

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 π -extension of such resulting TTF derivatives.

Keywords: Tetrathiafulvalene, MagtrieveTM, Wittig, HWE olefination, π -conjugation

Introduction

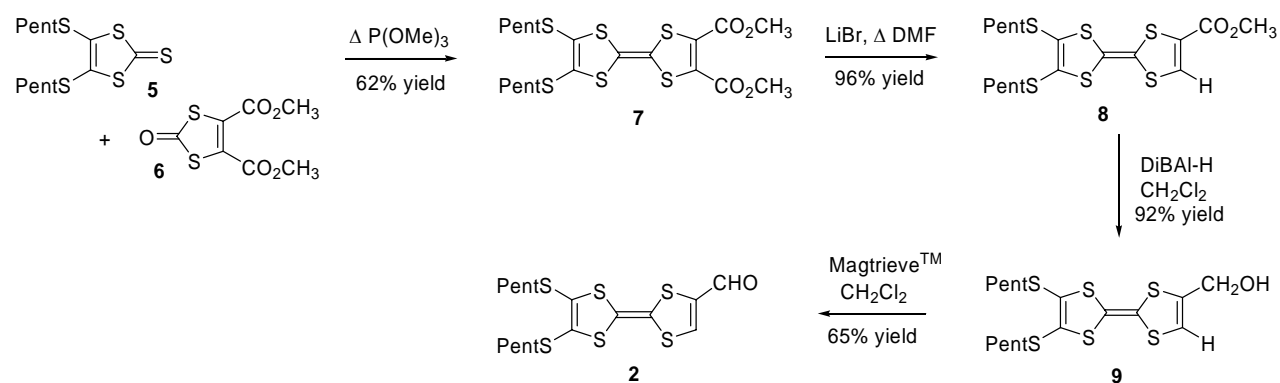
There is currently an important interest in achieving the syntheses of tetrathiafulvalene (TTF) derivatives in order to improve the electroconducting properties of the corresponding charge-transfer complexes or cation radical salts.¹ It is well established that stabilization of the metallic state of these materials may be reached by increasing their dimensionality,² which can be achieved chemically by subtle molecular engineering around the electroactive TTF framework.^{3,4,5} An active trend consists in the synthesis of highly extended and/or S-rich TTF analogues.⁵ The effects which are expected from such extended π -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

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.

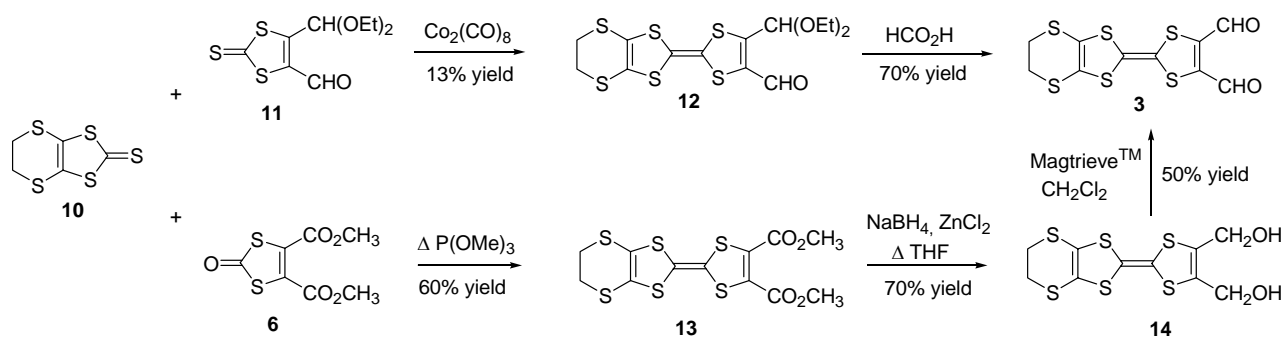
Synthesis of monoformyl TTF **2** was carried out according to a multi-step strategy (Scheme 3). The initial trimethylphosphite-mediated cross-coupling of the two corresponding 2-(thi)oxo-1,3-dithiole moieties **5** and **6** afforded 2,3-*bis*(methoxycarbonyl)TTF **7** in 62% yield, according to a known 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 MnO₂¹⁰ or SeO₂¹¹ 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 MagtrieveTM (CrO₂) 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 Co₂(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 MagtrieveTM 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.



