Coupling of Chromophores: Carotenoids and Photoactive Diarylethenes – Photoreactivity versus Radiationless Deactivation

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New photochromic carotenoid-like chromophores containing the dithienylperfluorocyclopentene fragment have been synthesized and characterized by UV/Vis spectroscopy. The quantum yields of the photochromic forward and back reactions of these compounds have been determined and are found to decrease sharply with increasing chain length of the substituent. This decrease in quantum yield can be rationalized in terms of a decrease of the excitation density at the central photoreactive unit and of the excited state lifetime, which is known to shorten in carotenoids with increasing chain length.

Introduction

Carotenoids play a key role in photosynthetic systems. They act as antennae and favor energy transfer to the various chlorophylls. They also protect the photosynthetic apparatus by quenching the excited triplet states of chlorophylls as well as singlet oxygen. Under conditions of excess excitation, xanthophylls deactivate excited chlorophyll in the course of the so-called xanthophyll cycle[1].

In order to examine this photoprotective and energy dissipating behavior of carotenoids on photoactive materials, we have developed novel carotenoid-like chromophores[2], either by attaching further photochemically active light-absorbing systems to natural carotenoids, or by incorporating these units into polyenic chromophores in a π-conjugated manner. Here, we report on the syntheses of novel carotenoids and polyenes possessing a central 1,2-dithienylperfluorocyclopentene unit (DTFCP), which is known to be an excellent photochrome[3][4][5][6][7][8][9][10][11][12][13][14][15]. These compounds act as photoswitches, and the objective of these syntheses is to elucidate the influence of polyene and carotenoid substituents as well as chain lengths on the photochromic reactivity of DTFCP.

Irie et al.[3][4][5][6][7][8][9] as well as Lehn and co-workers[10][11][12][13][14] have recently developed various 1,2-diarylethene derivatives, which constitute a class of photochromic compounds that show very promising properties for technical applications, for example, as optical switches or as optical data-processing materials. To date, DTFCP derivatives fulfil the best a priori conditions with regard to technical applications, in so far as these derivatives are thermally stable and exhibit excellent photofatigue resistance, the high reversibility of the photochromic reaction being preserved over 10^4 cycles[3][4][5][6][7][8][9][10][11][12][13][14]. The photochromic reaction of these compounds belongs to the class of electrocyclic reactions according to Woodward and Hoffmann, and can be viewed as a reversible interconversion between a π-conjugated "closed form" and a cross-conjugated "open form" (the π conjugation across the central DTFCP unit is actually interrupted in this isomer, cf. as an example the difference between 2-vinylbuta-1,3-diene and 1,3,5-hexatriene) when irradiated in the visible and UV-spectral ranges, respectively.

Figure 1 illustrates the photochromic reaction of "polyenyl"-disubstituted DTFCP **1**: excitation with UV light induces the ring-closure reaction of the twisted anti-parallel open isomer **1a** (according to AM1 calculations, the preferred ground-state geometry is a twisted conformation with an anti-parallel orientation of larger substituents[15]), while the reverse ring-opening reaction of the closed, π-conjugated isomer **1b** occurs upon irradiation with visible light. The ring-opening and ring-closure reactions can be regarded as switch "off" and switch "on" of the π conjugation of **1**.

The changes in electronic structure and the resulting spectra that accompany the ring-closure and ring-opening reactions of these photochromic compounds can be conveniently monitored by UV/Vis absorption spectroscopy. The ring-closure reaction allows an efficient delocalization

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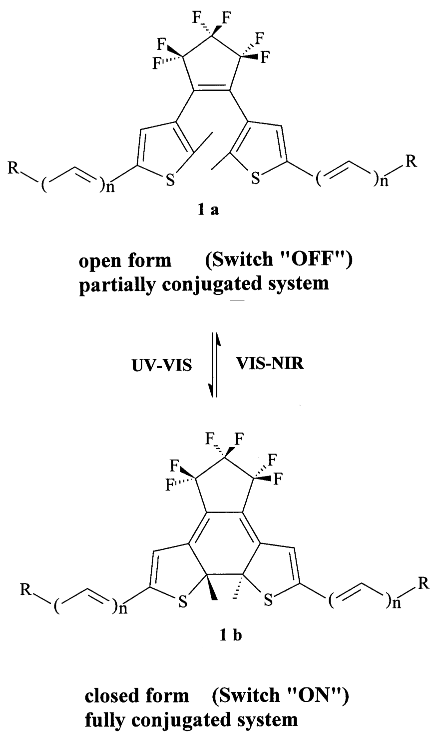
Figure 1. Photochromic reactions of 1,2-bis(2-methyl-5-“polyenyl”-thien-3-yl)perfluorocyclopentene **1**



of the π-electron system, with a low energy S_0-S_2 transition [$S_0-S_1(A_g)$ is a forbidden transition in polyenes with C_{2h} symmetry] that gives rise to a strong absorption band in the visible spectral range. The reverse ring-opening reaction interrupts the conjugation of the π-electron system and leads to a large increase in the energy of the S_0-S_2 transition, which consequently appears in the UV region (at $\lambda < 300$ nm for unsubstituted DTFCP). The structural differences between the open and closed forms are obvious from the ^{19}F-NMR signals of the CF_2 groups of the hexafluorocyclopentene ring.

