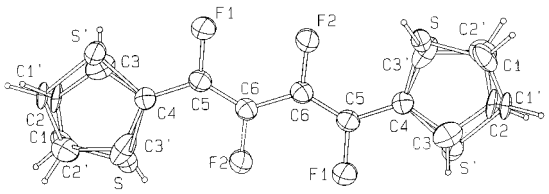


Figure 1. ORTP drawing of (*E*,*E*)-1,4-bis(2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (**4a**).

2-thienyl and from −132.5 to −133.6 Hz for that near the dibenzo[*b*,*d*]thienyl group. The $^4J_{F(1)F(3)}$ coupling constants increase from nearly 12 Hz in diaryl *F*-butadienes up to 16.3 Hz in bis(2-thienyl) **4a** and 23.1 Hz in bis(5-nitro-2-thienyl) **24** derivatives.

Interestingly, the X-ray results[22] of **4a** (Figure 1) show a planar s-transoid conformation of the *F*-1,3-butadienylene chain and a statistical disorder with equal contribution of *syn* and *anti* conformers of terminal thienyl rings. The observed s-transoid conformation of **4a** in crystal state, which brings a better degree of π-conjugation, contrasts with the unplanar s-cisoid conformation of the (*E*,*E*)-1,4-bis(4-tolyl)-*F*-1,3-butadiene.[3] The found s-transoid conformation of **4a** is similar to that in (*E*,*E*)-1,4-bis(2-thienyl)-1,3-butadiene.[23]

The s-transoid conformation of **4a** probably causes the larger difference (60 °C) in melting points between **4a** and s-cisoid (*E*,*E*)-1,4-diphenyl-*F*-1,3-butadiene[24] than was found between both of their s-transoid unfluorinated analogues (23 °C).[25] The MS (EI) fragmentation of **5** was dominated by a peak at *m*/*e* 133, corresponding to the ion $[C_4H_3SCF_2]^+$, presumably formed by cleavage β to the thiophene ring and by rearrangement including fluorine shift to α carbon. Interestingly, the peak at *m*/*e* 133 also dominated in patterns of linear α,ω-bis(2-thienyl)perfluoroalkanes.[20] This and relative $[ThioarylCF_2]^+$ peaks are very characteristic, and they were found in the spectra of the examined thienyl and aryl[3] derivatives, with an intensity of 43% for *m*/*z* 147, $[CH_3C_4H_2SCF_2]^+$ in **21**, and average values of 5−28% for the others.

Conclusion

A variety of novel, chemically stable conjugated *F*-polyene model systems containing thienyl rings were prepared. They have promising chemical, spectral, and structural dispositions to find application in material research chemistry and advanced technologies.

Experimental Section[26]

Yields are given for isolated *E*,*E* isomers and summarized in the reaction schemes. The UV absorption maxima (dioxane) of **4b**, **8**, **9**, and **23** are collected in Table 1 and for **4a**,**e**−**g** in Table 2. ^{19}F NMR data of **4a**−**c**,**e**−**g**, **11a**,**b**, **12a**,**b**, **8**, **9**, **23**, and **24** are collected in Table 3 (Supporting Information). ^{19}F NMR data and ratios of isomers of **17a**−**c** and **19a**,**b** are summarized in Table 4 (Supporting Information).

General Procedure for the Preparation of Symmetric 1,4-Diheteroaryl-1,2,3,4-tetrafluoro-1,3-butadienes 4a−**g.** The solution of organometallic compound[27] was cooled to −78 °C, and **2** (0.55 equivalent as a solution in THF) was added via a dropping funnel equipped with a jacket cooled with a CO_2−ethanol mixture. For the preparation of **4a**,**c**,**d**,**f** compound **2** was bubbled into the organometallic mixture from the bulb at −70 °C during 30 min. The mixture was stirred at −78 °C for 2.5 h. After being warmed to 0 °C, the mixture was worked up with NH_4Cl aqueous solution and extracted with ether. The organic phase was separated, washed with water and brine, and dried over $MgSO_4$. The solvent was rotary evaporated. The products were isolated by crystallization from a suitable solvent.

***(E,E)*-1,4-Bis(2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4a). 1a**[10] was prepared from thiophene (4.2 g, 0.05 mol) and BuLi in a THF−ether mixture. Crystallization from benzene gave crude **5** (0.15 g, yield 2%). Compound **4a** was obtained from the mother liquor by crystallization from methanol (2.55 g) and purified by column chromatography on SiO_2, eluted with a hexane−benzene (10:1) mixture: $R_f = 0.7$; yellow crystals; mp 118 °C (recryst hexane); IR (cm^{-1}) 1660, 1626 (CF═CF); 1359, 1267, 1217, 1178, 1128; ^{1}H NMR δ 7.14 (dd, 2H), 7.48−7.53 (m, 6H); ^{13}C {^{1}H} NMR δ 127.49 (m), 127.57, 128.94 (tm, $J = 4$ Hz), 130.30 (dm, $J \approx 24$ Hz), 137.10 (dm, $J \approx 240$ Hz), 147.13 (dm, $J \approx 240$ Hz). Anal. Calcd for $C_{12}H_6F_4S_2$: C, 49.65; H, 2.08. Found: C, 49.56; H, 1.98.

***(E,E)*-1,4-Bis(5-methyl-2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4b).** 2-Methylthiophene (**3b**) solution (1.38 g, 0.014 mol) in 15 mL of THF was treated with BuLi (13 mL, 0.7 M) in hexane at 30−35 °C for 1.5 h. A solution of **2** (1.46 g, 9 mmol) in 15 mL of THF was added at −70 °C and the resulting mixture stirred for 1.5 h. Crystallization from methanol gave 0.42 g of **4b**: mp 90 °C; yellow crystals (recryst hexane); IR (cm^{-1}) 1663 (CF═CF); 1270, 1222, 1166, 1117; MS *m*/*z* 319 (18), 318 (100) M^+, 303 (18), 296 (26), 283 (8), 265 (7), 259 (7), 220 (9), 202 (9), 171 (6), 159 (9), 147 (28), 127(7), 97 (23), 69 (14), 59 (66); ^{1}H NMR δ 2.53 (3H), 6.79 (m, 2H), 7.26 (d, 2H, $J = 3.7$ Hz). Anal. Calcd for $C_{14}H_{10}F_4S_2$: C, 52.82; H, 3.17. Found: C, 52.48; H, 3.21.

