New synthetic routes to highly-extended tetrathiafulvalenes

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Dedicated to Prof. Armand LATTES on the occasion of his 50th anniversary of teaching and research activities and for his involvement as a President of the “Société Française de Chimie”

Abstract

Various synthetic routes to highly extended tetrathiafulvalene (TTF) derivatives are presented. They generally involve a (poly)olefination reaction in the last step, thanks to Wittig-type or Horner-Wadsworth-Emmons (HWE) reactions. Two complementary strategies have been carried out by reacting a (poly)formyl-TTF with a phosphorous (P-ylide or phosphonate) reagent, or on the contrary, by the preparation of (poly)phosphonate-TTF derivatives prone to react with aldehydes. An X-ray structural determination of one of these systems confirms the high \( \pi \)-extension of such resulting TTF derivatives.

Keywords: Tetrathiafulvalene, Magtrieve\textsuperscript{TM}, Wittig, HWE olefination, \( \pi \)-conjugation

Introduction

There is currently an important interest in achieving the syntheses of tetrathiafulvalene (TTF) derivatives in order to improve the electroconducting properties of the corresponding charge-transfer complexes or cation radical salts.\textsuperscript{1} It is well established that stabilization of the metallic state of these materials may be reached by increasing their dimensionality,\textsuperscript{2} which can be achieved chemically by subtle molecular engineering around the electroactive TTF framework.\textsuperscript{3,4,5} An active trend consists in the synthesis of highly extended and/or S-rich TTF analogues.\textsuperscript{5} The effects which are expected from such extended \( \pi \)-donating molecules are: a) the enhancement of the dimensionality, in the solid state, thanks to the multiplication of sulfur atoms in the molecular structure allowing multi intra- and inter-chain S...S contacts; b) strong intermolecular interactions in the stacking mode of related materials, due to the lowering of the
charge density in the oxidized states and consequently due to a decrease of the coulombic repulsions between the positively charged oxidized neighbours; c) the lowering of the intramolecular coulombic repulsions in the oxidized species which may also provide an easy access to unusual stable multicationic species upon full oxidation, giving rise to organic salts of unconventional stoichiometries; d) finally, a higher \( \pi \)-donor ability in solution compared to parent TTF itself. TTF dimers and higher oligomers, in which the TTF units are linked by conjugated \( \pi \)-systems, were also identified as a possibility to increase the dimensionality of corresponding materials.\(^6\) These systems display multi-stage redox behavior thanks to intramolecular through-bond or through-space interactions between TTF units.

Considering the different modes of extension of the TTF framework, the retrosynthetic methodology involves olefination reactions using Wittig-type reactions under basic conditions with various ylides or Horner-Wadsworth-Emmons (HWE) reactions with phosphonate anions (Scheme 1).\(^7\) Therefore, there is a need for a controlled access to mono- or poly-formyl TTF derivatives, prone to undergo olefinations with various P-ylids or phosphonate anions (Route 1). Alternatively, similar highly extended systems can be built from the reciprocal strategy, i.e. the reaction of TTF-phosphonates with aldehydes (Route 2).

![Scheme 1](image1)

**Scheme 1**

In this work we will present successively our efforts concerning the preparation of (poly)formyl TTF derivatives 1-4 (Scheme 2), the access to TTF-phosphonate derivatives, and finally we will present different families of extended TTF derivatives obtained by (poly)olefinations using these reagents.

![Scheme 2](image2)

**Scheme 2**
Results and Discussion

Synthesis of the mono and polyformyl-TTF derivatives
TTF derivative 1 was prepared according to the described procedure,\(^8\) by formylation of TTF using LDA and N-methylformanilide.

Synthesis of monoformyl TTF 2 was carried out according to a multi-step strategy (Scheme 3). The initial trimethylphosphite-mediated cross-coupling of the two corresponding 2-(thi)oxo-1,3-dithiole moieties 5 and 6 afforded 2,3-bis(methoxycarbonyl)TTF 7 in 62% yield, according to a known procedure.\(^9\) Further monodecarboxymethoxylation to 8 was cleanly achieved in 96% yield by treatment with LiBr salt in refluxing DMF. Attempts to reduce selectively, using DiBAl-H, the ester functionality into the corresponding aldehyde failed. In fact, we could obtain efficiently in 92% yield the mono(hydroxymethyl)TTF 9. At this stage, different oxidizing reagents were tested such as MnO\(_2\)\(^{10}\) or SeO\(_2\)\(^{11}\) since these reagents have already been used successfully for the conversion of hydroxymethyl-TTFs into the corresponding aldehyde. In our case, best results were obtained taking advantage of the easy to handle Magtrieve\textsuperscript{TM} (CrO\(_2\)) reagent.\(^{12}\) Thus, transformation of the hydroxymethyl group to the formyl group (compound 2) was achieved in 65% yield using this reagent.

Scheme 3

Two different routes were used to reach bis(formyl) TTF derivative 3 (Scheme 4). The first one involves a Co\(_2\)(CO)\(_8\) mediated cross-coupling of compound 10 with thione 11\(^{13}\) bearing vicinal formyl and di(ethyl)acetal functions. Yields are rather low in this desulfuration-coupling step, but the resulting TTF derivative 12 could be transformed in reasonable yields into the corresponding bis(formyl) derivative 3 by simple formolysis. Alternatively, we synthesized in good yield 2,3-bis(methoxycarbonyl)TTF 13 according to the literature.\(^9,14\) As described above in the monofunctionalized series (to compound 2), selective reduction of 13 into 3 could not be achieved. Instead, reduction into the corresponding bis(hydroxymethyl)TTF 14 and subsequent smooth oxidation with Magtrieve\textsuperscript{TM} reagent proved to be the best alternative strategy to reach
bis(formyl)TTF 3. The latter was obtained in 50% yield after separation from a mixture consisting in the monoformyl intermediate and various overoxidation products.

Scheme 4

Tetraformyl-TTF 4 was prepared according to literature from the Co$_2$(CO)$_8$ mediated self-coupling of 11 and subsequent formolysis.$^{13}$

**Synthesis of TTF-phosphonate derivatives**

It is now clearly established that the powerful synthetic potential of phosphonate derivatives is the source of varied applications (Scheme 5). Indeed their higher nucleophilic character compared to ylids was exploited to achieve the required olefination of conjugated aldehyde to reach TTF vinylogue derivatives (reaction 1, Scheme 5).$^{15}$ The HWE reaction could be performed on $p$-benzoquinone after a decrease of its accepting quinonic character using the Yamashita’s methodology of protection-deprotection with cyclopentadiene (reaction II).$^{16}$ Another utilization of the phosphonate anion was recently shown with the creation of the central TTF double bond directly from the 2-oxo-1,3-dithiole moiety (reaction III).$^{17}$ The high reactivity of the phosphonate anion was finally demonstrated with the synthesis of spatial extended fused T-shaped TTF which involved a three-fold HWE olefination process (reaction IV).$^{18}$

We were interested in developing new phosphonate reagents derived from 1,3-dithiole or TTF moieties to reach highly sulfur-rich extended TTF-based architectures. Consequently, we now present a new approach to extend the TTF framework using HWE-type reagents (compounds 15-18). These reagents associate in their structure (dimethylphosphono)methyl groups to the 1,3-dithiole or TTF units (Scheme 6).
Scheme 5

Scheme 6

The reactivity of the vicinal bis(bromomethyl) group has been demonstrated with the possibility of generating the corresponding diene by reductive elimination or to perform its transformation into the pyrrolo group. The versatile synthetic reactivity of this group is now extended to the Arbuzov-type reaction to reach bis 15, 16 or tetrakis 17 phosphonate derivatives respectively. Considering this methodology, this vicinal bis(bromomethyl) group can act as a dicationic synthetic equivalent (Scheme 7).