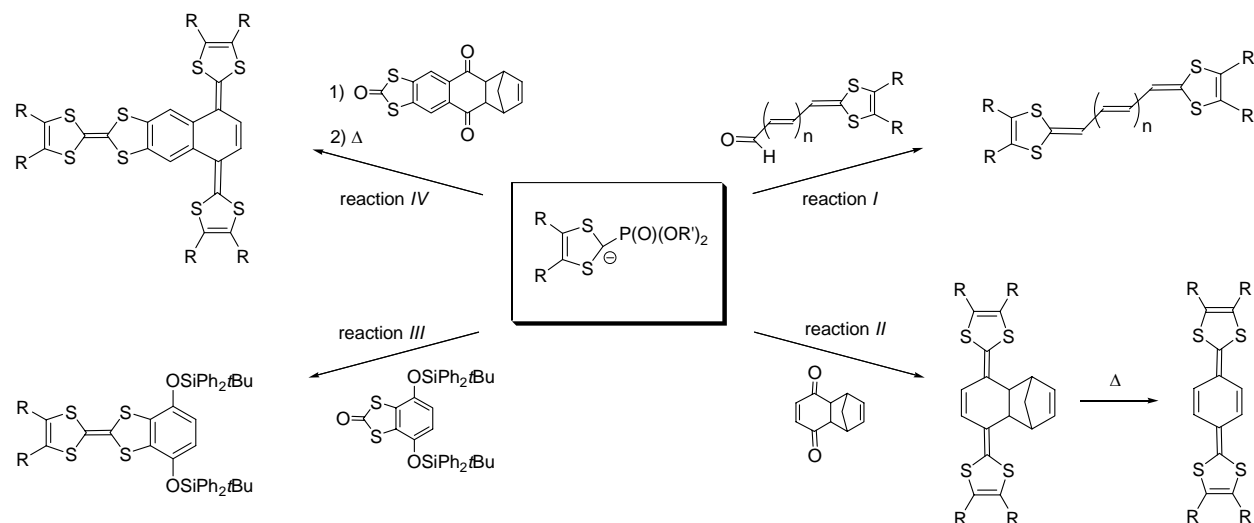
Scheme 4

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

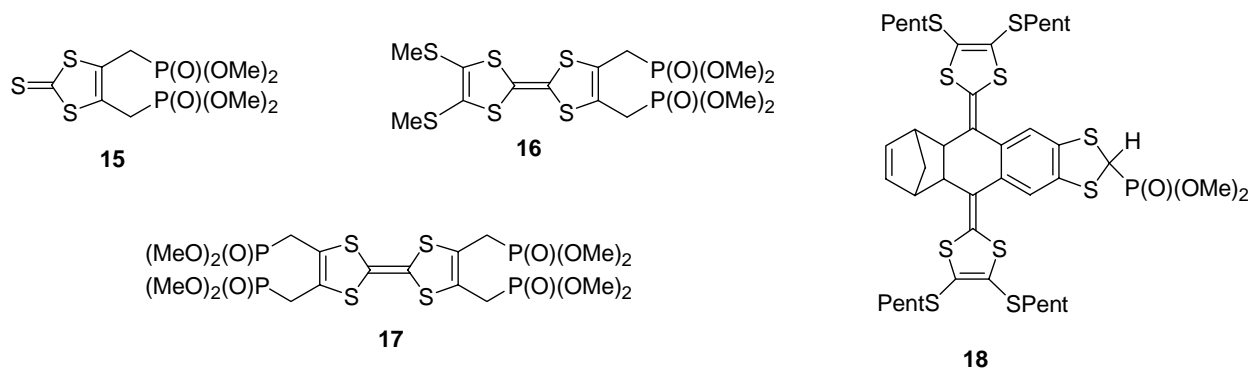
Synthesis of TTF-phosphonate derivatives

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 *I*, 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).

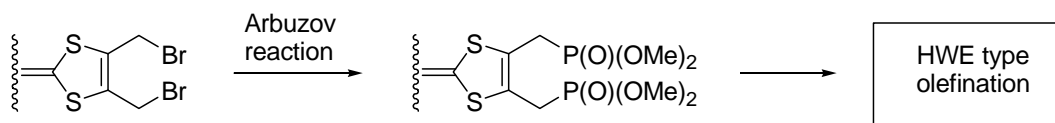


Scheme 5



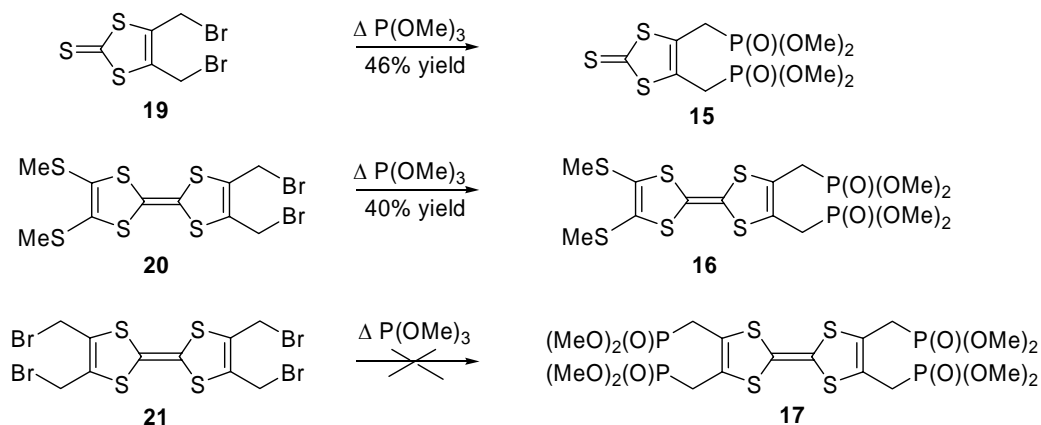
Scheme 6

The reactivity of the vicinal *bis*(bromomethyl) group has been demonstrated with the possibility of generating the corresponding diene by reductive elimination^{18,19} or to perform its transformation into the pyrrolo group.²⁰ 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).



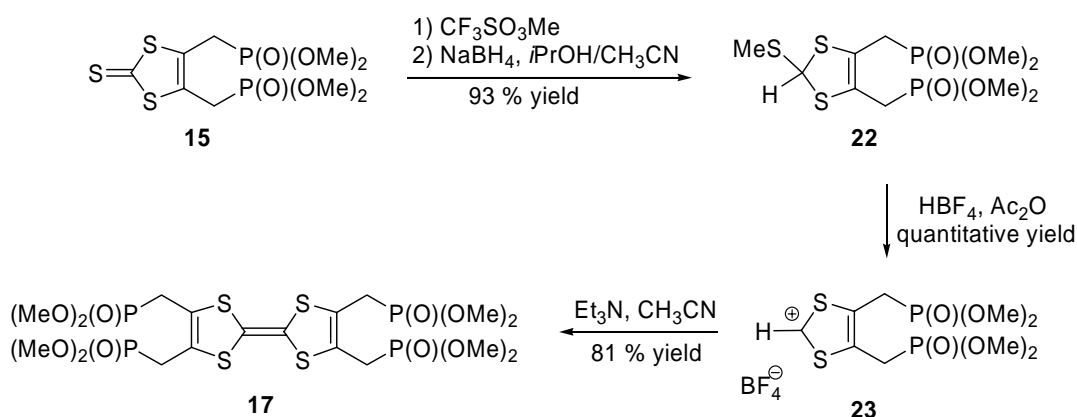
Scheme 7

The Arbuzov reaction was achieved by treatment of 2,3-bis(bromomethyl)-2-thioxo-1,3-dithiole **19**¹⁴ or TTF **20**²¹ in refluxing trimethylphosphite. The corresponding phosphonate derivatives **15** and **16** were isolated in 46 % and 40% yield respectively. Unfortunately, starting from *tetrakis*(bromomethyl)TTF **21**²¹ and using the same experimental procedure, we were not able to obtain the tetraphosphonate **17** (Scheme 8).