***(E,E)*-1,4-Bis[5-(trimethylsilyl)-2-thienyl]-1,2,3,4-tetrafluoro-1,3-butadiene (4c). 1c** was obtained from 5-(trimethylsilyl)thiophene (3c) and BuLi in ether:[28] mp 72 °C; yellow crystals (methanol); λ_{max}, (nm) 349 ($\epsilon = 2.6 \times 10^4$); IR ($cm^{-1}$) 1623 (CF═CF), 1325, 1206, 1178, 1167, 1128; ^{1}H NMR δ 0.36 (9H), 7.24 (m, 1H), 7.53 (d, 1H); ^{13}C {^{1}H} NMR δ 0.54, 128.92 (d, $J = 3.4$ Hz), 134.67, 135.48 (dm, $J \approx 22$ Hz), 137.61 (dm, $J \approx 240$ Hz), 145.46 (t, $J = 4$ Hz), 147.57 (dm, $J \approx 240$ Hz). Anal. Calcd for $C_{18}H_{22}F_4S_2Si_2$: C, 49.74; H, 5.10; S, 14.75. Found: C, 49.59; H, 4.91; S, 14.72.

***(E,E,E,E)*, *(Z,E,E,E)*, *(Z,E,E,Z)*-1,4-Bis[5-(2-chloro-1,2-difluorovinyl)-2-thienyl]-1,2,3,4-tetrafluoro-1,3-butadiene (4d). 17a** was treated with BuLi at −70 to −60 °C for 1.5 h. **4d** was crystallized from methanol and purified by column chromatography on silica gel. **4d** (85% of *E*,*E*,*E*,*E* isomer): mp 110 °C; yellow crystals (methanol); λ_{max}, (nm) 396 ($\epsilon = 5.3 \times 10^4$); IR ($cm^{-1}$) 1670, 1616 (CF═CF), 1352, 1310, 1258, 1218, 1182; ^{19}F NMR δ AA′XX′ system, −157.3 (m, 2F), −140.5 (m, 2F), −145.6 (d, 2F, ((*Z*)-**4d**), $J = 128$ Hz), −114.0 (d, 2F, ((*Z*)-**4d**), $J = 128$ Hz), −131.4 (d, 2F, ((*E*)-**4d**), $J = 11$ Hz), −101.6 (d, 2F, ((*E*)-**4d**), $J = 11$ Hz); ^{1}H NMR δ 7.39 (dm, 2H), 7.52 (dm, 2H). Anal. Calcd for $C_{16}H_4C_{12}F_8S_2$: C, 39.77; H, 0.83; S, 13.27. Found: C, 39.39; H, 0.92; S, 13.01.

***(E,E)*-1,4-Bis(3-thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4e). 3e** was treated with BuLi at −70 °C for 1 h[9] and further reacted with **2**: mp 66 °C; yellow crystals (methanol); purity 95% by ^{1}H NMR; IR (cm^{-1}) 1673, 1639, 1619 (CF═CF), 1322, 1286, 1262, 1207, 1170, 1129; MS *m*/*z* 291 (16), 290 (100) M^+, 270 (48), 257 (7), 245 (7), 225 (23), 207 (18), 157 (8), 145 (12), 133 (28), 113 (5), 81 (6), 69 (14); ^{1}H NMR δ ABX-system, 7.42 (m, 2H), 7.46 (dm, 2H), 7.74 (d, 2H, $J = 3$ Hz).

***(E,E)*-1,4-Bis(2-benzo[*b*]thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4f).** BuLi (20 mL of 1 M solution in ether) was added to benzo[*b*]thiophene (2.68 g, 0.02 mmol) in 28 mL of

(22) The X-ray crystallographic data of **4a** will be published separately.

(23) Buschmann, J. F.; Ruban, G. *Acta Crystallogr. Sect. B* **1978**, *34*, 1923.

(24) Yagupolskii, L. M.; Sevastiyan, A. P. *Zh. Obsch. Khim.* **1968**, *38*, 1500.

(25) Koszmehl, G.; Bohn, B. *Angew. Chem.* **1973**, *85*, 230.

(26) See ref 3 for general instrument specifications.

(27) For practical considerations and safety precautions concerning organolithium reagents see: Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988; pp 8−16.

(28) Benkeser, R. A.; Currie, R. B. *J. Am. Chem. Soc.* **1948**, *70*, 1780.

ether and stirred at room temperature overnight to give (2-benzo[*b*]thienyl)lithium (**1f**)[7] (48 mL), which was used for further reactions. **2** (0.5 g, 3 mmol) was condensed to a solution of **1f** (9.6 mL) at −70 to −60 °C and stirred at this temperature for 2.5 h. (*E*,*E*)-**4f** (0.3 g, mp 243−245 °C, chloroform): IR (cm^{-1}) 1621 (CF═CF), 1333, 1297, 1176, 1159; ^1H NMR δ 7.43 (m, 2H), 7.76 (1H), 7.88 (m, 2H). Anal. Calcd for $C_{20}H_{10}F_4S_2$: C, 61.53; H, 2.58. Found: C, 61.19; 2.88.