Scheme 7
The Arbuzov reaction was achieved by treatment of 2,3-bis(bromomethyl)-2-thioxo-1,3-dithiole 19 or TTF 20 in refluxing trimethylphosphite. The corresponding phosphonate derivatives 15 and 16 were isolated in 46% and 40% yield respectively. Unfortunately, starting from tetakis(bromomethyl)TTF 21 and using the same experimental procedure, we were not able to obtain the tetraphosphonate 17 (Scheme 8).

Scheme 8

To circumvent this difficulty, another synthetic method was developed to reach compound 17. Methylation of 15 with methyl triflate followed by reduction with sodium borohydride afforded compound 22 in an overall 93% yield. The 1,3-dithiolium salt 23 was produced in quantitative yield by dethiomethylation with tetrafluoroboric acid in acetic anhydride. Treatment with an excess of triethylamine afforded TTF 17 by carbenoid coupling in 81% yield (Scheme 9).

Scheme 9
Application to the synthesis of various families of extended-TTF derivatives $p$-N,N-Dimethylaminostyrenyl- TTF derivatives 25, 26 and 27

The N,N-dimethylaminostyrenyl moiety is a well-known electrodonating system. We have introduced this group on the periphery of the TTF framework in order to enhance the $\pi$-donating ability of the resulting extended system. The general synthetic strategy involved a Wittig-type mono-, di- or tetraolefination between the P-ylide generated using tBuOK from 24 and TTF aldehyde 1, 3 or 4 (Scheme 10). Corresponding highly extended systems 25, 26 and 27 were isolated in good yields (>75 %), if one considers that up to four simultaneous olefinations took place in the case of 27. Only the $E$ configuration was observed by $^1$H-NMR analysis for each double bond created.

Scheme 10

Single crystals of 26 could be grown as orange needles from a dichloromethane – methanol mixture, and the X-ray structure was determined (Figure 1). It appears that in the solid state, compound 26 presents a conformation close to planarity, giving rise to a highly extended $\pi$-system where the different units are therefore conjugated. The configuration of both double bonds generated during the Wittig olefination process is confirmed to be $E$. A transoid
conformation is observed for both \(p\)-\(N,N\)-dimethylamino styrenyl moieties relatively to the TTF framework, as expected from the steric demand generated by the vicinity of these groups.

\[\text{Figure 1} : \text{Molecular structure of 26 according to X-ray diffraction: a) space-filling model; b) 2D-extension of the } \pi \text{-system; c) projection onto the } ac \text{ plane.}\]

\textbf{Styrenyl- TTF derivatives 28, 29 and 30}

The reactivity of phosphonates 15-17 was first evaluated by deprotonation followed by olefination reaction using benzaldehyde as the electrophile. The corresponding 2-thioxo-1,3-dithiole 28 and TTFs 29-30 derivatives conjugated with styrenyl groups were isolated in satisfactory yields (Scheme 11). As for the above \(N,N\)-dimethylstyrenyl analogues 25-27, which were prepared via the reverse strategy (TTF-(CHO)\(_n\) + ylide), it should be noted that \(^1\)H NMR spectroscopy of compounds 28-30 was consistent with the \(E\) configuration for all double bonds created.

\[\text{Scheme 11}\]
This reactivity was extended to novel conjugated dimeric and trimeric TTF. Deprotonation using $t$BuOK or BuLi followed by the addition of adequately substituted monoformylTTTF 2 led to the corresponding dimeric TTF 31 and trimeric TTF 32 (Scheme 12). Yields in the HWE reaction were notably improved when $t$BuOK was added to a solution of electrophilic aldehyde 2 and diphosphonate 15 or 16 at 0°C (31 : 79%; 32 : 55% yields) instead of generating first the anion of diphosphonate 16 followed by the addition of the aldehyde 2.

Scheme 12

The synthesis of phosphonate 18 started from compound 19 (Scheme 13). Subsequent reductive elimination carried out using Et$_4$N$^+$ $\Gamma$ afforded the resulting transient diene 33 which reacted with $p$-benzoquinone according to a [4+2] Diels-Alder cycloaddition. Aromatization of the cycloadduct into compound 34 was carried out by treatment with DDQ. In order to perform further olefinations, it was necessary to decrease the accepting quinonic character of 34. The methodology of protection-deprotection developed by Yamashita using Diels-Alder cycloaddition with cyclopentadiene was applied. Consequently, we submitted the raw material to a [4+2] cycloaddition by treatment with cyclopentadiene in THF. Compound 35 was then isolated as yellow crystals in 59% yield (calculated from 19) after purification by silica gel column chromatography. HWE olefination of both carbonyl functionalities of compound 35 was carried out using an excess of phosphonate 36 in the presence of $n$-BuLi. Resulting bis-olefinated product 37 could be isolated as an analytically pure compound in 93% yield after precipitation with MeOH. Treatment of 2-thioxo-1,3-dithiole derivative 37 with trimethylphosphite afforded the expected TTF 38 resulting from the self-coupling reaction accompanied with phosphonate 18 according to a phenomenon appearing under high dilution conditions. We noted also the transformation of the thioxo derivative onto the oxo analogue 39. These three compounds were easily separated by silica gel column chromatography affording successively TTF derivative 38, then the oxo derivative 39 (petroleum ether/CH$_2$Cl$_2$ : 7/3) and finally, phosphonate 18 (petroleum...
ether/EtOAc : 1/1). Corresponding yields depending on experimental conditions are reported in Table 1. Moreover, note that we were able to transform the oxo derivative 39 into the expected phosphonate 18 in 41% yield (with only traces of TTF) using a diluted solution of trimethylphosphite in toluene.

Scheme 13

This phosphonate 18 allows to prepare novel extended TTF-based donors with increased dimensionality and prone to undergo multistep redox systems. In particular, we developed the HWE reaction to reach highly extended architectures presenting the C$_2$ or C$_3$ symmetry, using the suitable polyformylated aromatic spacer. Thus, the reaction of the phosphonate anion generated from 18 with terephthaldehyde gave a mixture of both mono-olefinated and bis-olefinated 40 and 41 compounds respectively (Scheme 14). These products were separated by chromatography on silica gel and compound 41 was isolated as orange crystals in 51% yield. The structure of 41 was confirmed by spectroscopic data and it should be noted that the mass spectrum presents the molecular peak as well as fragment peaks resulting from the successive retroDiels-Alder reactions eliminating cyclopentadiene molecules. We took advantage of this
peculiarity to carry out the thermal deprotection of quinonic double bonds. The conversion into extended-TTF 42 was performed efficiently by refluxing an \(\alpha\)-dichlorobenzene solution of product 41.

**Table 1.** Influence of experimental parameters for the transformation of 2-(thi)oxo-1,3-dithiole 37 or 39 with trimethylphosphite

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Concentration of 37 or 39 in P(OMe)(_3)</th>
<th>Time (h)</th>
<th>Reaction temperature (°C)</th>
<th>Yield of phosphonate 18 (%)</th>
<th>Yield of TTF 38 (%)</th>
<th>Yield of 39 (%)</th>
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<tr>
<td>37</td>
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<td>3</td>
<td>90</td>
<td>28</td>
<td>0</td>
<td>34</td>
</tr>
<tr>
<td>37</td>
<td>0.04 M</td>
<td>4</td>
<td>140</td>
<td>31</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
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<td>1</td>
<td>140</td>
<td>35</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>37</td>
<td>0.22 M</td>
<td>1.5</td>
<td>140</td>
<td>28</td>
<td>21</td>
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</tr>
<tr>
<td>39</td>
<td>0.037 M</td>
<td>24</td>
<td>140</td>
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<td>39</td>
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<td>24</td>
<td>140</td>
<td>33</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

![Scheme 14](image)

**Scheme 14**

The synthesis of TTF-based molecules with three-fold symmetry was previously investigated involving a Wittig reaction of both 1,3,5-

\(tris((\text{triphenylphosphonium})\text{methyl})\text{benzene tribromide and monoformyl-TTF 1}^{25}\). In our case, we have considered the reverse strategy by achievement of the HWE reaction using phosphonate
18 and 1,3,5-triformylbenzene\(^{25}\) as the electrophile. Following the procedure described for the synthesis of 41, the expected product 43 was isolated in 60\% yield (Scheme 15). *Retro* Diels-Alder was carried out by refluxing an \(\alpha\)-dichlorobenzene solution of 43 affording quantitatively the three-fold symmetry molecule 44 in which the benzene core is substituted in the 1,3,5-positions by extended-TTF units.