Scheme 8

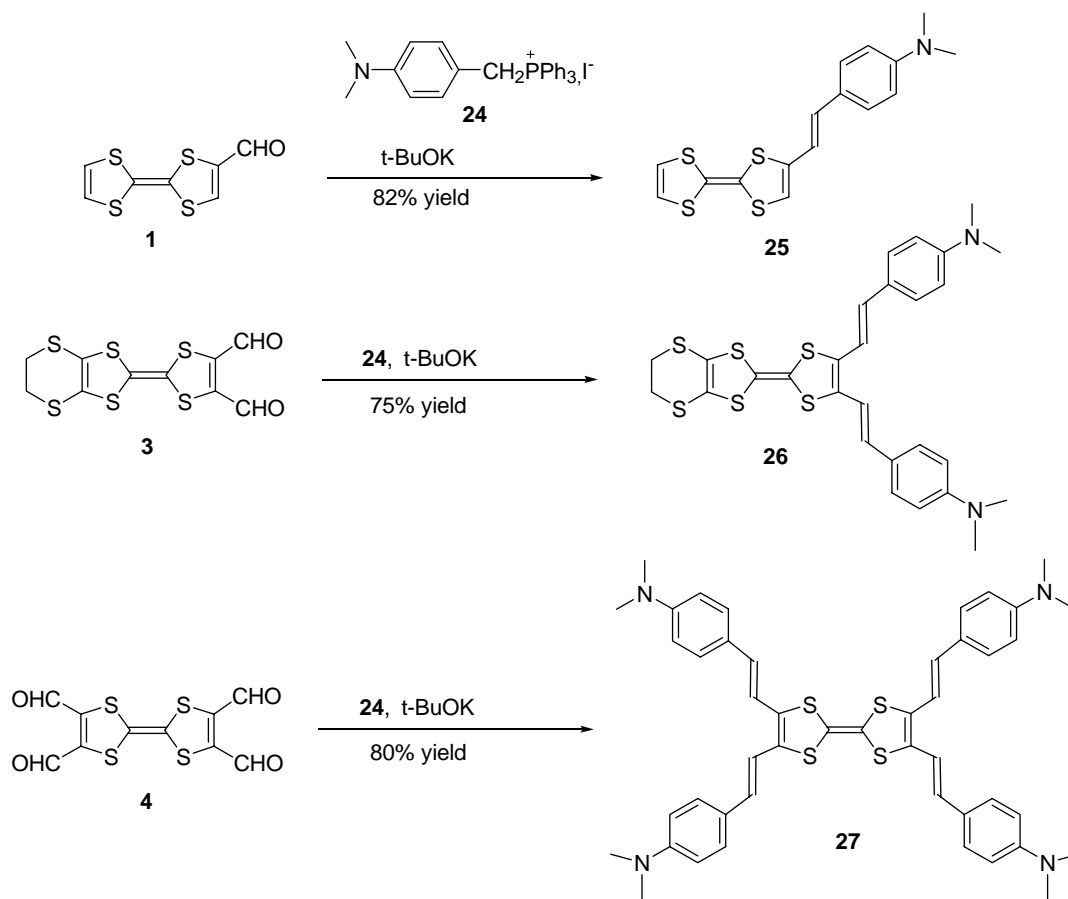
To circumvent this difficulty, another synthetic method was developed to reach compound **17**. Methylation of **15** with methyl triflate followed by reduction with sodium borohydride afforded compound **22** in an overall 93% yield. The 1,3-dithiolium salt **23** was produced in quantitative yield 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 π -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 *t*BuOK from **24**²² 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 ¹H-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 π -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.

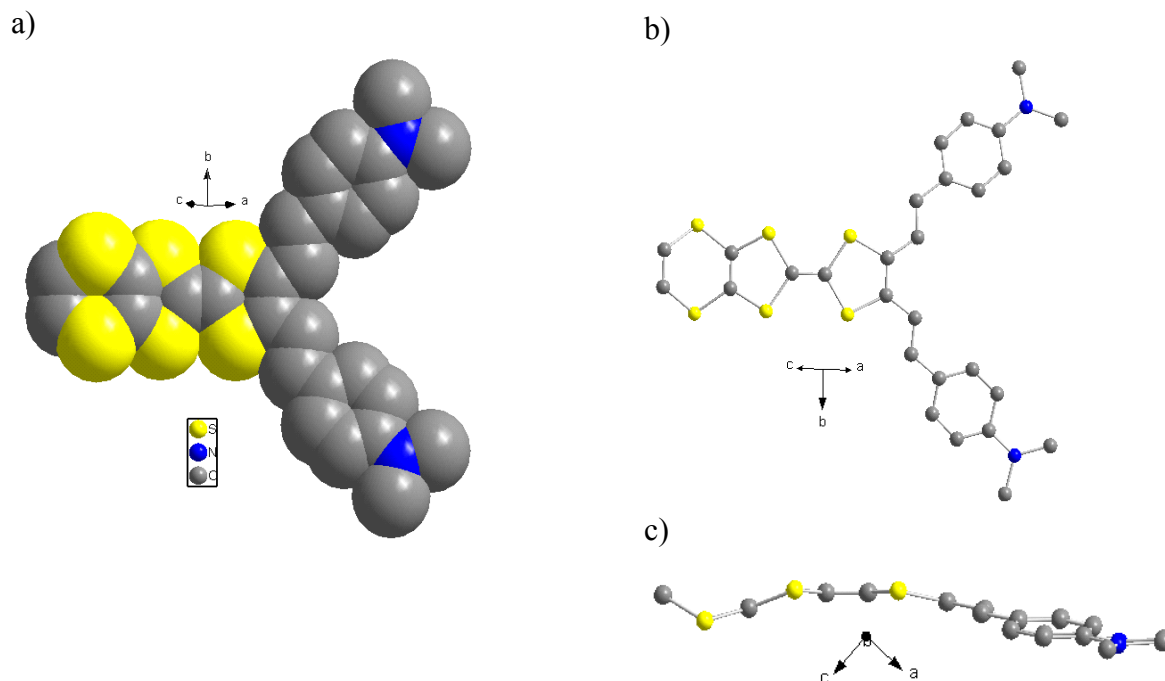
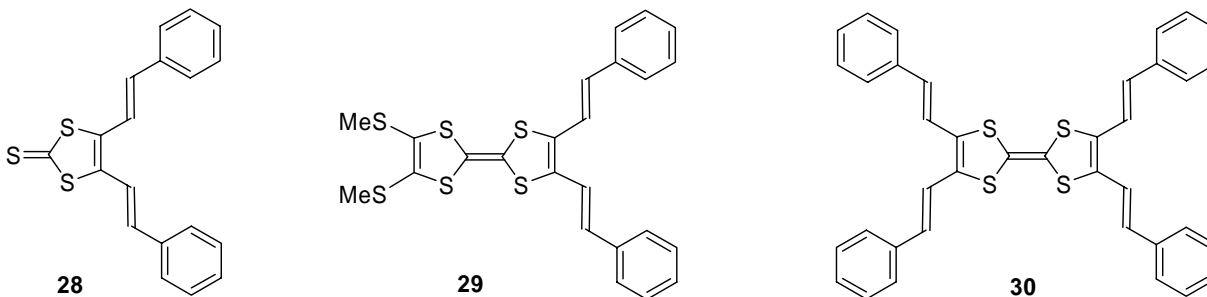


Figure 1 : Molecular structure of **26** according to X-ray diffraction: a) space-filling model; b) 2D-extension of the π -system; c) projection onto the *ac* plane.