(*E*,*Z*)-1,4-Bis(2-benzo[*b*]thienyl-1,2,3,4-tetrafluoro-1,3-butadiene (4f). Part of mother liquor was soluble in heptane−benzene (8:1) mixture ((*E*,*E*)-**4f** was found to be insoluble) and worked up by column chromatography on silica gel to obtain (*E*,*Z*)-**4f**: 68 mg; R_f 0.43; yield 6%; yellow solid; mp 96−98 °C; λ_{max} (nm) 334 ($\epsilon = 2.27 \times 10^4$), 288.5 ($2.16 \times 10^4$), 260 ($1.47 \times 10^4$); IR ($cm^{-1}$) 1655 (CF═CF); 1333, 1300, 1262, 1241, 1183, 1158, 1126; ^1H NMR δ 7.36 (m, 2H), 7.44 (m, 2H), 7.65 (1H), 7.72 (m, 1H), 7.75 (1H), 7.78 (m, 1H), 7.88 (m, 2H). Anal. Calcd for $C_{20}H_{10}F_4S_2$: C, 61.53; H, 2.58. Found: C, 61.20; H, 2.86.

(*E*,*E*)-1,4-Bis(4-dibenzo[*b*,*d*]thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4g). 4-Lithiodibenzo[*b*,*d*]thiophene (**1g**, 73 mL) was prepared following the known procedure[8] from BuLi (17.4 mL of 1.15 M solution in ether) and **3g** (3.68 g, 0.02 mol) and used for further reactions. **4g** was prepared from **2** (1.3 g, 8 mmol) and **1g** (38 mL): mp 199−200 °C; MS *m*/*z* 492 (4), 490 (14) M^+, 470 (28), 450 (5), 306 (3), 235 (5), 184 (12), 85 (65), 83 (100); λ_{max} (nm) 349.8 ($\epsilon = 1.2 \times 10^4$), 294 ($1.89 \times 10^4$), 266 ($2.61 \times 10^4$); IR ($cm^{-1}$) 1656 (CF═CF), 1327, 1304, 1274, 1199, 1156, 1145; ^1H NMR δ 7.52 (m, 2H), 7.59 (dd, 1H, J = 8, 8 Hz), 7.91 (m, 1H), 7.94 (d, 1H, J = 8 Hz), 8.20 (m, 1H), 8.27 (d, 1H, J = 8 Hz).

Preparation of (*E*,*E*,*E*,*E*)-2,5-Bis[4-(2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadienyl]thiophene (5). Compound **6a** (0.55 g) in THF at −70 °C was added to 2,5-dilithiothiophene. The last was prepared from thiophene (0.1 g) and BuLi/TMEDA (2.4 mmol, hexane, reflux 0.5 h).[10] Compound **5** was crystallized from benzene−hexane mixture and purified by column chromatography as **4a**. Compound **5**: R_f = 0.45; thermal data:[29] C → 154 °C − nematic (marbled) −158 °C → I → 156 °C − nematic (marbled − 121 °C → C; λ_{max} (nm) 398 ($\epsilon = 5.5 \times 10^4$); IR ($cm^{-1}$) 1659, 1623 (CF═CF), 1130, 1181, 1223, 1268, 1361; MS *m*/*z* 497 (20), 496 (73) M^+, 476 (5), 456 (4), 368 (10), 351 (10), 319 (6), 270 (5), 248 (39), 225 (9), 207 (7), 188 (18), 133 (100), 115 (10), 83 (9), 63 (10); ^1H NMR δ (400 MHz) 7.16 (ddt, 2H, J = 5.1, 3.7, 1.6 Hz), 7.50−7.56 (m, 6 H).

(*E*,*Z*)-1-(2-Thienyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (6a). BuLi (40 mL, 1.9 M in hexane) was added dropwise to solution of thiophene (6.3 g, 0.075 mol) in 10 mL of ether for 30 min and stirred at 40 °C for 3 h. The solution of organometallic was precooled and added by transfer tube to a solution of **2** (12.5 g, 0.077 mol) in 40 mL of THF at −78 °C for 1 h. After being stirred at this temperature for 2.5 h, the reaction mixture was hydrolyzed and extracted with ether. The organic phase was separated and dried over $MgSO_4$. The residue after rotary evaporation of the solvent was distilled in vacuum to obtain **6a** (5.9 g, bp 57 °C (8 Torr), yield 35%, 96−92% content of *E*-isomer). The analytical sample was purified by column chromatography: MS *m*/*z* 226 (100) M^+, 207 (70), 181 (18), 175 (20), 163 (37), 157 (70), 143 (18), 132 (23), 113 (16), 99 (23), 93 (26), 69 (35), 45 (50); λ_{max} 291 (1.80×10^4); IR (cm^{-1}) 1773, 1684 (CF═CF); 1428, 1370, 1349, 1315, 1280, 1231, 1202, 1164, 1120; ^1H NMR δ 7.1 (dd, 1H), 7.2 (d, 1H), 7.42 (m, 1H); ^{19}F NMR δ ((*E*)-**6a**) −139.85 (dddd, 1F, J = 127, 21, 11, 5 Hz), −157.5 (dddd, 1F, J = 127, 36, 13.5, 3 Hz) −180.6 (dddd, 1F, J = 118, 36, 11, 3 Hz), −94.80 (dddd, 1F, J = 50.5, 30, 5, 3 Hz), −107.1 (dddd, 1F, J = 118, 50.5, 21, 13.5 Hz); ^{13}C {^1H} NMR δ 120.14 (ddddd, J = 230.4, 50.2, 30.0, 24.9, 5.5 Hz), 128.20, 128.71 (t, J = 4.8 Hz), 130.00 (d, J = 8.8 Hz), 130.4 (ddd, C-Q, J = ∼56, 35.5, 8.8 Hz), 135.50 (ddddd, J = 236.5, 51.3, 24.9, 7.2, 4.1 Hz), 148.54 (ddddd, J = 241.3, 48.0, 4.5, 2.7, 2.7 Hz), 154.37 (ddddd, J = 295.4, 286.3, 47.5, 6.0, 2.7 Hz); ^{19}F NMR δ ((*Z*)-**6a**) −116.71 (dm, 1F, J = 15 Hz), −141.50 (dddd, 1F, J = 36, 15, 15, 4.8 Hz), −175.43 (ddd, 1F, J = 118, 36, 28 Hz), −92.95 (dddd, 1F, J = 44, 28, 4.8, 3 Hz), −107.6 (ddd, 1F, J = 118, 44, 15 Hz). Anal. Calcd for $C_8H_3F_5S$: C, 42.49; H, 1.34. Found: C, 42.86; 1.72.