**Scheme 15**

**Conclusions**

In this work, two complementary approaches to build extended-TTF derivatives by polyolefinations are illustrated. On this basis, new powerful functionalized TTF synthons have been prepared, bearing either formyl or phosphonate groups. The Magtrieve\textsuperscript{TM} reagent proved to constitute an appropriate smooth oxidant to allow the formation of (poly)formyl-TTF derivatives from the corresponding hydroxymethyl groups, without observation of TTF oxidation. Illustration of the wide applicability of these TTF synthons (poly(formyl) and...
poly(phosphonate)) is given by the construction of various original families of extended TTF derivatives. Work is now in progress to generate oxidized salts from these different families, in particular using the electrocrystallization technique.26

**Experimental Section**

**General Procedures.** Unless otherwise noted, chemicals were purchased from commercial suppliers and used without further purification. All solvents were distilled prior to use (THF and toluene from Na/benzophenone, CH₂Cl₂ from P₂O₅, CH₃CN from CaH₂). Column chromatography was performed on silica gel 60 from Merck (40-63 µm).

**Equipment.** Kugelrohr distillation was performed using a Büchi B-580 apparatus. Melting points were determined using a microscope RCH (C. Reichert) with a Kofler hot stage and are uncorrected. ^1^H and ^13^C NMR spectra were recorded on a Brucker AC 200 (200 MHz), Brucker ACX 400 (400 MHz) or Brucker Avance DRX 500 (500 MHz) spectrometer and chemical shifts are reported in ppm using TMS as an internal standard. Infrared spectra were recorded on a FT-IR Brucker Vector 22 spectrometer. Mass spectra were recorded on a VG Autospec spectrometer (Zaragoza) and on Kratos Kompact MALDI 2 spectrometer (Barcelona). X-ray diffraction:

Data collection was carried out on an Enraf-Nonius CAD4 diffractometer. Elemental microanalyses were performed by the Central Service of Microanalysis of the CNRS (Vernaison, France).

**Compound characterization**

2-Formyl-tetrathiafulvalene (1) was prepared according to ref. 8.

2-Formyl-6,7-bis(pentylsulfanyl)tetrathiafulvalene (2). A solution of 2-(hydroxymethyl)TTF (9) (204 mg; 0.46 mmol) and a large excess of Magtrieve™ (716 mg) in CH₂Cl₂ (2.5 mL) was refluxed for 1 h 30. After cooling and dilution with CH₂Cl₂, the solution was filtered. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel using CH₂Cl₂/petroleum ether (1/1) as the mixture of eluents affording a red oil which crystallized by standing in the freezer giving red crystals (130 mg; 65% yield). M.p. = 44°C (CH₂Cl₂/petroleum ether). ^1^H NMR (CDCl₃) δ : 0.90 (t, 6H, CH₂C₃H₇, ^3^J = 7 Hz), 1.25-1.45 (m, 8H, C₆H₄CH₃), 1.63 (qu, 4H, SCH₂CH₃, ^3^J=7 Hz), 2.80 and 2.81 (2t, 4H, CH₂S, ^3^J = 7 Hz), 3.74 (s, 1H, =CH), 9.47 (s, 1H, CHO). ^13^C NMR (CDCl₃) δ : 14.6 (CH₂C₃H₇), 22.8 (CH₂CH₃), 30.0 (SCH₂CH₂), 31.2 (CH₂CH₂CH₃), 37.0 (SCH₂), 110.2 and 111.6 (cent. C=C), 127.7 and 129.3 (SC=CS), 140.2 (C=C-H), 141.9 (=C=CHO), 180.2 (C=O). MS EI m/e (%): 436 (M⁺, 100), 364 (21), 331 (39), 294 (36), 174 (31).

6,7-Bis(ethylenedisulfanyl)-2,3-bis(formyl)TTF (3). Method A. A solution of acetal TTF derivative 12 (212 mg; 0.50 mmol) in CH₂Cl₂ (20 mL) was treated with formic acid (99%) (5 mL). The initial red solution turned immediately to deep blue. After 30 min of stirring, CH₂Cl₂ and Na₂CO₃ were successively added. The resulting organic layer was washed with water, dried...
over MgSO₄ and the solvent was removed in vacuo. Blue needles of 3 were collected from recrystallization in toluene (122 mg; 70% yield).

**Method B.** To a solution of diol 14¹⁴ (200 mg; 0.56 mmol) in a THF (20 mL) /CH₂Cl₂ (20 mL) mixture at room temperature, was added Magtrieve™ (1.5 g). The reaction mixture was refluxed overnight, and the oxidizing agent was discarded by filtration. The filtrate was evaporated and purified by column chromatography using CH₂Cl₂/petroleum ether (7/3) as the mixture of eluents to afford dialdehyde 3 as deep blue needles (101 mg; 50%). M.p. = 201-211°C (toluene). ¹H NMR (CDCl₃) δ : 3.30 (s, 4H, CH₂), 10.21 (s, 2H, CHO). IR (KBr) : 1650 and 1690 cm⁻¹ (C=O). MS m/e (I%) : 350 (M⁺, 100). Elemental analysis for C₁₀H₁₆O₅S₆ (349.87) calcd. C 34.26 H 1.73 O 9.13; found C 34.08 H 1.58 O 9.30.

**2,3,6,7-Tetraformyl-TTF (4)** was prepared according to ref.13.

**2,3-Dimethoxycarbonyl-6,7-bis(pentylsulfanyl)tetrathiafulvalene (7).** A solution of 2-oxo-1,3-dithiole 6 (4.68 g; 20 mmol) and 2-thioxo-1,3-dithiole 5 (6.76 g; 20 mmol) in trimethyolphosphite (200 mL) was heated at 80°C for 4 h. Trimethyolphosphite was removed in vacuo and the residue was purified by chromatography on silica gel using CH₂Cl₂/petroleum ether (1/4) as the mixture of eluents to remove 2,3,6,7-tetakis(pentylsulfanyl)TTF. Further elution using CH₂Cl₂/petroleum ether (7/3) as the mixture of eluents afforded 6.50 g (62% yield) of dissymmetrical TTF as a purple oil. ¹H NMR (CDCl₃) δ : 0.89 (t, 6H, CH₂), 1.20-1.50 (m, 8H, CH₂), 1.55-1.65 (m, 4H, C), 7.34 (s, 1H, CH). ¹³C NMR (CDCl₃) δ : 14.6 (CH₂CH₃), 22.8 (CH₂CH₂), 30.1 (CH₂CH₂CH₃), 37.0 (SCH₂), 53.4 (CH₃O), 110.7 and 111.6 (cent. C=C), 128.0 (=C=CO₂Me), 128.8 and 129.0 (SC=CS), 132.6 (C=C-H), 160.4 (C=O). MS EI m/e (I%) : 466 (M⁺, 100), 394 (14), 361 (30), 324 (22), 204 (21).