While the ring-closure reaction of DTFCP derivatives was found to occur within 10 ps[9], a femtosecond absorption spectroscopy study of benzophenone-ethenyl-substituted DTFCP led to a time constant for the ring-opening reaction of about 2.1 ps[15]. Recently, Irie et al.[8] reported that the photochromic reactivity of oligothiophene-substituted DTFCP decreases with increasing chain length of the oligothiophene substituent.

The design and synthesis of substituted DTFCP is interesting in several respects. For technical applications, adjustable spectral properties of these switches are desirable. A particular goal of molecular design is to shift the excitation wavelength of the open form to a spectral region accessible to LED devices. However, substituents that lower the excitation energy of DTFCP also have the effect of decreasing the excitation density at the reactive region of the molecule and of changing the lifetimes of the S_2 and S_1 states. Both factors influence the reactivity, since alternative pathways of excitation-energy flow become available.

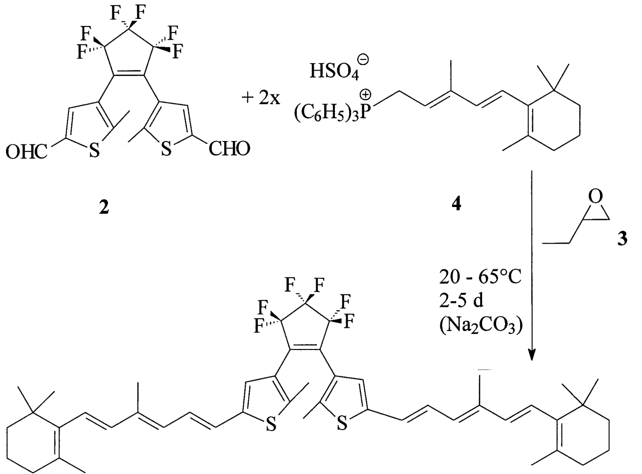
The sensitivity of the photochromic properties of DTFCP to substituents has prompted our systematic synthesis and spectroscopic investigations of new derivatives containing carotenoid-like or polyenic substituents of varying chain lengths. We describe herein the syntheses of seven new chromophores, together with their spectroscopic characterization, along with measurements of the photoreaction quantum yields in the case of the disubstituted DTFCP derivatives.

Results and Discussion

Syntheses

Compounds **5d**−**8d** (disubstituted DTFCPs) and **5m**−**8m** (monosubstituted DTFCPs) were synthesized by means of Wittig reactions[16] in the presence of epoxybutane **3** from the appropriate triphenylphosphonium salts (e.g. **4**) and 1,2-bis(5-formyl-2-methylthien-3-yl)perfluorocyclopentene **2**. The general route for compound **5d** (m.p. 51−53°C, 81% yield) is shown in Scheme 1.

Scheme 1. Synthesis of compound **5d**

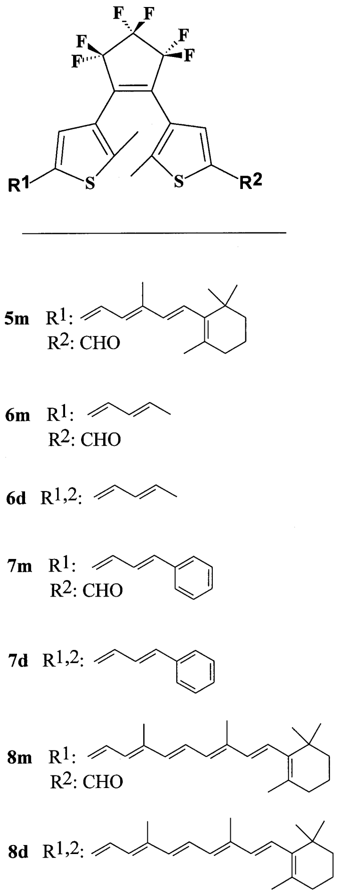


Following this reaction scheme, the dithienylethene derivatives with polyenic and carotenoid-like substituents depicted in Figure 2 were synthesized. The monoaldehydes **5m**, **7m**, and **8m** were obtained by reactions of the appropriate phosphonium salts with the bis(aldehyde) **2** in a 1:1 ratio. Details of the procedures are given in the Experimental Section.