(*E*)-1-(2-Benzo[*b*]thienyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (6b). A precooled solution of **1f** (17 mL, see synthesis of **4f**) was added by transfer tube to the solution of **2** (1.5 g, 9.3 mmol in THF) at −78 °C and the resulting mixture stirred for 2.5 h. The reaction mixture was worked up by the usual procedure. The crude product was purified by column chromatography on silica gel (50 g, 40/100) using a heptane−benzene (8:1) mixture to obtain (*E*)-**6b** (0.66 g, R_f 0.71, yield 35% on **3f**): yellow crystals; mp 49 °C; IR 1772, 1745 (CF═CF); 1311, 1245, 1181, 1113. λ_{max} 307 (2.42×10^4), 255.4 (0.94×10^4); ^{19}F NMR δ (*E*) −140.33 (dddd, 1F, J = 129, 21.4, 11.5, 5.5 Hz), −156.14 (dddd, 1F, J = 129, 35.6, 13.5, 3 Hz), −181.52 (dddd, 1F, J = 115.6, 35.5, 29, 11.5 Hz), −93.79 (dddd, 1F, J = 47.5, 29, 5.5, 3 Hz), −106.06 (dddd, 1F, J = 115.6, 47.5, 21.4, 13.5 Hz); ^1H NMR δ 7.43 (m, 2H), 7.73 (s, 1H, $t_{1/2}$ = 3 Hz), 7.87 (m, 2H). A minor quantity of **4f** (*E*,*Z*) (0.15 g, yield 5%) was obtained. The mixture of **6b** isomers (*Z*:*E* = 61:39) was found after storage of (*E*)-**6b** ethereal solution at ambient conditions. (*Z*)-**6b** ^{19}F NMR δ −118.17 (ddt, 1F, J' = 15.8 Hz, J'' = 4.2 Hz, J''' = 2.5 Hz), −137.91 (ddt, 1F, J' = 38.1 Hz, J'' = 5.0 Hz, J''' = 15.5 Hz), −176.19 (dddd, 1F, J = 119.1, 38.1, 27.4, 4.2 Hz), −89.62 (dddd, 1F, J = 40.8, 27.4, 5, 2.5 Hz), −105.03 (dddd, 1F, J = 119.1, 40.8, 15.5, 2.7 Hz). Anal. Calcd for $C_{12}H_5F_5S$: C, 52.18; H, 1.82. Found: C, 52.18; H, 2.14.

(*E*,*E*)-1-(2-Thienyl)-1,2,3,4-tetrafluoro-1,3-octadiene (7). **6a** (0.24 g, 1.06 mmol, in 5 mL of THF) was added to syringe to BuLi (1 mL, 1.2 mmol, 1.2 M solution in hexane diluted with 3 mL of ether) at −70 °C for 30 min and stirred at −70 and −65 °C for 1.5 h. The reaction mixture was hydrolyzed and extracted with ether. The oil that remained after rotary evaporation of the solvent was worked up by column chromatography on SiO_2 (15 g, 40/100 mesh) using heptane−benzene (10:1) eluent. A yellow oil of **7**: R_f = 0.7, was isolated: MS *m*/*z* 265 (14), 264 (96) M^+, 235 (2), 221 (100), 207 (19), 201 (47), 187 (15), 176 (25), 152 (32), 133 (28), 127 (12), 115 (13), 71 (17), 69 (12), 57 (34), 45 (42), 43 (39), 41 (44); IR (cm^{-1}) 1714, 1679 (CF═CF); λ_{max} (nm) 294 ($\epsilon = 2.14 \times 10^4$); ^1H NMR δ 0.96 (t, 3H), 1.44 (m, 2H), 1.62 (q, 2H), 2.53 (m, 2H), 7.13 (m, 1H), 7.45 (d, 1H), 7.5 (m, 1H). Anal. Calcd for $C_{12}H_{12}F_4S$: C, 54.54; H, 4.58. Found: C, 54.76; H, 4.84.

Compounds **8**, **9**, **11a**,**b**, and **12a**,**b** were prepared by the treatment of **6a** and 1-aryl-1,2,3,4,4-pentafluoro-1,3-butadienes **10a**,**b**,**d**,**e**[3] with tolyl- and (thioaryl)lithiums.

(*E*,*E*)-1-(2-Thienyl)-4-(*p*-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (8). This was prepared from *p*-tolyllithium and **6a** at −78 °C: mp 78 °C (methanol); λ_{max} (nm), 324 ($\epsilon = 1.3 \times 10^4$); IR ($cm^{-1}$) 1626 (CF═CF), 1292, 1264, 1221, 1181, 1135; MS *m*/*z* 299 (18), 298 (100) M^+, 283 (32), 278 (25), 263 (11), 233 (14), 219 (8), 214 (16), 149 (13), 141 (6), 133 (20), 91 (6) 69 (4); ^1H NMR δ 2.42 (3H), 7.16 (m, 1H), 7.28 (d, 2H, J = 8 Hz), 7.52 (m, 2H), 7.66 (d, 2H, J = 8 Hz). Anal. Calcd for $C_{15}H_{10}F_4S$ C, 60.40; H, 3.38; S, 10.75. Found: C, 60.49; H, 3.29; S, 10.37.