**2-Methoxycarbonyl-6,7-bis(pentylsulfanyl)tetrathiafulvalene (8).** A solution of TTF diester 7 (3.00 g; 5.72 mmol), LiBr (8.93 g; 102.9 mmol) in DMF (60 mL) was heated for 2 h at 120°C. The reaction mixture was cooled, then brine (10 mL) and EtOAc (250 mL) were added. The organic layer was washed with brine (3x100 mL), dried (MgSO₄) and the solvent was removed in vacuo. The residue was purified by chromatography on silica gel using CH₂Cl₂ as the eluent affording a red oil (2.56 g; 96% yield). ¹H NMR (CDCl₃) δ : 0.89 (t, 6H, CH₂CH₃, 3J = 7 Hz), 1.20-1.50 (m, 8H, CH₂), 1.63 (qu, 4H, SCH₂CH₂, 3J = 7 Hz), 2.80 and 2.81 (2t, 4H, CH₂S, 3J = 7 Hz), 3.81 (s, 3H, OCH₃), 7.34 (s, 1H, CH). ¹³C NMR (CDCl₃) δ : 14.6 (CH₂CH₃), 22.8 (CH₂CH₂), 31.3 (SCH₂), 30.1 (CH₂CH₂CH₃), 37.0 (SCH₂), 53.4 (CH₃O), 110.7 and 111.6 (cent. C=C), 128.0 (=C=CO₂Me), 128.8 and 129.0 (SC=CS), 132.6 (C=C-H), 160.4 (C=O). MS EI m/e (I%) : 466 (M⁺, 100), 394 (14), 361 (30), 324 (22), 204 (21).

**2-Hydroxymethyl-6,7-bis(pentylsulfanyl)tetrathiafulvalene (9).** To a solution of TTF monoester 8 in dry CH₂Cl₂ (50 mL) (1.16 g; 2.49 mmol) was slowly added at -78°C under nitrogen DiBAl-H 1M solution in hexane (14.9 mL; 14.9 mmol). After stirring for 45 min at -78°C, the reaction mixture was hydrolysed using a solution of HCl 6M/MeOH (1/1) (2 mL). After dilution with CH₂Cl₂ (30 mL), the organic layer was extracted, then washed with an aqueous HCl 1M solution (30 mL), brine (3x50 mL) and dried (MgSO₄). The solvent was removed in vacuo and the residue was purified by chromatography on silica gel using CH₂Cl₂ as the eluent affording orange crystals of 2-(hydroxymethyl)TTF (1.00 g; 92% yield). M.p. = 31-32°C (CH₂Cl₂). ¹H NMR (CDCl₃) δ : 0.90 (t, 6H, CH₂CH₃, 3J = 7 Hz), 1.20-1.50 (m, 8H,
CH₃CH₂CH₃), 1.63 (qu, 4H, SCH₂CH₂), ³J = 7 Hz), 2.03 (br.s, 1H, OH), 2.81 (t, 4H, CH₂S, ³J = 7 Hz), 4.39 (s, 2H, CH₂OH), 6.22 (s, 1H, CH). MS EI m/e (I%): 438 (M⁺, 100), 366 (20), 333 (31), 296 (23), 176 (27).

6,7-Bis(ethylenedisulfanyl)-2-formyl-3-diethylacetal tetrathiafulvalene (12). To a freshly distilled (over CaH₂) toluene solution of thiones 10 (10 mmol) and 11 (30 mmol), was slowly added Co₂(CO)₈ under nitrogen. The mixture was refluxed for 5 h. After cooling to room temperature, the solution was filtered over a short silica gel column (CH₂Cl₂). The solvent was removed in vacuo and the residue corresponding to a mixture of symmetrical coupling products and the desired dissymmetrical one, was purified by column chromatography on silica gel (CH₂Cl₂ then CH₂Cl₂/Et₂O; 9/1) to afford 12 as a red solid (13% yield). M.p.= 73-77°C. ¹H NMR (CDCl₃) δ: 1.24 (t, 6H, CH₃), 3.29 (s, 4H, CH₂S), 3.65 (m, 4H, OCH₂), 5.73 (s, 1H, CH), 9.86 (s, 1H, CHO). IR (KBr) cm⁻¹: 1652 (C=O). MS (FAB) calcd for C₁₄H₁₆O₃S₆: 424.125; found: 424.321 (M⁺).

4,5-Bis(dimethylphosphono)methyl-2-thioxo-1,3-dithiole (15). A solution of 4,5-bis(bromomethyl)-2-thioxo-1,3-dithiole 19̅ (1 g; 3.12 mmol) in trimethylphosphite (10 mL) was heated for 2 h at 100°C. The excess of trimethylphosphate was removed in vacuo then dimethyl methylphosphonate was eliminated by distillation under reduced pressure using a Kugelrohr apparatus. The residue was purified by chromatography on silica gel using EtOAc/MeOH (4/1) as the eluent. Recrystallization in CH₂Cl₂/petroleum ether afforded 540 mg of orange crystals (46% yield). M.p. = 105-107°C. ¹H NMR (CDCl₃) δ: 3.23 (d, 4H, CH₂, ²J_H-P = 18.3 Hz), 3.75 (d, 12H, CH₃, ³J_H-P = 10.8 Hz). ¹³C NMR (CDCl₃) δ: 26.4 and 26.5 (2d, CH₂, ¹J_C-P = 145 Hz), 53.9 and 54.0 (2d, CH₃, ²J_C-P = 4.4 Hz), 132.2 (C=C), 210.8 (C=S). IR (KBr) cm⁻¹: 1250 (P=O), 1051 (C=S), 1028 (P-O-C). MS EI m/e (I%): 377 ((M-H)⁺, 60), 301 (82), 269 (44), 193 (100).

2,3-Bis(dimethylphosphono)methyl-6,7-dimethylsulfaltetraethiafulvalene (16). A solution of 2,3-bis(bromomethyl)TTF 20̅ (200 mg; 0.41 mmol) in trimethylphosphite (10 mL) was heated for 1 h 30 at 140°C. After evaporation of the excess trimethylphosphite and elimination of dimethyl methylphosphonate by distillation using the Kugelrohr apparatus (60°C, 9 mm Hg), the residue was purified by chromatography on silica gel using EtOAc/MeOH (9/1) as the mixture of eluents. Recrystallization in CH₂Cl₂/MeOH afforded 90 mg of brown crystals (40% yield). M.p. = 138-140°C. ¹H NMR (CDCl₃) δ: 2.41 (s, 6H, CH₃S), 3.05 (d, 4H, CH₂P, ²J_H-P = 17.8 Hz), 3.78 (d, 12H, CH₃O, ³J = 10.9 Hz). ³¹P NMR (CDCl₃) δ: 25.57. ¹³C NMR (CDCl₃) δ: 19.1 (CH₃S), 26.0 (d, CH₂P, ¹J_C-P = 146 Hz), 53.2 (CH₂O), 107.0 and 112.3 (cent. C=C), 120.8 (C=C-CH₂), 127.5 (S₂C=CS₂). IR (KBr) cm⁻¹: 1253 (P=O), 1029 (P-O-C). MS EI m/e (I%): 540 (M⁺, 45), 525 (9), 390 (12), 91 (66), 45 (100). Elemental analysis for C₁₄H₂₂O₆S₆ P₂ (539.92) calcd. C 31.10 H 4.10 S 35.58 P 11.46; found C 30.75 H 3.88 S 34.10 P 11.12.

Compound (22). To a solution of 2-thioxo-1,3-dithiole 15 (500 mg; 1.32 mmol) in CH₂Cl₂ (15 mL) were added methyl trifluoromethanesulfonate (152 µL; 1.38 mmol). After stirring for 3 h at room temperature, the solvent was removed in vacuo. The residue was dissolved in CH₃CN (5 mL) and propan-2-ol (0.7 mL), then sodium borohydride (52 mg; 1.39 mmol) was added and
stirring was pursued for 15 min. After concentration, the residue was diluted with EtOAc and washed with brine. The organic layer was dried (MgSO₄) and concentrated. The residue was purified by chromatography on silica gel using EtOAc/MeOH (4/1) as the mixture of eluents affording 484 mg of colourless oil (93% yield). ¹H NMR (CDCl₃) δ: 2.26 (s, 3H, CH₃S), 3.04 and 3.06 (2d, 4H, CH₂, ³J_H-P = 18 Hz), 3.78 and 3.80 (2d, 12H, CH₃O, ³J_H-P = 7.3 Hz), 5.83 (s, 3H, CH₃S). ¹³C NMR (CDCl₃) δ: 12.1 (CH₃S), 27.43 and 27.5 (2d, CH₂, ¹J_C-P = 145 Hz), 53.3 (2d, CH₃O, ¹J_C-P = 3 Hz), 58.0 (CH), 117.9 (C=C). IR (KBr) cm⁻¹: 1265 (P=O), 1034 (P-O-C).