Optical Spectra and Photochromic Reactions

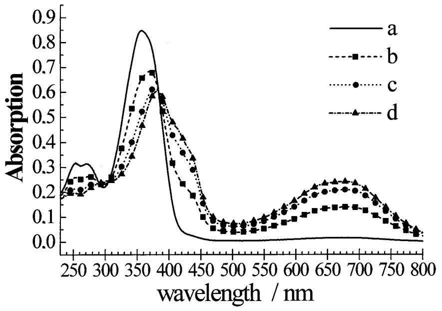
UV/Vis spectra of the open isomers and of mixtures of both isomers (open and closed) of compounds **5d** to **8d** were recorded in *n*-hexane. Figures 3 and 4 show absorption spectra (a) of the open isomers of **5d** and **8d**, respectively, together with spectra (b to d) recorded after irradiation at 366 nm with increasing duration. The respective irradiation times are 5 s, 10 s, and 15 s for **5d**; 10 min, 30 min, and 90 min for **8d**. The open forms of **5d** and **8d** are characterized

Figure 2. Photochromic compounds **5**−**8** (m: monosubstituted DTFCP; d: disubstituted DTFCP)



by absorption maxima at 357 nm (lg ε = 4.89) and 400 nm (lg ε = 5.02), respectively, while the corresponding absorption maxima of the closed forms lie at 678 nm (lg ε = 4.54) and 682 nm (lg ε = 4.66).

Figure 3. UV/Vis absorption spectra of **5d** (3.33×10^{-5} mol dm^{-3} in *n*-hexane), prior (a, open isomer) and subsequent to irradiation at 366 nm for 5 s (b), 10 s (c), and 15 s (d)



The energies and extinction coefficients of the absorption bands characterizing closed and open isomers of all compounds studied here are summarized in Table 1.

Comparison of the observed spectral shifts of the absorption maxima of the mono- and disubstituted compounds confirms the extended π conjugation across the central DTFCP unit in the closed isomers. In the case of the open isomers, where the π conjugation across the central DTFCP unit is interrupted (actually it is cross-conjugated), the positions of the absorption maxima of the mono- and disubstituted compounds in the near UV region are approximately the same. The maxima are, as expected, located at longer wavelengths for compounds **8m** and **8d**, with substituents containing the longer π-conjugated chain. In contrast, for the closed isomers, the π conjugation across the closed central unit is evident from the significant shift of the absorption maxima into the visible region of the spectra of the disubstituted compounds compared to the monosubstituted ones. In this case, the position of the absorption maxima depends only little on the conjugation length of the carotenoid substituent, since the overall π conjugation of the chromophore is already large. The effect on the photoreactivity is also clearly apparent in the spectra shown in Figures 3 and 4, from the evolution as a function of irradiation time.

For compound **8d**, an increase in the irradiation time of two orders of magnitude is required to induce changes of the absorption spectra comparable to those obtained in the case of **5d**. This observation clearly indicates a significant decrease of the quantum yield of the ring-closure reaction for **8d**. Measurements of the quantum yields, performed for both the ring-closure and the ring-opening reactions, confirm this finding. Results of these measurements, performed by standard methods and described in the Experimental Section below, are reported in Table 2.

The photochromic reactions of all the investigated compounds show only slight solvent and wavelength dependences. These effects are irrelevant in the context of the present work and will be discussed elsewhere. The polyene-disubstituted DTFCP derivatives **6d** and **7d** exhibit rather large ring-closure quantum yields [ϕ_{313}(**6d**) = 0.73 and ϕ_{313}(**7d**) = 0.54], as well as good reversibility and fatigue resistance during many irradiation cycles using alternately visible and UV light. In contrast, the carotenoid derivatives **5d** and **8d** irreversibly undergo the ring-closure reaction. The very large decrease of the quantum yield of the ring-closure reaction on going from **5d** to **8d** [ϕ_{313}(**5d**) = 0.34; ϕ_{313}(**8d**) = 5.3×10^{-3}] merits some discussion. Two factors contribute to this effect. One is a reduced excitation density at the central DTFCP unit (this is supported by PPP-SCF-CI calculations and configurational analysis of **5d**), and the other is a shorter excited-state lifetime of compound **8d** compared to that of **5d**. The aforementioned spectral shifts, together with the fact that the lowest excited state of unsubstituted DTFCP absorbs at wavelengths shorter than 300 nm, clearly indicate that the excitation density resides mainly on the carotenoid substituent. As a consequence, a reduction of the reaction rate is to be expected. The lifetime of the lowest excited singlet state S_1 of carotenoids is known to decrease with increasing chain length. The following empirical relationship between decay rate, k [s^{-1}], and the number of π-conjugated double bonds, n, of the chain has been derived[1][17]:

$$\log k = 0.395\, n + 6.70 \qquad (1)$$

Table 1. UV/Vis absorption spectroscopy data of the compounds **5**−**8**[a]

compound	solvent	n fully conjugated double bonds in the closed form	λ_{max} [nm] (lg ε) open form	λ_{max} [nm] (lg ε) closed form	$\Delta\lambda_{max}$ [nm]
6d	CH_2Cl_2	8	315 (4.54)	626 (4.22)	311
7m	CH_2Cl_2	6	350 (4.47)	618	268
7d	CH_2Cl_2	8	354 (4.90)	661 (4.43)	307
5m	*n*-hexane	8	354 (4.09)	634	280
5d	*n*-hexane	12	357 (4.89)	678 (4.54)	321
8m	*n*-hexane	10	401 (4.72)	633	232
8d	*n*-hexane	16	400 (5.02)	682 (4.66)	282

[a] **m** and **d** denote mono- and disubstituted compounds, respectively.

Figure 4. UV/Vis absorption spectra of **8d** (1.00×10^{-5} mol dm^{-3} in *n*-hexane), prior (a, open isomer) and subsequent to irradiation at 366 nm for 10 min (b), 30 min (c) and 90 min (d)

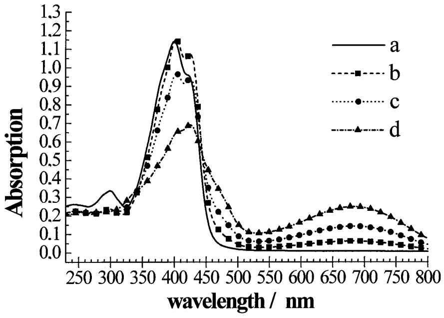


Table 2. Quantum yields of the compounds **5d**−**8d**

compound	solvent	$\Phi_{ring\text{-}closure}$ (open → closed)	$\Phi_{ring\text{-}opening}$ (closed → open)
6d	toluene	0.76	2.8×10^{-4}
	dichloromethane	0.73	4.7×10^{-4}
7d	toluene	0.59	3×10^{-5}
	dichloromethane	0.54	3×10^{-5}
5d	dichloromethane	0.34 irreversible	0
8d	dichloromethane	5.3×10^{-3} irreversible	0

The number of conjugated double bonds n increases by four on going from **5d** to **8d**. However, since the π conjugation in the open form is cross-conjugated, an actual conjugation length increase of $\Delta n = 2$ is a more realistic value. Therefore, a decrease in the lifetime of about one order of magnitude would be predicted. This, together with a more delocalized excitation density, reasonably accounts for the observed decrease of quantum yield by almost two orders of magnitude [ϕ_{313}(**8d**)/ϕ_{313}(**5d**) = 0.016]. It is assumed that the photoisomerization starts from the comparatively long-lived S_1 state (lifetime in carotenoids about 1−1000 ps[1][17]), and not from the extremely short-lived S_2 state (lifetime in carotenoids about 100−200 fs[1][17]), as befits the observed reaction times of 2−10 ps[9][15] (see Introduction). The fact that, within the limits of experimental error, the measured quantum yields show only very small dependences on the excitation wavelength, supports this rationalization: The S_1 state is not populated by direct excitation, but by rapid internal conversion from S_2. The latter corresponds to the strong UV/Vis absorption band, whereas the former transition is optically forbidden ($2A_g$ state in C_{2h} symmetry) and therefore does not contribute to the conventional absorption spectrum.

Clearly, the closed isomers of **5d** and **8d** are true polyenic carotenoid-like chromophores, in which the π conjugation extends over the entire molecule. Therefore, it is hardly surprising that the ring-opening reaction is not observed for these isomers, since the radiationless decay rate is even higher in these systems than in the corresponding open isomers.