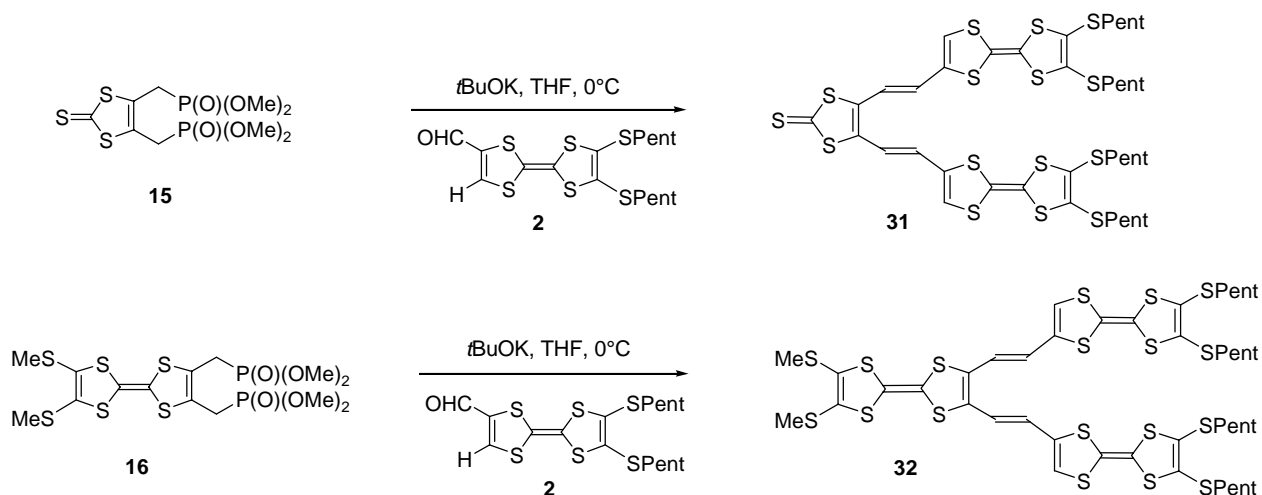
Styrenyl- TTF derivatives **28**, **29** and **30**

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 ¹H NMR spectroscopy of compounds **28-30** was consistent with the *E* configuration for all double bonds created.



Scheme 11

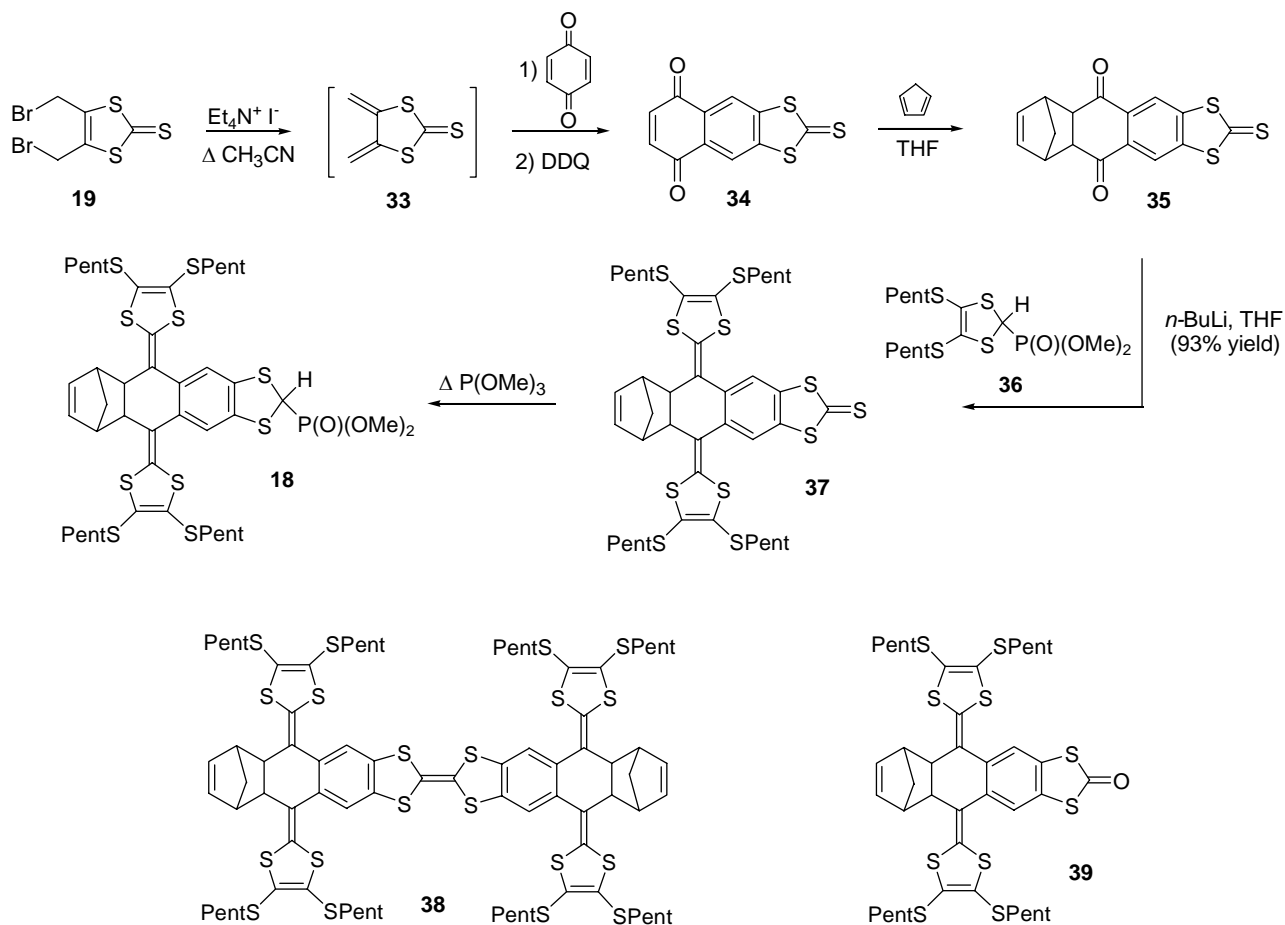
This reactivity was extended to novel conjugated dimeric and trimeric TTF. Deprotonation using *t*BuOK or BuLi followed by the addition of adequately substituted *monoformyl*TTF **2** led to the corresponding dimeric TTF **31** and trimeric TTF **32** (Scheme 12). Yields in the HWE reaction were notably 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**¹⁴ (Scheme 13). Subsequent reductive elimination carried out using $\text{Et}_4\text{N}^+ \text{I}^-$ 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.¹⁶ 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.²³ We noted also the transformation of the thioxo derivative onto the oxo analogue **39**.²⁴ These three compounds were easily separated by silica gel column chromatography affording successively TTF derivative **38**, then the oxo derivative **39** (petroleum ether/ CH_2Cl_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.