**Tetrakis(dimethylphosphono)methyltetrathiafulvalene (17).** To a solution of compound 22 (336 mg; 0.85 mmol) in acetic anhydride (2 mL) was added at 0°C HBF₄.Et₂O 54% (0.23 mL; 0.93 mmol). The reaction mixture was stirred for 4 h at room temperature. After addition of dry Et₂O (40 mL), the dithiolium salt was crystallized overnight at -18°C. The precipitate was filtered. After dissolution in CH₂CN (3 mL), triethylamine (1.3 mL) was added. After stirring for 15 min, the reaction mixture was diluted with CH₂Cl₂, washed with brine and the organic layer was dried and concentrated to afford 230 mg of colourless oil (81% yield). ¹H NMR (CDCl₃) δ: 3.03 (d, 8H, CH₂, ²J_H-P = 18 Hz), 3.75 (d, 48H, CH₃O, ³J_H-P = 10 Hz).

**p-N,N-Dimethylamino styrenyl tetrathiafulvalene (25).** A solution of phosphonium salt 24 (209 mg; 0.40 mmol) in dry THF (10 mL) was cooled to 0°C under nitrogen. t-BuOK (56 mg, 0.50 mmol) was added in one portion, and the resulting red solution was stirred for 15 min before adding a solution of formyl-TTF 1 (46 mg; 0.2 mmol) in dry THF (5mL). The mixture was stirred overnight at room temperature, and the solvent was removed in vacuo. After addition of CH₂Cl₂, the organic layer was washed twice with water, and dried over MgSO₄. The solvent was concentrated and the residue was purified by chromatography on silica gel using CH₂Cl₂/petroleum ether (10/1) as the mixture of eluents. Compound 25 was obtained as small orange pellets (82% yield). M.p. = 205-208°C (CH₂Cl₂). ¹H NMR (CDCl₃) δ: 2.98 (s, 6H, NCH₃), 6.22 (s, 1H, SCH), 6.32 (s, 2H, SCH=CHS), 6.34 (d, 1H, TTFCH=CHR, ³J = 16 Hz), 6.67 (d, 2H, ArH, ³J = 9 Hz), 6.69 (d, 1H, TTFCH=CHR, ³J = 16 Hz), 7.29 6.67 (d, 2H, ArH, ³J = 9 Hz). (HRMS, FAB) m/e 349.006943; C₁₆H₁₅NS₄ requires : 349.008737.

**2,3-Bis(p-N,N-dimethylamino styrenyl)-6,7-bis(ethylenedisulfanyl) tetrathiafulvalene (26).** A solution of phosphonium salt 24 (418 mg; 0.80 mmol) in dry THF (20 mL) was cooled to 0°C under nitrogen. t-BuOK (112 mg; 1.00 mmol) was added in one portion, and the resulting red solution was stirred for 15 min before the addition of a solution of diformyl-TTF 3 (70 mg; 0.2 mmol) in THF (10 mL). The mixture was stirred at room temperature for 2 h, and the solvent was evaporated. After addition of CH₂Cl₂, the organic phase was washed twice with water, and dried over MgSO₄. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel using CH₂Cl₂/cyclohexane (5/1) as the mixture of eluents to give 26 as a red powder (75% yield). One fraction was recrystallized by slow diffusion of MeOH in a CH₂Cl₂ solution of 26 affording orange needles. M.p. = 210-214°C (CH₂Cl₂/MeOH). ¹H NMR
(CDCl₃) δ  3.01 (s, 12H, NCH₃), 3.30 (s, 4H, SCH₂), 6.48 (d, 2H, TTFCH=CHAr, ³J = 16 Hz), 6.70 (d, 4H, ArH, ³J = 9 Hz), 7.05 (d, 2H, TTFCH=CHAr, ³J = 16 Hz), 7.36 (d, 4H, ArH, ³J = 9 Hz). IR (KBr) cm⁻¹: 1590, 1510, 1350, 1165. (MS, FAB+) m/e (I%) : 584 (M⁺, 55), 482 (35), 460 (35), 379 (35).

Crystallographic data: C₂₈N₂S₆, M = 556.70, red needle, 0.60 x 0.23 x 0.20 mm³, monoclinic, space group P₂₁/m, a = 5.754(2) Å, b = 25.392(9) Å, c = 9.862(5) Å, β = 90.90(5)°, V = 1441(1) Å³, Z = 2, ρcalc = 1.280 g/cm³, µ(MoKα) = 0.493 mm⁻¹, F(000) = 556, θmin = 2.5°, θmax = 29.98°, 4606 data unique, parameters = 166, R1 = 0.055 and wR2 = 0.063 using 1687 reflections with I>3σ(I), R1 = 0.119 and wR2 = 0.101 using all data, GOF = 1.042, -0.177 < ∆ρ < 0.229 e.Å⁻³. X-ray data were collected at 293K on a Enraf Nonius Mach3 four circles diffractometer equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SIR) using MolEN package programs and refined on F by full matrix least-squares method with anisotropic thermal parameters for all non-H atoms. Absorption was corrected by DIFABS. CCDC 292490 contains the supplementary crystallographic data for this paper.

Tetrakis(p-N,N-dimethylaminostyrenyl)TTF (27). A solution of phosphonium salt 24 (2.092 g; 4 mmol) in dry THF (30 mL) was cooled to 0°C under nitrogen. t-BuOK (494 mg; 4.40 mmol) was added in one portion, and the resulting red solution was stirred for 15 min before the addition of a solution of tetraformyl-TTF 4 (158 mg; 0.50 mmol) in dry THF (30 mL). The mixture was stirred overnight at room temperature. The reaction mixture was poured onto a magnetically stirred MeOH solution (200 mL). Stirring was pursued for two additional hours. The precipitate obtained was filtered through a frit-glass (N°4) to afford a red-purple microcrystalline powder (312 mg; 80% yield). M.p. = 266-268°C (MeOH). ¹H NMR (CDCl₃) δ 3.01 (s, 24H, NCH₃), 6.53 (d, 4H, TTFCH=CHAr, ³J = 16 Hz), 6.72 (d, 8H, ArH, ³J = 9 Hz), 7.09 (d, 4H, TTFCH=CHAr, ³J = 16 Hz), 7.39 (d, 8H, ArH, ³J = 9 Hz). IR (KBr) cm⁻¹: 1595, 1515, 1350, 1165. (MS, FAB+) m/e (I%) : 784 (M⁺, 40), 639 (40), 538 (60), 470 (60).

4,5-Distyrenyl-2-thioxo-1,3 dithiole (28). To a solution of diphosphonate 15 (450 mg; 1.19 mmol) and freshly distilled benzaldehyde (0.36 mL; 3.55 mmol) in dry THF (10 mL) was added at 0°C a solution of t-BuOK (400 mg; 3.55 mmol) in dry THF (5 mL). After stirring for 45 min, the solvent was removed and the residue was purified by chromatography on silica gel using CH₂Cl₂ as the eluent affording orange crystals (282 mg; 80% yield). M.p. = 266-268°C (MeOH). ¹H NMR (CDCl₃) δ 6.65 (d, 2H, CH, ³J = 16 Hz), 7.18 (d, 2H, CH, ³J = 16 Hz), 7.30-7.60 (m, 10H, H arom.). ¹³C NMR (CDCl₃) δ : 116.7 (S-C-CH=CH-C), 127.0 and 129.1 (C-CH=CH-CH), 129.2 (S-C-CH=CH-C), 134.6 (S-C-CH=CH-C), 135.8 (C-CH=CH-CH), 139.2 (C-CH=CH-CH), 208.6 (C=S). IR (KBr) cm⁻¹: 1068 (C=S). MS EI m/e (I%) : 338 (M⁺, 60), 261 (56), 229 (41), 228 (40).