Conclusion

The main finding of the synthetic and spectroscopic investigations on the dithienylethene derivatives described herein is the evidence for an upper limit of π-conjugation length, beyond which a fully reversible photochromic reaction no longer occurs. Compound **8d**, bearing the "longest" carotenoid substituents with 6 conjugated double bonds on either side of the dithienylethene chromophore, still undergoes the ring-closing reaction with a low quantum yield. In contrast, the ring-opening back reaction is no longer observed for **5d** or **8d**. These compounds act as unidirectional photoswitches only, generating photostable, closed isomers, in which radiationless deactivation of the π-electron system is very efficient. In compound **8d**, the small quantum yield of the ring-closure reaction gives an indication of the limit beyond which the conjugation length cannot be increased further without losing this reactivity. Studies on DTFCP with other novel subchromophores[15], which also have low-lying excited states but longer excited state lifetimes, are currently under way in order to establish which factors are dominant in promoting or inhibiting the photoreactivity. These studies are of key importance with regard to the spectral adjustments required for the successful operation of such systems in technical applications. The influence of temperature and of environment (e.g. polymer matrices) on the reactivity, two factors which are also expected to depend on the nature of the substituents, have yet to be investigated and these issues will be addressed in further studies.

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Experimental Section

General: All syntheses were carried out under argon or nitrogen and were monitored by TLC using aluminium-backed silica gel (230−400 mesh) or by HPLC using a Hewlett-Packard ChemStation 1040 and 1050 Series II instrument. The reaction mixtures were rigorously protected from light. The salts [3-methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienyl]triphenylphosphonium hydrogen sulfate (C_{15}-phosphonium salt) and [3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-enyl)nona-2,4,6,8-tetraenyl]triphenylphosphonium hydrogen sulfate (C_{20}-phosphonium salt) were obtained as gifts from the *BASF AG*. The other triphenylphosphonium salts were synthesized according to literature procedures as described below. 1,2-Bis(5-formyl-2-methylthien-3-yl)perfluorocyclopentene **2** was synthesized according to a procedure described by Lehn[12], starting with octafluorocyclopentene, donated by the *Bayer AG*, and commercially available 5-methyl-2-thiophenecarboxaldehyde (Aldrich). Solvents and other reagents were used as purchased without further purification, unless stated otherwise. Column chromatography was performed on silica gel (230−400 mesh) using nitrogen-flushed *n*-hexane and dichloromethane as eluents. − Melting points: Uncorrected, Reichardt THERMOVAR. − NMR: Bruker Avance DRX 200 and Varian VXR 300 at frequencies of 200 MHz for ^{1}H, and 300 MHz for ^{1}H, and 188.3 MHz for ^{19}F, respectively, with TMS (^{1}H) and $CFCl_3$ (^{19}F) as references. − UV/Vis: Perkin-Elmer Lambda 19 spectrophotometer. − IR: Perkin-Elmer 1420 spectrometer. − EI MS: Varian MAT 311A and MAT 8000. − Microanalytical data were obtained at the *Institute of Pharmaceutical Chemistry of the University of Düsseldorf.*

Quantum Yields: Quantum yields were determined by recording absorption spectra after irradiating solutions for various lengths of time. The following, suitably filtered spectral lines were used to induce the ring-closure and ring-opening reactions, respectively: 313 nm and 546 nm of a 200-W mercury high-pressure arc, 351/364 nm and 514 nm of an Ar+ laser, 633 nm of an He−Ne laser, and 575 nm of a dye laser. The intensities of the sources were calibrated using a furylfulgide actinometer (aberchrome 540)[18]. Extinction coefficients of the visible absorptions of the closed isomers were determined by measuring the relative concentrations of the two isomers in the irradiated solutions by ^{19}F NMR or ^{1}H NMR, where the total concentration of the mixture of the two isomers was known. Measurements of the ring-opening quantum yields were in some cases slightly affected by photochemical decomposition.