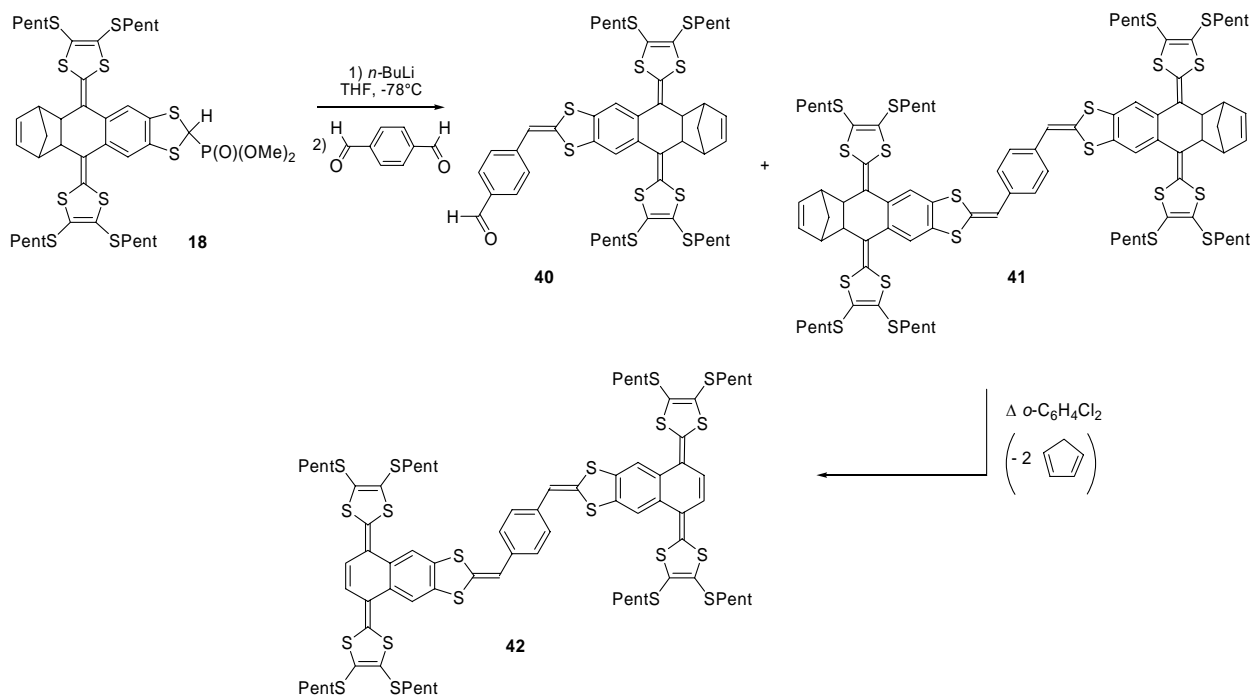
Scheme 13

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 terephthalaldehyde 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 *retro*Diels-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 *o*-dichlorobenzene solution of product **41**.

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

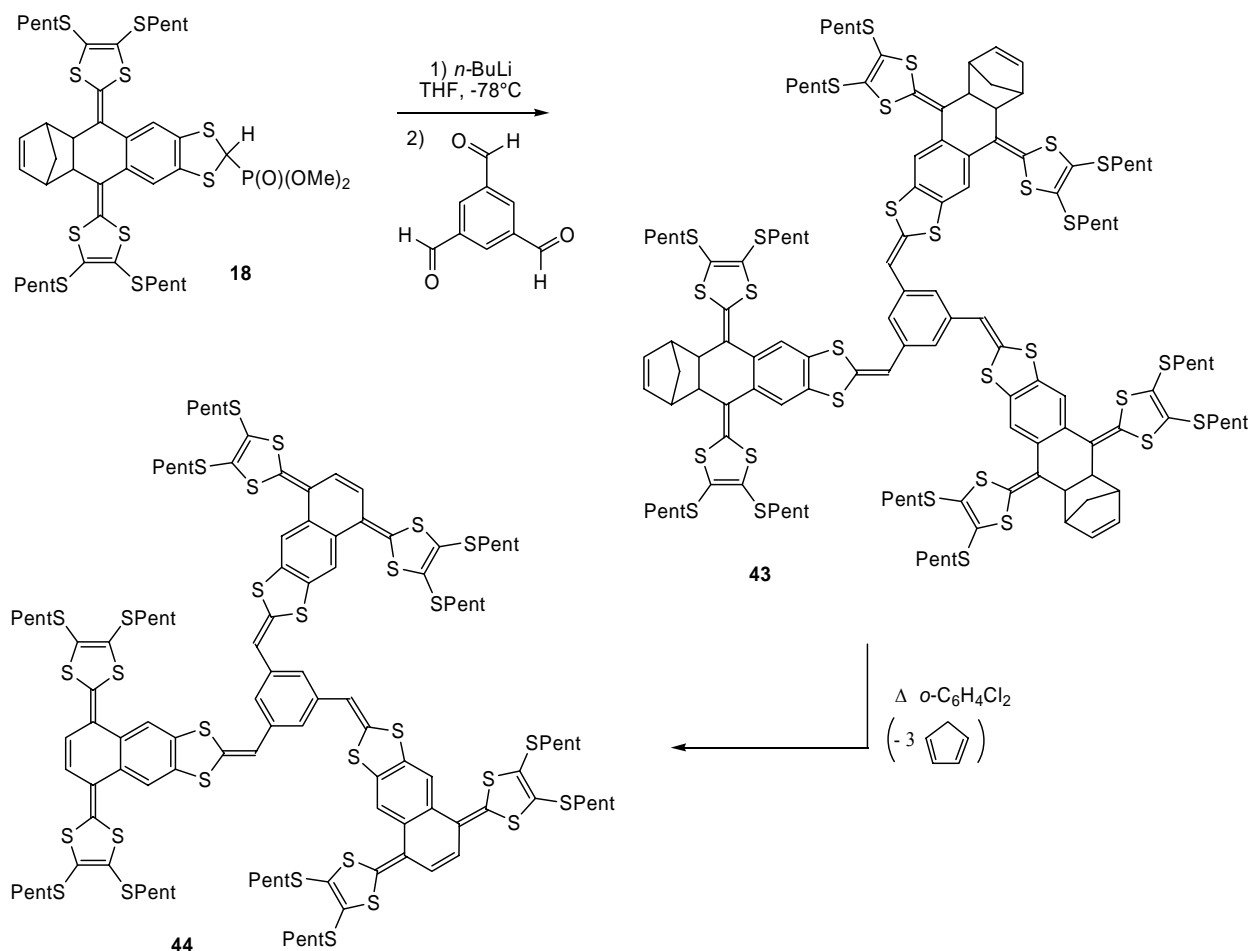
Starting material	Concentration of 37 or 39 in P(OMe) ₃	Time (h)	Reaction temperature (°C)	Yield of phosphonate 18 (%)	Yield of TTF 38 (%)	Yield of 39 (%)
37	0.04 M	3	90	28	0	34
37	0.04 M	4	140	31	9	14
37	0.11 M	1	140	35	21	4
37	0.22 M	1.5	140	28	21	0
39	0.037 M	24	140	41	traces	0
39	0.11 M	24	140	33	2	0