2,3-Distyrenyl-6,7-bis(methylsulfanyl)tetrathiafulvalene (29). A solution of n-BuLi 1.4 M in hexane (0.26 mL; 0.37 mmol) was added dropwise at -78 °C under argon to a solution of phosphonate 16 (90 mg, 0.166 mmol) in dry THF (4 mL). After stirring for 15 min at -78°C, freshly distilled benzaldehyde (50 µL; 0.5 mmol) was added dropwise. After stirring for 2 h at
room temperature, the solvent was removed. The residue was purified by chromatography on silica gel using petroleum ether/CH₂Cl₂ (4/1) as the mixture of eluents affording red crystals (25 mg; 30% yield). ¹H NMR (CDCl₃) δ: 2.45 (s, 6H, CH₃S), 6.58 (d, 2H, S-C-CH=CH, ³J = 15.7 Hz), 7.22 (d, 2H, S-C-CH=CH, ³J = 15.7 Hz), 7.28–7.50 (m, 12H, C₆H₅-CH=). ¹³C NMR (CDCl₃) δ: 19.9 (CH₃S), 110.8 (cent. C-C), 118.5 (S-C-CH=), 128.1 (S₂C=CS₂), 127.4 and 129.1 (CH-CH-CH=C), 129.5 (S-C-CH=CH), 133.2 (C-⁻C-CH=), 133.6 (CH-CH-CH=C), 137.1 (CH-CH-CH=C).

**2,3,6,7-Tetrahydroxytetrathiafulvalene (30).** To a solution of compound 22 (208 mg; 0.53 mmol) in acetic anhydride (1.2 mL) was added at 0°C HBF₄.Et₂O 54% (0.15 mL; 0.57 mmol. The reaction mixture was stirred for 4 h at room temperature. After dilution with dry Et₂O (25 mL), the dithiolium salt 23 was crystallized overnight at -18°C. The precipitate was filtered. After dissolution in dry CH₂CN (1.8 mL), triethylamine (0.8 mL) was added. After stirring for 15 min, the reaction mixture was diluted with CH₂Cl₂, washed with brine and the organic layer was dried and concentrated. In this case, compound 17 was used without further purification. After addition of dry THF (1.3 mL), freshly distilled benzaldehyde (0.12 mL) and a mixture of CH₂Cl₂/Et₂O (4/1) as the mixture of eluents affording red crystals (25 mg; 40% yield for three steps); Spectroscopic analyses were in agreement with reported data for compound 30, previously synthesized from tetraformylTTF 4 and the corresponding phosphonium salt in a Wittig-type reaction.

**Bis-TTF (31).** To a solution of diphosphonate 15 (58 mg; 0.15 mmol) and monoformalTTF 2 (200 mg; 0.46 mmol) in dry THF (1 mL) was added at 0°C a solution of t-BuOK (51 mg; 0.46 mmol) in dry THF (0.5 mL). After stirring for 30 min, the solvent was removed and the residue was purified by chromatography on silica gel using CS₂ as the eluent. After precipitation using a mixture of CH₂Cl₂/MeOH then filtration, 120 mg (79% yield) of black crystals were isolated (bordeaux in solution). M.p. = 41–42°C. ¹H NMR (CDCl₃) δ: 0.91 and 0.92 (2t, 12H, CH₃-CH₂, ³J = 7 Hz), 1.22-1.44 (m, 16H, CH₂-CH₂), 1.66 (q, 8H, CH₂-CH₂S, ³J = 7 Hz), 2.84 and 2.85 (2t, 8H, CH₂S, ³J = 7 Hz), 6.25 (d, 2H, S-C-CH=CH-C=CH, ³J = 15 Hz), 6.40 (d, 2H, S-C-CH=CH-C=CH), 13.9 and 14.0 (CH₃-CH₂), 22.1 and 22.2 (CH₃-CH₂), 29.3 and 29.4 (CH₂-CH₂S), 30.6 (CH₂-CH₂-CH₂), 36.2 and 36.3 (CH₂S), 110.3 and 110.8 (cent. C=C), 118.1 (S-C-CH=CH-C=CH), 123.6 (S-C-CH=CH-C=CH), 125.4 (S-C-CH=CH-C=CH), 127.6 and 128.0 (PentS-C), 134.3 (S-C-CH=CH=C=CH), 138.6 (S-C-CH=CH=C=CH), 206.5 (C=S). Elemental analysis for C₅₉H₅₀S₁₅ (997.97) calcd. C 46.85 H 5.04 S 48.11; found C 45.66 H 5.00 S 47.41.

**Tris-TTF (32).** To a solution of diphosphonate 16 (53 mg; 0.1 mmol) and monoformalTTF 2 (130 mg; 0.29 mmol) in dry THF (4 mL) was added at 0°C a solution of t-BuOK (32 mg; 0.29 mmol) in dry THF (3 mL). After stirring for 2 h, the solvent was removed and the residue was purified by chromatography on silica gel using CS₂ as the eluent. After precipitation using a mixture of CH₂Cl₂/MeOH then filtration, 63 mg (55% yield) of purple crystals were isolated. M.p. = 70–75°C. ¹H NMR (CDCl₃) δ: 0.90 and 0.91 (2t, 12H, CH₃-CH₂, ³J = 7 Hz), 1.22-1.44
(m, 16H, CH₂-CH₃-CH₂), 1.64 (qu, 8H, CH₂-CH₂S, 3J = 7 Hz), 2.43 (s, 6H, CH₃S), 2.82 and 2.85 (2t, 8H, CH₂S, 3J = 7 Hz), 6.31 (d, 2H, S-C-CH=CH-C=CH, 3J = 15 Hz), 6.32 (d, 2H, S-C-CH=CH-C=CH, 3J = 15 Hz), 6.44 (s, 2H, S-C-CH=CH-C=CH). 13C NMR (CDCl₃) δ: 14.6 (CH₃S), 19.9 (CH₂S), 22.9 (CH₂-CH₂), 30.1 (CH₂-CH₂S), 31.3 (CH₃-CH₂-CH₂), 37.0 (CH₂S), 109.0 and 112.1 (cent. C=C TTF), 110.6 and 112.3 (cent. C=C lateral TTF), 120.4 (S-C=S), 12.9 (CH₂S), 128.1 (CH₂S), 128.5 and 128.7 (PentS-C), 133.2 (S=C-CH=CH-C=CH), 135.6 (S=C-CH=CH-C=CH). MS m/e (I%) 1160 (M⁺, 20), 778 (17), 350 (100).

2-Thioxo-naphtho[2,3-d][1,3]dithiole-5,8-dione (34). To a solution of compound 19 (1.10 g; 3.43 mmol) in dry CH₃CN (60 mL) was added p-benzoquinone (0.38 g; 3.5 mmol) then tetraethylammonium iodide (2.77 g; 11 mmol). The resulting mixture was refluxed under nitrogen for 45 min. After addition of DDQ (1.62 g; 7.1 mmol), the solution was again refluxed for 7 h. The solvent was removed in vacuo and compound 34 was precipitated by addition of MeOH (150 mL). The precipitate was filtered, then washed with MeOH (100 mL), water (100 mL) and Et₂O (100 mL). At this step of purification, the crude material can be used without further purification for subsequent Diels-Alder cycloaddition with cyclopentadiene (see the synthesis of compound 35).

In order to improve its purity, the resulting material was dissolved in CH₂Cl₂, filtered on silica gel using CH₂Cl₂ as the eluent. The filtrate was washed with an aqueous solution of sodium thiosulfate, dried (MgSO₄) and concentrated to afford compound 34 as yellow-orange crystals. M.p. = 240-242°C (CH₂Cl₂). 1H NMR (CDCl₃) δ: 7.05 (s, 2H, H-C=C-H), 8.16 (s, 2H, H-C=C-C=O). IR (KBr) cm⁻¹: 1657 (C=O), 1076 (C=S). MS EI m/e (I%) 264 (M⁺, 100), 220 (45), 192 (18).