Syntheses

1,2-Bis{2-methyl-5-[4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-trienyl]thien-3-yl}perfluorocyclopentene (**5d**): 1,2-Bis(5-formyl-2-methylthien-3-yl)perfluorocyclopentene (**2**, 424 mg, 1.0 mmol) was added to a suspension of the C_{15}-phosphonium salt (vide supra, 1310 mg, 2.3 mmol) and sodium carbonate (300 mg) in 50 ml of 1,2-epoxybutane (**3**) under argon. The suspension was stirred for 48 h at room temperature in the dark, giving a brown solution, which was refluxed at 75°C for 8 h. The solvent was then removed and the product was purified by CC on silica gel using *n*-hexane/dichloromethane, 2:1 (v/v), as eluent. The first fraction contained **5d**. After removal of the solvent in vacuo, the resulting green solid was dried in vacuo at 0.1 mbar (647 mg, 81%), m.p. 51−53°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 12 H, CH_3 at C-6′′′), 1.47 (dt, $^{3}J_{4'''5'''}$ = 6 Hz, 4 H, 5′′′-H), 1.62 (m, 4 H, 4′′′-H), 1.73 (s, 6 H, CH_3 at C-2′′′), 1.90 (m, 6 H, CH_3 at C-2′), 1.99 (s, 6 H, CH_3 at C-4′′), 2.03 (m, 4 H, 3′′′-H), 6.15 (AB*X*, $^{3}J_{2''3''}$ = 11.3 Hz, 2 H, 3′′-H), 6.18 (d, $^{3}J_{5''6''}$ = 18 Hz, 2 H, 5′′-H), 6.28 (d, $^{3}J_{5''6''}$ ≈ 17 Hz, 2 H, 6′′-H), 6.40−6.64 (*AB*X, 4 H, 1′′-H and 2′′-H), 6.88 and 6.99 (s, 2 H, 4′-H). − ^{19}F NMR (188.3 MHz, $CDCl_3$, ref. $CFCl_3$): δ (open form) = −132.29 (m, 2 F, 4-F), −110.53 (m, 4 F, 3-F and 5-F). The following changes are observed after ring closure: δ (closed form) = −133.47 (m, 2 F, 4-F), −113.07 (m, 4 F, 3-F and 5-F). − IR (KBr): $\tilde{\nu}$ = 975, 990 cm^{-1} (conj. C=C), 1280 (C−F), 2880, 2945, 2985 (C−H), 3040 (C−H conj. C=C). − MS (70 eV): *m/z* (%) = 797 (67) $[M^{+} + 1]$, 796 (100) $[M^{+}]$, 781 (3) $[M^{+} - CH_3]$, 398 (4) $[M^{2+}{}_{2e-}]$, 91 (8) $[C_7H_7{}^{+}]$, 43 (13) $[C_3H_7{}^{+}]$, 32 (3) $[S^{+}]$. − HRMS (70 eV): $C_{47}H_{54}F_6S_2$ (796.36): calcd. 796.3571; found 796.3602.

1-(5-Formyl-2-methylthien-3-yl)-2-{2-methyl-5-[4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-trienyl]thien-3-yl}-perfluorocyclopentene (**5m**): The DTFCP-bis(aldehyde) **2** (vide supra, 424 mg, 1.0 mmol) was added to a suspension of the C_{15}-phosphonium salt (vide supra, 655 mg, 1.2 mmol) and sodium carbonate (150 mg) in 50 ml of 1,2-epoxybutane (**3**). The suspension was stirred for 48 h at room temperature in the dark under argon, giving a brown solution, which was refluxed at 75°C for 8 h. The solvent was then removed using a rotary evaporator. Care was taken to protect the product from daylight at all times. Purification by CC on silica gel using *n*-hexane/dichloromethane, 2:1 (v/v), as eluent yielded compound **5d** (210 mg, 26%) in the first fraction and the monoaldehyde **5m** in the second fraction. Evaporation of the solvent from the latter left a pale-green solid, which was dried in vacuo at 0.1 mbar (345 mg, 57%), m.p. 33−35°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 6 H, CH_3 at C-6′′′), 1.47 (dt, $^{3}J_{4'''5'''}$ = 6 Hz, 2 H, 5′′′-H), 1.61 (m, 2 H, 4′′′-H), 1.73 (s, 3 H, CH_3 at C-2′′′), 1.89 (m, 3 H, CH_3 at C-2′), 1.99 (s, 3 H, CH_3 at C-4′′), 2.02 (m, 2 H, 3′′′-H), 6.15 (AB*X*, $^{3}J_{2''3''}$ = 11.3 Hz, 1 H, 3′′-H), 6.18 (d, $^{3}J_{5''6''}$ = 18 Hz, 1 H, 5′′-H), 6.28 (d, $^{3}J_{5''6''}$ ≈ 17 Hz, 1 H, 6′′-H), 6.40−6.65 (*AB*X, 2 H, 1′′-H, 2′′-H), 6.86 and 6.96 (s, 2 H, 4′-H), 9.85 (s, 1 H, CHO). − IR (KBr): $\tilde{\nu}$ = 975, 990 cm^{-1} (C−H conj. C=C), 1280 (C−F), 1690 (CHO), 2880, 2940, 2985 (C−H), 3040 (C−H conj. C=C). − MS (70 eV): *m/z* (%) = 610 (100) $[M^{+}]$, 595 (12) $[M^{+} - CH_3]$, 305 (5) $[M^{2+}{}_{2e-}]$, 91 (12) $[C_7H_7{}^{+}]$, 43 (77) $[C_3H_7{}^{+}]$, 32 (20) $[S^{+}]$. − HRMS (70 eV): $C_{32}H_{32}F_6OS_2$ (610.18): calcd. 610.1798; found 610.1812.