(*E*,*E*)-1-(5-Methyl-2-thienyl)-4-(2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadiene (9). This was prepared from 2-methylthiophene (**3b**) and **6a**: mp 65 °C; yellow unstable crystals; λ_{max} (nm), 343 ($\epsilon = 3.45 \times 10^4$); IR ($cm^{-1}$) 1629 (CF═CF), 1297, 1265, 1224, 1178, 1124; MS *m*/*z* 305 (17), 304 (100) M^+, 289 (15), 284 (21), 256 (7), 239 (6), 220 (6), 152 (21), 147 (6), 133 (26), 97 (9), 69 (6), 59 (22), 41 (18); ^1H NMR δ 2.55 (3H), 6.81 (m, 1H), 7.15 (m, 1H), 7.29 (d, 1H, J = 4 Hz), 7.51 (m, 2 H). Anal. Calcd for $C_{13}H_8F_4S_2$: C, 51.31; H, 2.65. Found: C, 51.19; H, 2.96.

(*E*,*E*)-1-(2-Benzo[*b*]thienyl)-4-(*p*-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (11a). This was prepared from **1f** (8 mL, see preparation of **4f**) and 1-(*p*-tolyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (**10b**)[3] (0.7 g, 3 mmol). **11a**: mp 163−165 °C; λ_{max} (nm) 336.6 ($\epsilon = 4.41 \times 10^4$), 274 ($\epsilon = 0.93 \times 10^4$); IR ($cm^{-1}$) 1660, 1631, 1606 (CF═CF), 1383, 1333, 1294, 1264, 1246, 1187−1115; MS *m*/*z* 349 (24), 348 (100), M^+, 333 (11), 328 (54), 313 (24), 294 (8), 256 (21), 183 (11), 174 (24), 141 (14), 134 (21), 91 (7); ^1H NMR δ 2.43 (3H), 7.29 (d, 2H, J = 8.2 Hz),

(29) The nematic textures were characterized as in: Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed.; Blackie and Sow: Glasgow and London, 1991; pp 369−372.

7.68 (d, 2H, J = 8.2 Hz), 7.41 (m, 2H), 7.73 (1H), 7.86 (m, 2H). Anal. Calcd for $C_{19}H_{12}F_4S$: C, 65.51; H, 3.47. Found: C, 65.14; H, 3.72.

(*E*,*E*)-1-(2-Benzo[*b*]thienyl)-4-[4-(*N*,*N*-dimethylamino)-phenyl]-1,2,3,4-tetrafluoro-1,3-butadiene (11b). This was prepared from **1f** (8 mL, see preparation of **4f**) and 1-[4-(*N*,*N*-dimethylamino)phenyl]-1,2,3,4,4-pentafluoro-1,3-butadiene (**10e**)[3] (0.79 g, 3 mmol). **11b**: mp 228-229 °C; λ_{max} (nm) 380 (ϵ = 4.60 × 10^4); IR (cm^{-1}) 1662, 1641, 1606 (CF═CF), 1371, 1335, 1293, 1234, 1203−1112; MS *m*/*z* 378 (27), 377 (100) M^+, 358 (10), 356 (47), 332 (10), 312 (12), 294 (7), 244 (4), 188 (26), 178 (7), 170 (7), 78 (9); ^{1}H NMR δ 3.06 (6H), 6.75 (d, 2H, J = 9 Hz), 7.67 (d, 2H, J = 9 Hz), 7.70 (1H), 7.40 (m, 2H), 7.86 (m, 2H). Anal. Calcd for $C_{20}H_{15}F_4NS$: C, 63.65; H, 4.01; N, 3.71. Found: C, 63.53; H, 4.30; N, 3.67.

(*E*,*E*)-1-(4-Dibenzo[*b*,*d*]thienyl)-4-phenyl-1,2,3,4-tetrafluoro-1,3-butadiene (12a). This was prepared from **3g** and 1-phenyl-1,2,3,4,4-pentafluoro-1,3-butadiene (**10a**).[3] **12a**: mp 88 °C; λ_{max} (nm) 296 (ϵ = 2.93 × 10^4), 270.7 (3.07 × 10^4); IR (cm^{-1}), 1652 (CF═CF), 1387, 1329, 1304, 1273, 1188, 1148; MS *m*/*z* 385 (25), 384 (100) M^+, 364 (80), 344 (20), 306 (19), 288 (6), 257 (16), 233 (5), 192 (8), 184 (73), 172 (10), 139 (16), 127 (15), 85 (12), 71 (18); ^{1}H NMR δ 7.51 (m, 5H), 7.57 (ddd, 1H, J = 8, 8, 1.5 Hz), 7.83 (m, 2H), 7.90 (dm, 2H, J = 8 Hz), 8.20 (m, 1H), 8.27 (d, 1H, J = 8 Hz). Anal. Calcd for $C_{22}H_{12}F_4S$; C, 68.74; H, 3.15. Found: C, 68.39; H, 3.49.

(*E*,*E*)-1-(4-Dibenzo[*b*,*d*]thienyl)-4-[4-(cyclohexyloxy)-phenyl]-1,2,3,4-tetrafluoro-1,3-butadiene (12b). This was prepared from **3g** and 1-[4-(cyclohexyloxy)phenyl]-1,2,3,4,4-pentafluoro-1,3-butadiene (**10d**).[3] **12b**: mp 111 °C; λ_{max} (nm) 318 (ϵ = 2.74 × 10^4), 296.7 (2.85 × 10^4), 271.8 (2.5 × 10^4); IR (cm^{-1}) 1665, 1640, 1606 (CF═CF), 1389, 1287, 1259, 1170, 1143, 1106; MS *m*/*z* 483 (15), 482 (60) M^+, 461 (2), 400 (84), 380 (100), 361 (12), 349 (12), 331 (15), 306 (16), 257 (7), 233 (6), 184 (28), 143 (25), 139 (12), 83 (16), 55 (84); ^{1}H NMR δ 1.37−2.03 (m, 10H), 4.36 (m, 1H), 7.00 (d, 2H, J = 9 Hz), 7.51 (m, 2H), 7.57 (ddd, 1H, J = 8, 8, 1.5 Hz), 7.74 (d, 2H, J = 9 Hz), 7.90 (m, 2H), 8.19 (m, 1H), 8.25 (d, 1H, J = 8 Hz). Anal. Calcd for $C_{28}H_{22}F_4OS$: C, 69.70; H, 4.60. Found: C, 69.50; H, 4.76.