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*((triphenylphosphonium)methyl)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-triformylbenzene²⁵ 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 *o*-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 MagtrieveTM 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. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 200 (200 MHz), Bruker ACX 400 (400 MHz) or Bruker 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 Bruker 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). ¹H NMR (CDCl₃) δ : 0.90 (t, 6H, CH₂CH₃, ³J = 7 Hz), 1.25-1.45 (m, 8H, CH₂CH₂CH₃), 1.63 (qu, 4H, SCH₂CH₂, ³J=7 Hz), 2.80 and 2.81 (2t, 4H, CH₂S, ³J = 7 Hz), 7.44 (s, 1H, =CH), 9.47 (s, 1H, CHO). ¹³C NMR (CDCl₃) δ : 14.6 (CH₂CH₃), 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=C), 140.2 (C=C-H), 141.9 (=C-CHO), 180.2 (C=O). MS EI m/e (I%) : 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 MgSO_4 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 **14**¹⁴ (200 mg; 0.56 mmol) in a THF (20 mL) / CH_2Cl_2 (20 mL) mixture at room temperature, was added MagtrieveTM (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 CH_2Cl_2 /petroleum ether (7/3) as the mixture of eluents to afford dialdehyde **3** as deep blue needles (101 mg; 50%). M.p. = 210-211°C (toluene). ¹H NMR (CDCl_3) δ : 3.30 (s, 4H, CH_2), 10.21 (s, 2H, CHO). IR (KBr): 1650 and 1690 cm^{-1} (C=O). MS *m/e* (*I*%) : 350 (M^+ , 100). Elemental analysis for $\text{C}_{10}\text{H}_6\text{O}_2\text{S}_6$ (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 trimethylphosphite (200 mL) was heated at 80°C for 4 h. Trimethylphosphite was removed *in vacuo* and the residue was purified by chromatography on silica gel using CH_2Cl_2 /petroleum ether (1/4) as the mixture of eluents to remove 2,3,6,7-tetrakis(pentylsulfanyl)TTF. Further elution using CH_2Cl_2 /petroleum ether (7/3) as the mixture of eluents afforded 6.50 g (62% yield) of dissymmetrical TTF as a purple oil. ¹H NMR (CDCl_3) δ : 0.89 (t, 6H, $\text{CH}_3\text{-CH}_2$, ³J = 7 Hz), 1.30-1.40 (m, 8H, $\text{CH}_3\text{-CH}_2\text{-CH}_2$), 1.55-1.65 (m, 4H, $\text{CH}_2\text{-CH}_2\text{S}$), 2.80 (t, 4H, CH_2S , ³J = 7 Hz), 3.83 (s, 6H, CH_3O).

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 (MgSO_4) and the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel using CH_2Cl_2 as the eluent affording a red oil (2.56 g; 96% yield). ¹H NMR (CDCl_3) δ : 0.89 (t, 6H, CH_2CH_3 , ³J = 7 Hz), 1.20-1.50 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.63 (qu, 4H, SCH_2CH_2 , ³J = 7 Hz), 2.80 and 2.81 (2t, 4H, CH_2S , ³J = 7 Hz), 3.81 (s, 3H, OCH_3), 7.34 (s, 1H, CH). ¹³C NMR (CDCl_3) δ : 14.6 (CH_2CH_3), 22.8 (CH_2CH_3), 31.3 (SCH_2CH_2), 30.1 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 37.0 (SCH_2), 53.4 (CH_3O), 110.7 and 111.6 (cent. C=C), 128.0 ($=\text{C-CO}_2\text{Me}$), 128.8 and 129.0 ($\text{SC}=\text{CS}$), 132.6 ($\text{C}=\text{C-H}$), 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 CH_2Cl_2 (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 CH_2Cl_2 (30 mL), the organic layer was extracted, then washed with an aqueous HCl 1M solution (30 mL), brine (3x50 mL) and dried (MgSO_4). The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel using CH_2Cl_2 as the eluent affording orange crystals of 2-(hydroxymethyl)TTF (1.00 g; 92% yield). M.p. = 31-32°C (CH_2Cl_2). ¹H NMR (CDCl_3) δ : 0.90 (t, 6H, CH_2CH_3 , ³J = 7 Hz), 1.20-1.50 (m, 8H,

$\text{CH}_2\text{CH}_2\text{CH}_3$), 1.63 (qu, 4H, SCH_2CH_2 , $^3J = 7$ Hz), 2.03 (br.s., 1H, OH), 2.81 (t, 4H, CH_2S , $^3J = 7$ Hz), 4.39 (s, 2H, CH_2OH), 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 CaH_2) toluene solution of thiones **10** (10 mmol) and **11** (30 mmol), was slowly added $\text{Co}_2(\text{CO})_8$ under nitrogen. The mixture was refluxed for 5 h. After cooling to room temperature, the solution was filtered over a short silica gel column (CH_2Cl_2). 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 (CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$; 9/1) to afford **12** as a red solid (13% yield). M.p. = 73-77°C. $^1\text{H NMR}$ (CDCl_3) δ : 1.24 (t, 6H, CH_3), 3.29 (s, 4H, CH_2S), 3.65 (m, 4H, OCH_2), 5.73 (s, 1H, CH), 9.86 (s, 1H, CHO). *IR (KBr) cm^{-1}* : 1652 (C=O). *MS (FAB) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}_8$* : 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 **19**¹⁴ (1 g; 3.12 mmol) in trimethylphosphite (10 mL) was heated for 2 h at 100°C. The excess of trimethylphosphite 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 CH_2Cl_2 /petroleum ether afforded 540 mg of orange crystals (46% yield). M.p. = 105-107°C. $^1\text{H NMR}$ (CDCl_3) δ : 3.23 (d, 4H, CH_2 , $^2J_{\text{H-P}} = 18.3$ Hz), 3.75 (d, 12H, CH_3 , $^3J_{\text{H-P}} = 10.8$ Hz). $^{13}\text{C NMR}$ (CDCl_3) δ : 26.4 and 26.5 (2d, CH_2 , $^1J_{\text{C-P}} = 145$ Hz), 53.9 and 54.0 (2d, CH_3 , $^2J_{\text{C-P}} = 4.4$ 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-dimethylsulfanyltetrathiafulvalene (16). A solution of 2,3-bis(bromomethyl)TTF **20**²¹ (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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ afforded 90 mg of brown crystals (40% yield). M.p. = 138-140°C. $^1\text{H NMR}$ (CDCl_3) δ : 2.41 (s, 6H, CH_3S), 3.05 (d, 4H, CH_2P , $^2J_{\text{H-P}} = 17.8$ Hz), 3.78 (d, 12H, CH_3O , $^3J = 10.9$ Hz). $^{31}\text{P NMR}$ (CDCl_3) δ : 25.57. $^{13}\text{C NMR}$ (CDCl_3) δ : 19.1 (CH_3S), 26.0 (d, CH_2P , $^1J_{\text{C-P}} = 146$ Hz), 53.2 (CH_3O), 107.0 and 112.3 (cent. C=C), 120.8 ($\text{C}=\text{C}-\text{CH}_2$), 127.5 ($\text{S}_2\text{C}=\text{CS}_2$). *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 $\text{C}_{14}\text{H}_{22}\text{O}_6\text{S}_6$ 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 CH_2Cl_2 (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 CH_3CN (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, ²J_{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, ²J_{C-P} = 3 Hz), 58.0 (CH), 117.9 (C=C). IR (KBr) cm⁻¹: 1265 (P=O), 1034 (P-O-C). MS EI m/e (I%): 394 (M⁺, 1), 346 (100), 221 (33).