1,2-Bis[2-methyl-5-(penta-1,3-dienyl)thien-3-yl]-perfluorocyclopentene (**6d**): The DTFCP-bis(aldehyde) **2** (vide supra, 106 mg, 0.25 mmol) was added to a suspension of (but-2-enyl)triphenylphosphonium chloride[19] (185 mg, 0.52 mmol) in 15 ml of 1,2-epoxybutane (**3**). The suspension, which slowly darkened, was stirred for 16 h at room temperature, and then, to complete the reaction, was refluxed at 60−70°C for 7 h. Removal of the solvent in vacuo, followed by trituration with dichloromethane, and purification by CC on silica gel using *n*-hexane/dichloromethane, 2:1 to 3:1 (v/v), as eluent, gave a pale yellow-green oil, which was dried in vacuo at 0.1 mbar (102 mg, 82%).− ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.82 (q, ^{3}J = 7 Hz, 6 H, CH_3), 1.86 and 1.92 (s, 6 H, thiophene CH_3), 5.78−6.90 (m, 8 H, olefinic H), 6.92 and 6.93 (s, 2 H, 4-H). − IR (film): $\tilde{\nu}$ = 990 cm^{-1} (conj. C=C), 1260 (C−F), 2940 (C−H), 3040 (C−H conj. C=C). − MS (70 eV): *m/z* (%) = 500 (44) $[M^{+}]$, 485 (15) $[M^{+} - CH_3]$, 250 (9) $[M^{2+}{}_{2e-}]$, 57 (100), 43 (90), 32 (45) $[S^{+}]$. − $C_{25}H_{22}F_6S_2$ (500.56): calcd. C 59.99, H 4.43; found C 59.27, H 4.60.

1,2-Bis[2-methyl-5-(4-phenylbuta-1,3-dienyl)thien-3-yl]perfluorocyclopentene (**7d**) *and 1-(5-Formyl-2-methylthien-3-yl)-2-[2-methyl-5-(4-phenylbuta-1,3-dienyl)thien-3-yl]perfluorocyclopentene* (**7m**): Cinnamyltriphenylphosphonium bromide[20] (1010 mg, 2.2 mmol) was suspended in 50 ml of a solution of **2** (424 mg, 1.0 mmol) in 1,2-epoxybutane under argon. The white suspension was stirred for 24 h at room temperature, whereupon it became yellow-brown, and then the mixture was refluxed for a further 6 h under nitrogen. Removal of the solvent left a brown residue, which was triturated with dichloromethane, and subsequently purified by CC on silica gel using *n*-hexane/dichloromethane, 3:1 (v/v), as eluent. The first fraction contained the disubstituted DTFCP **7d**. The pale-green solid was dried in vacuo at 0.1 mbar (286 mg, 46%), m.p. 63°C. The second fraction contained the monoaldehyde **7m**, which was obtained as a yellow-brown solid (89 mg, 17%), m.p. 37°C. − Characterization of **7d**: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.91 and 1.96 (s, 6 H, thiophene CH_3), 6.25−6.90 (m, 8 H, olefinic H), 6.94 and 7.02 (s, 2 H, 4-H), 7.23−7.51 (m, 10 H, aromatic H). − IR (film): $\tilde{\nu}$ = 755, 990 cm^{-1} (C−H conj. C=C), 1280 (C−F), 1500, 1580, 1600 (ar.), 2870, 2930 (C−H), 3040 (C−H conj. C=C), 3080, 3100 (ar. C−H). − MS (70 eV): *m/z* (%) = 624 (100) $[M^+]$, 609 (4) $[M^+ - CH_3]$, 312 (13) $[M^{2+}{}_{2e-}]$, 91 (22) $[C_7H_7^+]$, 32 (10) $[S^+]$. − $C_{35}H_{26}F_6S_2$ (624.70): calcd. C 67.30, H 4.20; found C 67.31, H 4.02. − Characterization of **7m**: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.89 and 1.94 (s, 6 H, thiophene CH_3), 6.27−7.04 (m, 4 H, olefinic H), 6.92 and 6.99 (s, 2 H, 4-H), 7.24−7.48 (m, 5 H, aromatic H), 9.85 (s, 1 H, CHO). − IR (film): $\tilde{\nu}$ = 765, 990 cm^{-1} (C−H conj. C=C), 1280 (C−F), 1500, 1550, 1580 (ar.), 2870, 2940, 2980 (C−H), 3040 (C−H conj. C=C), 3080, 3100 (ar. C−H). − MS (70 eV): *m/z* (%) = 524 (100) $[M^+]$, 509 (5) $[M^+ - CH_3]$, 262 (13) $[M^{2+}{}_{2e-}]$, 91 (22) $[C_7H_7^+]$, 32 (10) $[S^+]$. − $C_{35}H_{26}F_6S_2$ (624.70): calcd. C 59.53, H 3.46; found C 59.60, H 3.67.