(*E*,*E*),(*E*,*Z*)-2,5-(3-Methylthienylene)-1,2,3,4-tetrafluoro-1,3-butadienylene Oligomers (14). BuLi (60 mL, 44 mmol) and TMEDA (4.64 g, 0.04 mol) were added to the 3-methylthiophene (1.96 g, 0.02 mol) in hexane at 45−50 °C for 0.5 h. The reaction mixture was cooled to −70 °C, and 50 mL of THF was added. Precooled **2** (3.6 g, 0.02 mol) in 15 mL of THF was added at −70 to −55 °C and the resulting stirred for 1.5 h. The mixture was allowed to warm to −5 °C, hydrolyzed with aqueous HCl, and extracted with ether. A total of 1.70 g (39%, violet solid) of the polymer was filtered. After evaporation of ether and crystallization from benzene−heptane mixture, 2.15 g (49%, violet solid) of polymer **14** was obtained. (*E*,*E*):(*E*,*Z*) = 3:1 and n = 4−5 (by the content of −CF═CF_2 groups) by ^{19}F NMR: mp > 340 °C; IR (cm^{-1}) 1770, 1660 (CF═CF), 1319, 1269, 1202, 1172, 1122; λ_{max} (nm), 372 (ϵ = 4−5 × 10^4); ^{19}F NMR δ −93.3 (m), −106 (m), 118.1 (m), −136.5−142 (m), −149 to −158 (m), −182.0 (m); ^{1}H NMR δ 2.17−2.42 (broad, 3H), 6.5−7.2 (broad m, 1H). Anal. Calcd for $C_9H_4F_4S$: C, 49.09; H, 1.83; S, 14.56. Found: C, 47.76; H, 2.82; S, 10.25.

(*E*,*E*),(*E*,*Z*)-2,5-Thienylene-1,2,3,4-tetrafluoro-1,3-butadienylene Oligomers (15a). This was prepared from thiophene, BuLi/TMEDA, and **2**. Polymer (51%) that was insoluble in ether was filtered. The ether was evaporated, and the polymer was crystallized from a benzene−hexane mixture to obtain **15a** (21%, violet solid): mp > 310 °C; (*E*,*E*):(*E*,*Z*) = 3:1 and n = 3−5 (by the content of −CF═CF_2 groups) by ^{19}F NMR, which is similar to **15b**; IR (cm^{-1}) 1654, 1638 (CF═CF), 1312, 1282, 1221, 1177, 1154, 1132; λ_{max} (nm) 389 (ϵ = ∼4 × 10^4); ^{1}H NMR δ 7.2−7.55 (broad m). Anal. Calcd for $(C_8H_2F_4S)_n$; C, 46.61; H, 0.98. Found: C, 46.78; H, 1.48.

(*E*,*E*),(*E*,*Z*)-2,5-Thienylene-1,2,3,4-tetrafluoro-1,3-butadienylene Oligomer (15b). This was prepared from 2,5-dibromothiophene (12.1 g, 0.05 mol) and Mg (2.4 g, 0.1 mol) in 140 mL of THF (reflux 30 min) and further reaction with **2** (6.0 g, 0.04 mol) at −15 to +5 °C for 4 h and 60 h at room temperature. After the hydrolysis with aqueous HCl and extraction with ether, the crude reaction product was crystallized from a benzene−hexane mixture to obtain **15b** (1.1 g, 13%, violet solid): mp > 350 °C; (*E*,*E*):(*E*,*Z*) = 3:1 and n = 3−6 (by the content of −CF═CF_2 groups in ^{19}F NMR); IR (cm^{-1}) 1656, 1626 (CF═CF); 1316, 1279, 1216, 1173, 1153, 1126; λ_{max} (nm), 385 (ϵ = ∼4 × 10^4); ^{19}F NMR (benzene-d_6) δ −93.09 (m), −105.47 (m), −117.0 (m), −137−142 (m), −151−160 (m), −181.76 (m); ^{1}H NMR (benzene-d_6) δ 6.5−7.2 (broad m). Anal. Found: C, 47.30; H, 1.47; S, 17.76; Br, 8.04.

2,5-Thienylene-1,2-difluoroethylene Oligomers and (*E*,*E*)-2,5-bis[2-(2-thienyl)-1,2-difluoroethenyl]thiophene (16). This was prepared by lithiation of thiophene (2.5 g 0.03 mol) with BuLi/TMEDA and further reaction with **13**. Polymer that was insoluble in ether (2.9 g, 68%, violet solid) was filtered. Some soluble polymer (0.2 g, 5%) was recrystallized from hot benzene to obtain (*E*,*E*)-2,5-bis[2-(2-thienyl)-1,2-difluoroethenyl]thiophene (**16**): red solid; thermal data:[29] C → 214 °C − nematic → 233 °C − nematic (Schlieren) − 278 °C → I → 274 °C − nematic (Schlieren) − 172 °C → C; purity 84% by ^{19}F NMR; IR (cm^{-1}) 1636 (CF═CF), 1133; λ_{max} (nm), 436 (ϵ = 2.0 × 10^4), 463 (ϵ = 1.6 × 10^4); ^{19}F NMR δ −144.01 (d, J = 115 Hz); −147.27 (d, J = 115 Hz); ^{1}H NMR δ 7.15 (m, 2H), 7.40 (m, 2H), 7.44 (d, 2H, J = 3.3 Hz), 7.49 (tm, 2H, J = 4.1 Hz). Anal. Calcd for $C_{16}H_8F_4S_3$; C, 51.60; H, 2.14. Found: C, 51.26; H, 2.51.