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 CH₃CN (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, CH₃, ³J_{H-P} = 10 Hz). ¹³C NMR (CDCl₃) δ: 26.7 (d, CH₂, ²J_{C-P} = 140 Hz), 53.7 (CH₃), 108.4 (cent. C=C), 121.5 (C=C). MS EI m/e (I%): 692 (M⁺, 6), 110 (100).

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 (5 mL). 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=CHAr, ³J = 16 Hz), 6.67 (d, 2H, ArH, ³J = 9 Hz), 6.69 (d, 1H, TTFCH=CHAr, 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

($CDCl_3$) δ 3.01 (s, 12H, NCH_3), 3.30 (s, 4H, SCH_2), 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 : $C_{28}N_2S_6$, $M = 556.70$, red needle, $0.60 \times 0.23 \times 0.20$ mm³, monoclinic, space group $P2_1/m$, $a = 5.754(2)$ Å, $b = 25.392(9)$ Å, $c = 9.862(5)$ Å, $\beta = 90.90(5)^\circ$, $V = 1441(1)$ Å³, $Z = 2$, $\rho_{calc} = 1.280$ g/cm³, $\mu(MoK\alpha) = 0.493$ mm⁻¹, $F(000) = 556$, $\theta_{min} = 2.5^\circ$, $\theta_{max} = 29.98^\circ$, 4606 data unique, parameters = 166, $R1 = 0.055$ and $wR2 = 0.063$ using 1687 reflections with $I > 3\sigma(I)$, $R1 = 0.119$ and $wR2 = 0.101$ using all data, $GOF = 1.042$, $-0.177 < \Delta\rho < 0.229$ e.Å⁻³. X-ray data were collected at 293K on a Enraf Nonius Mach3 four circles diffractometer equipped with a graphite monochromator utilizing $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SIR) using MolEN package programs²⁷ 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**²² (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-violet microcrystalline powder (312 mg; 80% yield). M.p. = 266-268°C (MeOH). ¹H NMR ($CDCl_3$) δ 3.01 (s, 24H, NCH_3), 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 CH_2Cl_2 as the eluent affording orange crystals (282 mg; 70% yield). M.p. = 154-155°C (CH_2Cl_2). ¹H NMR ($CDCl_3$) 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 ($CDCl_3$) δ : 116.7 (S-C- $\underline{C}H=CH-C$), 127.0 and 129.1 (C- $\underline{C}H=CH-CH$), 129.2 (S-C- $\underline{C}H=CH-C$), 134.6 (S-C- $\underline{C}H=CH-C$), 135.8 (C- $\underline{C}H=CH-CH$), 139.2 ($\underline{C}-CH=CH-CH$), 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 μ L; 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 (S-C-CH=), 133.6 (CH-CH-CH-C), 137.1 (CH-CH-CH-C).

2,3,6,7-Tetrastirenyltetrathiafulvalene (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 CH₃CN (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; 1.15 mmol) and a solution of *t*-BuOK (129 mg; 1.15 mmol) in dry THF (0.7 mL) were added successively. After stirring for 30 min at room temperature, the purple precipitate was filtered and washed with THF (65 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.^{13b}

Bis-TTF (31). To a solution of diphosphonate **15** (58 mg; 0.15 mmol) and monoformylTTF **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, CH₃-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, ³J = 15 Hz), 6.55 (s, 2H, S-C-CH=CH-C=CH). ¹³C NMR (CDCl₃) δ: 13.9 and 14.0 (CH₃-CH₂), 22.1 and 22.2 (CH₃-CH₂), 29.3 and 29.4 (CH₂-CH₂S), 30.6 (CH₃-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 C₃₉H₅₀S₁₅ (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 monoformylTTF **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, CH₃-CH₂-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 (CH₃-CH₂), 19.9 (CH₃S), 22.9 (CH₃-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-CH=CH-C=CH), 122.0 (S-C-CH=CH-C=CH), 125.0 (S-C-CH=CH-C=CH), 128.1 (CH₃S-C), 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 FAB⁺ (m-NBA) (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**¹⁴ (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-CO). 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 *retro*Diels-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.^{7f} M.p. = 47°C (EtOAc/petroleum ether). 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, CH₂CH₂S, ²J = 12.8 Hz, ³J = 6.7 Hz and ³J = 7.7 Hz),