Compound (35). To a suspension of compound 34 (1.15 g; 4.35 mmol) in dry THF (100 mL) was added freshly distilled cyclopentadiene (1.78 mL; 22 mmol). The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel using CH₂Cl₂ as the eluent to furnish yellow crystals (1.21 g; 59 % yield calculated from 19). M.p. = 198°C (The temperature of the retroDiels-Alder reaction from 35 was determined to start at 198°C with the formation of compound 34 as yellow-orange crystals for which the melting point was noted at 240-242°C). 1H NMR (CDCl₃) δ: 1.50-1.60 (m, 2H, CH₂), 3.50 (dd, 2H, CH-C=O, 3J = 2 Hz, 3J = 1.5 Hz), 3.65-3.72 (m, 2H, CH-CH₂), 5.97 (t, 2H, H-C=C-H, 3J = 2 Hz), 8.06 (s, 2H, H-C=C-C=O). 13C NMR (CDCl₃) δ: 50.1 (CH₂), 50.2 and 50.6 (CO-CH-CH), 120.5 (H-C=C-C=O), 134.7 (H-C=C-C=O), 136.3 (H-C=C-H), 148.2 (S=C=C=S), 196.8 (C=O), 224.0 (C=S). IR (KBr) cm⁻¹: 1674 (C=O), 1055 (C=S). MS EI m/e (I%) : 330 (M⁺, 35), 264 (100), 220 (39), 66 (37). Elemental analysis for C₁₆H₁₀O₂S₃ (329.98) calcd. C 58.16, H 3.05, S 29.11; found: C 57.41, H 3.08, S 28.74.

4,5-Bis(pentylsulfanyl)-2-dimethoxyphosphoryl-2-yl-1,3-dithiole (36). Phosphonate 36 was prepared as beige crystals according to the reported procedure. 1H NMR (CDCl₃) δ: 0.91 (t, 6H, CH₃CH₂), 3J = 7 Hz), 1.25-1.50 (m, 8H, CH₃CH₂CH₂), 1.60-1.80 (m, 4H, CH₂CH₂S), 2.75 (ddd, 2H, CH₃H₄S, 3J = 12.8 Hz, 3J = 6.7 Hz and 3J = 7.7 Hz), 2.82 and 2.85 (2t, 8H, CH₂S, 3J = 7 Hz), 6.31 (d, 2H, S-C-CH=CH-C=CH, 3J = 15 Hz), 6.32 (d, 2H, S-C-CH=CH-C=CH, 3J = 15 Hz), 6.44 (s, 2H, S-C-CH=CH-C=CH). 13C NMR (CDCl₃) δ: 14.6 (CH₃S), 19.9 (CH₂S), 22.9 (CH₂-CH₂), 30.1 (CH₂-CH₂S), 31.3 (CH₃-CH₂-CH₂), 37.0 (CH₂S), 109.0 and 112.1 (cent. C=C TTF), 110.6 and 112.3 (cent. C=C lateral TTF), 120.4 (S-C=S), 12.9 (CH₂S), 128.1 (CH₂S), 128.5 and 128.7 (PentS-C), 133.2 (S=C-CH=CH-C=CH), 135.6 (S=C-CH=CH-C=CH). MS m/e (I%) 1160 (M⁺, 20), 778 (17), 350 (100).
2.88 (dd, 2H, CH₃H₂S, ^2J = 12.8 Hz, ^3J = 6.7 Hz and ^4J = 7.7 Hz), 3.87 (d, 6H, CH₃O, ^3J_H-P = 10.6 Hz), 4.74 (d, 1H, CH, ^2J_H-P = 5.5 Hz). ^13C NMR (CDCl₃) δ: 13.8 (CH₃CH₂), 22.0 (CH₂CH₂), 29.2 (CH₂CH₂S), 30.5 (CH₃CH₂CH₂), 36.0 (CH₂S), 41.0 (d, CH-P, ^1J_C-P = 160 Hz), 54.4 (d, CH₃O, ^2J_C-P = 7.2 Hz), 125.3 (C=C). MS EI m/e (I%) : 416 (M⁺, 22), 307 (100), 237 (19), 167 (19), 43 (42). Elemental analysis for C₁₃H₂₅O₃S₄ (416.07) calc. C 43.24, H 7.02, S 30.79; found : C 43.36, H 6.81, S 30.92.

**Compound (37).** To a solution of phosphonate 36 (1.13 g; 2.72 mmol) in dry THF (20 mL) was added dropwise at -78°C under argon n-BuLi 1.5 M in hexane (2.0 mL; 3 mmol). After stirring for 15 min at -78°C, a solution of compound 35 (300 mg; 0.91 mmol) in dry THF (15 mL) was added dropwise. The reaction mixture was stirred for 2 h until the temperature arose to progressively -20°C. After addition of MeOH, the precipitate was filtered, then washed with MeOH and compound 37 was isolated as yellow lemon crystals (767 mg; 93% yield). M.p. = 130-132°C (MeOH/THF). ^1H NMR (CDCl₃) δ : 0.83 and 0.87 (2t, 12H, CH₃, ^3J = 7 Hz), 1.20-1.80 (m, 26H, CH₃-CH₂-CH₂-CH₂, CH-CH₂), 2.60-2.92 (m, 8H, CH₂S), 3.04 (br.s., 2H, =C-CH-CH), 3.32 (br.s., 2H, =C-CH-CH), 5.41 (br.s., 2H, H-C=CH, 7.24 (s, 2H, S-C=CH-C). ^13C NMR (CDCl₃) δ : 14.6 (CH₃), 22.8 (CH₃-CH₂), 30.0 and 30.1 (CH₃-CH₂-CH₂-CH₂), 31.3 and 31.4 (CH₃-CH₂-CH₂-CH₂), 36.9 (CH₂S), 47.7 (=C-CH-CH), 49.2 (=C-CH-CH), 50.2 (=C-CH-CH), 118.7 (S-C=CH-C), 123.9 (S₂=C=C-C), 126.7 and 127.4 (S₂=C=CS₂), 130.9 (S₂=C=C-C), 135.2 (H=C=C-H), 136.4 (S=C=CH-C), 139.4 (S=C=CH-C), 211.8 (C=S). IR (KBr) cm⁻¹ : 1060 (C=S). MS FAB⁺ m/e (I%) : 911 ((M+H)+, 10), 844 (100), 612 (27), 582 (39), 538 (33), 329 (46). Elemental analysis for C₄₂H₃₄S₁₁ (910.12) calc. C 55.34, H 5.97; found : C 55.06, H 6.10.