(*E*,*Z*)-2-(2-Chloro-1,2-difluorovinyl)thiophene (17a):[13] ^{1}H NMR δ 7.04 (dd, 1H, CH), 7.24 (dd, 1H, CH), 7.36 (m, 2H, CH).

(*E*,*Z*)-2-(2-Chloro-1,2-difluorovinyl)-5-methylthiophene (17b). Butyllithium (44 mL, 0.7 M in hexane) was added dropwise to the solution of 2-methylthiophene (**1b**) (2.75 g, 28 mmol) in 30 mL of THF and 15 mL of ether and heated to 40−45 °C for 45 min. The organometallic was cooled to −70 to −65 °C using a CO_2−ethanol bath. **18** (4 g, 34 mmol) was bubbled for 20 min and stirred at this temperature for 1.5 h. After being warmed to 0 °C, the mixture was hydrolyzed and extracted three times with ether. The organic layer was separated, washed with brine, and dried over $MgSO_4$, and the solvent was distilled off. After fractional distillation using a 10 cm Vigreux column, a compound **17b**, bp 72−75 °C (8 Torr) (4.2 g, purity 94% by GC, yield 80%, *E*/*Z* ratio 85:15) was obtained: IR (cm^{-1}, neat) 1684, 1608 (CF═CF), 1516, 1468, 1332, 1302, 1270, 1231, 1164; ^{1}H NMR δ 2.53 (3H), 6.74 (m, 2H), 7.23 (d, 2H, J = 3.7 Hz). Anal. Calcd for $C_7H_5F_2ClS$: C, 43.20; H, 2.59. Found: C, 42.94; H, 2.92.

(*E*,*Z*)-2-(2-Chloro-1,2-difluorovinyl)-5-(trimethylsilyl)-thiophene (17c):[14] bp 86 °C (3 Torr) (*E*/*Z* ratio 79:21); MS *m*/*z* 254 (11), 252 (27) M^+, 239 (42), 237 (100), 118 (7), 97 (8), 81 (8), 77 (27), 45 (7), 43 (7); ^{1}H NMR δ 0.34 (9H), 7.18 (d, 1H, J = 3.7 Hz), 7.32 (d, 1H, J = 3.7 Hz).

(*Z*,*E*)-1,4-Bis(5-methyl-2-thienyl)-1,2-difluorobut-1-en-3-yne (19a). A solution of **17b** (1.36 g, 7 mmol) in 8 mL of THF and 4 mL of ether was treated with BuLi (11 mL of 0.7 M solution in hexane) at −72 °C for 1 h. **2** (1.4 g, 8.6 mmol) was bubbled for 15 min and stirred for 2 h. After being warmed to 0 °C, the reaction mixture was hydrolyzed and extracted three times with ether. The organic layer was separated, dried over $MgSO_4$, and filtered and the solvent was distilled off. The methanol-soluble substance was separated and crystallized from pentane by low-temperature crystallization to obtain dark yellow crystals that gave upon warming a brown oil of **19a** (0.87 g 40%, *E*/*Z* ratio 35:65): IR (cm^{-1}, $CHCl_3$) 2192 (C≡C); 1648 (CF═CF); 1382, 1333, 1281, 1166, 1140; MS *m*/*z* $C_{14}H_{10}F_2S_2$ 281 (38), 280 (70) M^+, 279 (98), 278 (100), 264 (19), 247 (45), 245 (21), 221 (17), 207 (16), 201 (13), 183 (14), 163 (24), 139 (22), 135 (42), 81 (25), 69 (50), 59 (78); ^{1}H NMR δ 2.48 (3H), 2.51 (3H), 6.72 (m, 2H), 7.20 (m, 2H). Anal. Calcd for $C_{14}H_{10}F_2S_2$ C, 59.98; H, 3.60. Found: C, 59.58; H, 3.92.

(*Z*,*E*)-1,4-Bis[5-(trimethylsilyl)-2-thienyl]-1,2-difluorobut-1-en-3-yne (19b). This was prepared by a procedure similar to that for **19a** from **17c** (0.4 g, 1.6 mmol) and BuLi (1.6 mL, 1 M solution in hexane). A brown oil of **19b** (0.22 g, 35%, *E*/*Z* ratio 45:55) was obtained by low-temperature crystallization from methanol: IR (cm^{-1}, neat), 2190 (C≡C),

1645 (CF═CF), 1309, 1252, 1207, 1137; ^{1}H NMR δ 0.34 (9H), 0.35 (9H), 7.14 (d, 1H, J = 3.4 Hz), 7.18 (dd, 2H, J = 3.6 Hz), 7.23 (m, 1H), 7.39 (d, 1H, J = 3.5 Hz), 7.42 (d, 1H, J = 3.7 Hz), 7.44 (d, 1H, J = 3.7 Hz), 7.53 (d, 1H, J = 3.7 Hz). Anal. Calcd for $C_{18}H_{22}F_2S_2Si_2$: C, 54.50; H, 5.59. Found: C, 54.38; H, 5.76.