1,2-Bis{5-[4,8-dimethyl-10-(2,6,6-trimethylcyclohex-1-enyl)deca-1,3,5,7,9-pentaenyl]-2-methylthien-3-yl}perfluorocyclopentene (**8d**): Sodium (140 mg, 6.0 mmol) was dissolved in 5 ml of anhydrous methanol and the resulting solution was stirred for 10 min. Under nitrogen, a solution of the C_{20}-phosphonium salt (vide supra, 1586 mg, 2.5 mmol) in 10 ml of anhydrous *N,N*-dimethylformamide was added dropwise over a period of 20 min. The intensely red-orange-colored solution was stirred for a further 10 min, and then a solution of **2** (424 mg, 1.0 mmol) in 7 ml of anhydrous *N,N*-dimethylformamide was slowly added over a period of 20 min. The resulting mixture was stirred for 16 h, and then added to a vigorously stirred mixture consisting of 150 ml of dichloromethane and 100 ml of water. The organic phase was separated and washed with 100 ml of water. Evaporation of the dichloromethane afforded a brownish-yellow oil, which was redissolved in 2 ml of dichloromethane and chromatographed on silica gel (230−460 mesh) using *n*-hexane/dichloromethane, 2:1 (v/v), as eluent. The product, which was obtained as a yellow oil, was dried in vacuo at 0.1 mbar, yielding an intensely yellow-colored solid (m.p. 25−30°C), 275 mg **8d** (24% yield). In addition, a fraction containing **8m** (vide infra, 205 mg, 30%) was obtained. Characterization of **8d**: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 12 H, CH_3 at C-6′′′), 1.47 (m, 4 H, 5′′′-H), 1.62 (m, 4 H, 4′′′-H), 1.72 (s, 6 H, CH_3 at C-2′′′), 1.91 (m, 12 H, CH_3 at C-4′′ and at C-8′′), 1.98 (s, 6 H, CH_3 at C-2′), 2.01 (m, 4 H, 3′′′-H), 6.09−6.90 (m, 16 H, olefinic H), 6.90 and 6.99 (s, 2 H, 4′-H). − IR (film): $\tilde{\nu}$ = 975, 990 (C−H conj. C=C), 1280 (C−F), 2880, 2945, 2980 (C−H), 3040 (C−H conj. C=C). − MS (70 eV): *m/z* (%) = 738 (1) $[M^+ - C_{14}H_{23}]$, 551 (1) $[M^+ - C_{26}H_{33}S]$, 123 (11) $[C_9H_{15}^+]$, 91 (13) $[C_7H_9^+]$, 69 (30) $[C_5H_9^+]$, 43 (100) $[C_3H_7^+]$, 32 (30) $[S^+]$. − $C_{57}H_{66}F_6S_2$ (929.28): calcd. C 73.67, H 7.16; found C 72.78, H 7.38. More accurate combustion analytical data could not be obtained.

1-(5-Formyl-2-methylthien-3-yl)-2-{5-[4,8-dimethyl-10-(2,6,6-trimethylcyclohex-1-enyl)-2-methyldeca-1,3,5,7,9-pentaenyl]thien-3-yl}perfluorocyclopentene (**8m**): The procedure was analogous to the synthesis of **5m**. Isolated yield: 44% as a yellow oil. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 6 H, CH_3 at C-6′′′), 1.47 (m, 2 H, 5′′′-H), 1.62 (m, 2 H, 4′′′-H), 1.72 (s, 3 H, CH_3 at C-2′′′), 1.90 (m, 6 H, CH_3 at C-4′′ and at C-8′′), 1.98 (s, 6 H, CH_3 at C-2′), 2.03 (m, 2 H, 3′′′-H), 6.10−7.09 (m, 8 H, olefinic H), 6.88, 6.96 (s, 2 H, 4′-H), 9.85 (s, 1 H, CHO). − IR (film): $\tilde{\nu}$ = 975, 990 cm^{-1} (C−H conj. C=C), 1260 (C−F), 1680 (CHO), 2880, 2945, 2980 (C−H), 3040 (C−H conj. C=C). − MS (70 eV): *m/z* (%) = 676 (3) $[M^+]$, 380 (5) $[C_{16}H_{10}F_6S_2^+]$, 278 (4) $[C_{21}H_{26}^+]$, 91 (10) $[C_7H_7^+]$, 43 (100) $[C_3H_7^+]$, 32 (5) $[S^+]$. − $C_{37}H_{38}F_6OS_2$ (676.83): calcd. C 65.66, H 5.66; found C 65.60, H 5.44.

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