**Compound (18).** A solution of compound 37 (200 mg; 0.22 mmol) in trimethylphosphite (2 mL) was heated at 140°C for 1 h. The solution was cooled then concentrated in vacuo. The residue was purified by chromatography on silica gel using petroleum ether/CH₂Cl₂ (7/3) as the mixture of eluents to afford TTF 38 as orange crystals (40 mg; 21% yield), then the oxo derivative 39 as orange crystals (9 mg; 4% yield). Elution using petroleum ether/EtOAc (1/1) as the mixture of eluents afforded an orange oil corresponding to phosphonate 18 (77 mg; 35% yield) which was isolated as a mixture of two stereoisomers in a 68/32 ratio. ^1H NMR (CDCl₃) δ : 0.85-0.95 (m, 12H, CH₃-CH₂), 1.28-1.55 (m, 18H, CH₃-CH₂-CH₂-CH₂, CH-CH₂), 1.57-1.70 (m, 8H, CH₃-CH₂-CH₂-CH₂), 2.75-2.92 (m, 8H, CH₂S), 3.25 (br.s., 2H, =C-CH-CH), 3.31 (br.s., 2H, =C-CH-CH), 3.79 (68%) and 3.83 (32%) (2d, 6H, CH₃O, ^3J_H-P = 10.5 Hz), 4.90 (68%) and 5.05 (32%) (2d, 1H, H-C-P, ^2J_H-P = 5.2 Hz), 5.43 (68%) and 5.45 (32%) (2t, 2H, H-C=CH, ^3J = 1.6 Hz, ^4J = 1.6 Hz), 7.05 (68%) and 7.13 (32%) (s, 2H, CH arony). ^13C NMR (CDCl₃) δ : 14.6 (CH₃), 22.8 (CH₃-CH₂), 30.0 (CH₃-CH₂-CH₂-CH₂), 31.3 (CH₃-CH₂-CH₂-CH₂), 36.8 (CH₂S), 44.8 (d, H-C-P, ^1J_C-P = 159 Hz), 47.6 (=C-CH-CH), 48.8 (=C-CH-CH), 50.3 (=C-CH-CH₂-CH₂), 55.1 and 55.3 (CH₃O), 119.5 and 119.9 (S=C-CH-C), 124.5 and 124.7 (S₂=C=C-C), 126.8 and 127.0 (S₂=C=CS₂), 128.6 (S₂=C=C-C), 134.7 and 134.9 (S=C=CH-C), 135.2 (H=C=C-H). IR (KBr) cm⁻¹ : 1260 (P=O), 1034 (P-O-C). MS FAB⁺ m/e (I%) : 989 ((M+H)+, 10), 922 (100), 813 (17), 660 (15), 616 (7), 551 (7). MS Maldi-ToF m/e (I%) : 922 (M-C₆H₆, 100). Elemental analysis for C₄₄H₆₁O₅S₁₀P (988.16) calc. C 53.40, H 6.21; S 32.40; found : C 53.03, H 6.18; S 31.44.
**Compound (41).** To a solution of phosphonate 18 (245 mg; 0.25 mmol) in dry THF (6 mL) was added dropwise at -78 °C under argon n-BuLi 1.5 M in hexane (0.17 mL; 0.25 mmol). After stirring for 15 min at -78°C, a solution of 1,4-terephthaldehyde (11 mg; 0.08 mmol) in dry THF (1 mL) was added dropwise. The reaction mixture was stirred for 3 h at room temperature then concentrated in vacuo. The residue was purified by chromatography on silica gel using petroleum ether/CH₂Cl₂ (4/1) as the mixture of eluents to afford extended-TTF 41 as orange crystals (78 mg; 51% yield). Elution with CH₂Cl₂ furnished compound 40 as red crystals (12 mg; 15% yield). Compound 41 was isolated as a mixture of cis/trans stereoisomers in a ratio : 50/50. 

**Compound (40).** M.p. = 63-65°C (CH₂Cl₂/petroleum ether). ¹H NMR (CDCl₃) δ : 0.88 and 0.92 (2t, 12H, CH₂), 1.10-1.50 (m, 20H, CH₂-CH₂-S), 1.70-1.95 (8H, CH₂), 3.07 (br.s., 2H, =C-CH-CH₂), 5.48 (br.s., 2H, CHO-CH-CH₂), 6.64 (s, 1H, H-C=CS₂), 7.16 and 7.19 (2s, 2H, S-C-CH=C), 7.47 (d, 2H, CHO-C-CH=C, 3J = 8 Hz), 7.88 (d, 2H, CHO-C-CH=C, 3J = 8 Hz), 9.97 (s, 1H, CHO). IR (KBr) cm⁻¹ : 1695 (C=O). MS FAB⁺ m/e (I%): 1862((M+H)⁺, 19), 1794/1792 (M+C₃H₆, 26/19), 1728/1726 (M₂C₅H₆, 100/50), 1466 (50), 1438 (80). **Elemental analysis** for C₆₀H₁₄₄O₆S₁₀ (1858.33) calcd. C 59.37, H 6.17; found : C 58.66, H 6.15. **Compound (42).** A solution of TTF 41 (75 mg; 4.10⁻⁵ mol) in o-dichlorobenzene (3 mL) was refluxed for 15 min. The solvent was distilled using a Kugelrohr apparatus (50°C, 9 mm Hg). Extended-TTF 42 was isolated as bordeaux crystals (69 mg; quantitative yield). M.p. = 70-72°C. ¹H NMR (C₆D₆, 340 K) δ : 0.85-1.00 (m, 24H, CH₂), 1.00-1.80 (m, 48H, CH₃-CH₂-CH₂-CH₂), 2.50-2.90 (m, 16H, CH₂S), 6.42 (s, 4H, H-C=CS₂), 7.23 (s, 2H, C=CH=CS₂), 7.74 and 7.78 (2s, 4H, S-C=CH-C), protons of the central benzene ring are masked by the peak of the solvent. **MS Maldi-Tof m/e:** 1728 (M⁺). **Elemental analysis** for C₅₂H₁₀₂O₁₀S₂₀ (1726.24) calcd. C 56.96, H 5.95, S 37.09; found : C 56.61, H 5.89, S 36.84. **Compound (43).** To a solution of phosphonate 18 (240 mg; 0.24 mmol) in dry THF (4 mL) was added dropwise at -78 °C under argon atmosphere n-BuLi 2.2 M in hexane (0.11 mL; 0.24 mmol). After stirring for 15 min at -78°C, a solution of 1,3,5-triformylbenzene ²⁵ (10 mg; 0.06 mmol) in dry THF (1 mL) was added dropwise. The reaction mixture was stirred for 4 h at room temperature then concentrated in vacuo. The residue was purified by chromatography on silica
gel using petroleum ether/CH₂Cl₂ (7/3) as the mixture of eluents to afford compound 43 as orange crystals (101 mg; 60% yield). The product was isolated as a mixture of cis/trans stereoisomers in a ratio: 50/50. ¹H NMR (CDCl₃) δ: 0.80-1.10 (m, 36H, CH₃), 1.25-1.55 (m, 54H, CH₂CH₂CH₂CH₂, CH-CH₂), 1.55-1.75 (m, 24H, CH₃CH₂CH₂CH₂), 2.60-2.96 (m, 24H, CH₂S), 3.07 and 3.09 (2 br.s., 6H, =C-CH=CH), 3.34 (br.s., 6H, =C-CH=CH), 5.50 (br.s., 6H, H-C=C-H), 6.63 (50%) and 6.65 (50%) (2s, 3H, S₂C=CH-C), 7.10-7.20 (m, 3H, S-C=CH-C+ C₆H₃ arom.).

¹³C NMR (CDCl₃) δ: 14.6 (CH₃), 22.9 (CH₃CH₂), 30.1 (CH₃CH₂CH₂CH₂), 31.4 (CH₃CH₂CH₂CH₂), 36.9 (CH₂S), 47.8 (=C-CH=CH), 48.9 (=C-CH=CH), 50.4 (=C-CH=CH=CH₂), 115.5 (S₂C=CH-Ar), 118.4 and 119.2 (S-C=CH=C), 124.8 (S₂C=C-C), 126.8 and 127.0 (S₂C=CS₂), 128.7 (S₂C=C-C), 133.4, 134.3, 134.9, 135.1, 137.6, 137.7 (=C-CH=CS₂, H-C=C-H, S-C=CH-C, C₆H₃ arom.).

Elemental analysis for C₁₃₅H₁₆₈S₃₀ (2748.48) calcd. C 58.90, H 6.15, S 34.95; found : C 57.67, H 6.02, S 34.30.

**Compound (44).** A solution of TTF 43 (77 mg; 2.8.10⁻⁵ mol) in o-dichlorobenzene (3 mL) was refluxed for 15 min. The solvent was distilled using a Kugelrohr apparatus (50°C, 9 mm Hg). Extended-TTF was isolated as red bordeaux crystals (71 mg; quantitative yield). M.p. = 92-95°C. MS Maldi-Tof m/e : 2554 (M⁺). Elemental analysis for C₁₂₀H₁₁₈S₃₀ (2550.34) calcd. C 56.42, H 5.92, S 37.66; found : C 56.13, H 5.84, S 37.52.

**Supplementary Information Available**

X-ray crystallography data for compound 26 as CIF files.

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**References and Footnotes**