***(Z,E,E)*-1-(5-Methyl-2-thienyl)-4-(2-thienyl)-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (21).** This was prepared by the reaction of **17b** with BuLi (*E*:*Z* = 85:15) at −100 to −95 °C for 45 min and further reaction with **6a** at −95 to −65 °C for 2 h. The crude reaction mixture was separated by column chromatography on silica gel eluting with heptane−benzene (8:1) mixture to obtain **21** (75% of *Z*,*E*,*E* isomer), R_f 0.54. Some starting **6a** was also found: IR (cm^{-1}, $CHCl_3$) 1667 (CF═CF), 1321, 1271, 1176, 1115; MS *m*/*z* $C_{15}H_8F_6S_2$ 368 (10), 367 (18), 366 (100) M^+, 246 (12), 226 (8), 237 (7), 233 (6), 147 (43), 133 (30), 97 (4), 69 (7), 59 (9), 41 (15); ^{19}F NMR (376.5 MHz) δ −114.99 (m) −146.01 (dm), −148.69 (dm), −145.74 (dm), −161.92 (dm), −138.15 (dm); ^{1}H NMR (400 MHz) δ 2.49 (3H), 6.72 (dt, 1H, J = 3.7, 1.1 Hz), 7.15 (m, 1H), 7.16 (d, 1H, J = 3.7 Hz), 7.52 (d, 1H, J = 3.5 Hz), 7.56 (m, 1H).

***(E,Z,E)*-1,4-Bis(2-thienyl)-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (22).** This was prepared by the metalation of thiophene with BuLi/TMEDA (1 equiv) in ether (25 °C for 0.5 h)[10] and further addition of 0.5 equiv of perfluoro-1,3,5-hexatriene (*Z* isomer) at −75 °C. (*E*,*Z*,*E*)-**22**: yield 24%; yellow solid; mp 53−54.5 °C (hexane); λ_{max} (nm), 344.5 (ϵ = 1.89 × 10^4); IR (cm^{-1}, $CHCl_3$) 1669, 1636 (CF═CF); 1330, 1269, 1174, 1150; ^{1}H NMR δ 7.14 (m, 2H), 7.47 (d, 2H, J = 4 Hz), 7.55 (m, 2H); ^{19}F NMR δ −159.01 (m, 2F), −139.13 (m, 2F), −137.69 (m, 2F). Anal. Calcd for $C_{14}H_6F_6S_2$: C, 47.73; H, 1.72. Found: C, 48.02; H, 2.06.

***(E,E)*-1-(5-Nitro-2-thienyl)-4-(2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadienes (23).** Compound **4a** (55 mg, 0.19 mmol) in 3 mL of Ac_2O was treated with HNO_3 (0.27 mL, 0.21 mmol, 5% solution in Ac_2O) at −30 °C and stirred for 0.5 h. The orange precipitate of (*E*,*E*)-**23** was filtered from the cold reaction mixture in Ac_2O. A cold Na_2CO_3 aqueous solution was added, and the mixture was extracted with ether. The organic phase was separated and dried over $MgSO_4$, and the solvent was rotary evaporated to obtain an orange semicrystalline material. Additional crystallization from ethanol gave (*E*,*E*)-**23**, an orange solid, as 80% pure containing 20% of (*E*,*E*)-**24**. Further purification of it by column chromatography on silica gel eluting with benzene−PE (1:1) mixture gave (*E*,*E*)-**23**[30] (30 mg, 47%, R_f 0.77), purity > 90% by ^{1}H NMR and (*E*,*E*)-**24** (10%, R_f 0.51). (*E*,*E*)-**23**: mp 127 °C; λ_{max} (nm), 376 (ϵ = 1.18 × 10^4), 301 (ϵ = 1.38 × 10^4); IR (cm^{-1}) 1664, 1634 (CF═CF), 1534, 1334 (−NO_2), 1262, 1181, 1157; MS *m*/*z* 337 (17), 336 (16), 335 (100) M^+, 315 (3), 289 (7), 269 (5), 256 (22), 225 (26), 207 (6), 187 (5), 133 (12), 111 (14), 81 (4), 69 (9), 42 (22); ^{1}H NMR δ 7.18 (m), 7.39 (d, J = 4.4 Hz), 7.56 (d, J = 3.6 Hz), 7.60 (tm, J = 4.0 Hz), 7.93 (d, J = 4.5 Hz).

***(E,E)*-1,4-Bis(5-nitro-2-thienyl)-1,2,3,4-tetrafluoro-1,3-butadienes (24).** Compound **4a** (15 mg, 0.05 mmol) in 0.5 mL of Ac_2O was treated with HNO_3 (0.27 mL, 0.21 mmol, 5% solution in Ac_2O), storing at −20 °C overnight. The orange precipitate of (*E*,*E*)-**24** (10 mg, yield 51%) was filtered from the reaction mixture: mp 197 °C. IR (cm^{-1}) 1629, 1538, 1513, 1424, 1335, 1187, 1068, 1031, 875, 819, 730; λ_{max} (nm) 334 (ϵ = 1.1 × 10^4) and shoulder at 364 (ϵ = 1.0 × 10^4); ^{1}H NMR δ 7.45 (d, J = 4.4 Hz), 7.95 (d, J = 4.4 Hz). Anal. Calcd for $C_{12}H_4F_4N_2O_4S_2$: C, 37.90; H, 1.06; N, 7.37. Found: C, 37.96; H, 1.15; N, 7.00.

Acknowledgment. We thank Dr. M. M. Kremlev for his preliminary assistance and the Institute of Chemical Technology, Prague, for financial support of this work.

Supporting Information Available: ^{19}F NMR data, ratio of isomers and the assignments of **4a**−**c**,**e**−**g**, **11a,b**, **12a,b**, **8**, **9**, and **23**, and **24** (Table 3) and **17a**−**c** and **19a,b** (Table 5). ^{19}F NMR data and assignment of **6a,b** (Table 4) and **7**. ^{1}H NMR spectra of **4e**, **4g**, **21**, and **23** (12 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.

JO962325X

(30) The isomerization of (*E*,*E*)-**23** and (*E*,*E*)-**24** during the separation was observed once, which was probably caused by the exposure of a chromatography column and a solution to the sunshine, to give (*E*,*E*:*Z*,*E*:*E*,*Z* = 1:2:0.5)-**23** and (*E*,*E*:*E*,*Z* = 1:2)-**24** mixtures.

(31) Spectral simulation was performed by High-resolution NMR spectra analysis CALM version 2.00, 1991, Resonance Co.