2.88 (ddd, 2H, $\text{CH}_2\text{H}_b\text{S}$, $^2J = 12.8$ Hz, $^3J = 6.7$ Hz and $^3J = 7.7$ Hz), 3.87 (d, 6H, CH_3O , $^3J_{\text{H-P}} = 10.6$ Hz), 4.74 (d, 1H, CH, $^2J_{\text{H-P}} = 5.5$ Hz). ^{13}C NMR (CDCl_3) δ : 13.8 (CH_3CH_2), 22.0 (CH_3CH_2), 29.2 ($\text{CH}_2\text{CH}_2\text{S}$), 30.5 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 36.0 (CH_2S), 41.0 (d, CH-P, $^1J_{\text{C-P}} = 160$ Hz), 54.4 (d, CH_3O , $^2J_{\text{C-P}} = 7.2$ Hz), 125.3 (C=C). MS EI m/e ($I\%$): 416 (M^+ , 22), 307 (100), 237 (19), 167 (19), 43 (42). Elemental analysis for $\text{C}_{15}\text{H}_{29}\text{O}_3\text{PS}_4$ (416.07) calcd. 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 $n\text{-BuLi}$ 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. = $130\text{-}132^\circ\text{C}$ (MeOH/THF). ^1H NMR (CDCl_3) δ : 0.83 and 0.87 (2t, 12H, CH_3 , $^3J = 7$ Hz), 1.20-1.80 (m, 26H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$, CH-CH_2), 2.60-2.92 (m, 8H, CH_2S), 3.04 (br.s., 2H, =C-CH-CH), 3.32 (br.s., 2H, =C-CH-CH), 5.41 (br.s., 2H, H-C=C-H), 7.24 (s, 2H, S-C=CH-C). ^{13}C NMR (CDCl_3) δ : 14.6 (CH_3), 22.8 ($\text{CH}_3\text{-CH}_2$), 30.0 and 30.1 ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 31.3 and 31.4 ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 36.9 (CH_2S), 47.7 (=C-CH-CH), 49.2 (=C-CH-CH), 50.5 (=C-CH-CH-CH $_2$), 118.7 (S-C=CH-C), 123.9 ($\text{S}_2\text{C}=\text{C-C}$), 126.7 and 127.4 ($\text{S}_2\text{C}=\text{CS}_2$), 130.9 ($\text{S}_2\text{C}=\text{C-C}$), 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 $\text{C}_{42}\text{H}_{54}\text{S}_{11}$ (910.12) calcd. 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/ CH_2Cl_2 (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 (CDCl_3) δ : 0.85-0.95 (m, 12H, $\text{CH}_3\text{-CH}_2$), 1.28-1.55 (m, 18H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$, CH-CH_2), 1.57-1.70 (m, 8H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 2.75-2.92 (m, 8H, CH_2S), 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, CH_3O , $^3J_{\text{H-P}} = 10.5$ Hz), 4.90 (68%) and 5.05 (32%) (2d, 1H, H-C-P, $^2J_{\text{H-P}} = 5.2$ Hz), 5.43 (68%) and 5.45 (32%) (2t, 2H, H-C=C-H, $^3J = 1.6$ Hz, $^3J = 1.6$ Hz), 7.05 (68%) and 7.13 (32%) (s, 2H, CH arom). ^{13}C NMR (CDCl_3) δ : 14.6 (CH_3), 22.8 ($\text{CH}_3\text{-CH}_2$), 30.0 ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 31.3 ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 36.8 (CH_2S), 44.8 (d, H-C-P, $^1J_{\text{C-P}} = 159$ Hz), 47.6 (=C-CH-CH), 48.8 (=C-CH-CH), 50.3 (=C-CH-CH-CH $_2$), 55.1 and 55.3 (CH_3O), 119.5 and 119.9 (S-C=CH-C), 124.5 and 124.7 ($\text{S}_2\text{C}=\text{C-C}$), 126.8 and 127.0 ($\text{S}_2\text{C}=\text{CS}_2$), 128.6 ($\text{S}_2\text{C}=\text{C-C}$), 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 $^+$ $m\text{-NBA}$ 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-C $_3$ H $_6$, 100). Elemental analysis for $\text{C}_{44}\text{H}_{61}\text{O}_3\text{S}_{10}\text{P}$ (988.16) calcd. 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-terephthalaldehyde (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/ CH_2Cl_2 (4/1) as the mixture of eluents to afford extended-TTF **41** as orange crystals (78 mg; 51% yield). Elution with CH_2Cl_2 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. $^1\text{H NMR}$ (CDCl_3) δ : 0.88 and 0.92 (2t, 24H, CH_3), 1.10-1.50 (m, 40H, $\text{CH}_3\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}$), 1.50-1.80 (m, 16H, $\text{CH}_2\text{-CH}_2\text{-S}$), 1.70-1.95 (16H, CH_2S), 3.07 (br.s., 4H, $=\text{C-CH-CH-CH}_2$), 3.34 (br.s., 4H, $=\text{C-CH-CH-CH}_2$), 5.48 (br.s., 4H, CH-CH=CH-CH), 6.56 (s, 2H, H-C=CS_2), 7.11 and 7.13 (2s, 4H, S-C-CH=C), 7.35 (d, 1H, C=CH-CH=C). $^{13}\text{C NMR}$ (CDCl_3) δ : 14.6 (CH_3), 22.9 ($\text{CH}_3\text{-CH}_2$), 30.1 ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 31.4 ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 36.8 (CH_2S), 47.7 ($=\text{C-CH-CH}$), 48.9 ($=\text{C-CH-CH}$), 50.4 ($=\text{C-CH-CH-CH}_2$), 115.4 ($\text{S}_2\text{C=CH-Ar}$), 118.3 and 119.1 (S-C=CH-C), 124.8 and 124.8 ($\text{S}_2\text{C=C-C}$), 126.8 and 127.0 ($\text{S}_2\text{C=CS}_2$), 126.9 (C=CH-CH=C), 127.7 (C=CH-CH=C), 128.5 and 128.6 ($\text{S}_2\text{C=C-C}$), 133.0 and 133.4 ($=\text{C-CH=CS}_2$), 134.9 (H-C=C-H), 134.5, 134.7, 135.2 (S-C=CH-C *cis/trans*). *MS FAB*⁺ *m-NBA m/e (I%)* : 1862((M+H)⁺, 19), 1794/1792 ($\text{M-C}_3\text{H}_6$, 26/19), 1728/1726 ($\text{M-2C}_3\text{H}_6$, 100/50), 1466 (50), 1438 (80). *Elemental analysis* for $\text{C}_{92}\text{H}_{114}\text{S}_{20}$ (1858.33) calcd. C 59.37, H 6.17; found : C 58.66, H 6.15.

Compound (40). M.p. = $63\text{-}65^{\circ}\text{C}$ (CH_2Cl_2 /petroleum ether). $^1\text{H NMR}$ (CDCl_3) δ : 0.88 and 0.92 (2t, 12H, CH_3), 1.10-1.50 (m, 20H, $\text{CH}_3\text{-CH}_2\text{-CH}_2$, $\text{CH}_2\text{-CH}$), 1.50-1.80 (m, 8H, $\text{CH}_2\text{-CH}_2\text{S}$), 1.70-1.95 (8H, CH_2S), 3.07 (br.s., 2H, $=\text{C-CH-CH-CH}_2$), 3.34 (br.s., 2H, $=\text{C-CH-CH-CH}_2$), 5.48 (br.s., 2H, CH-CH=CH-CH), 6.64 (s, 1H, H-C=CS_2), 7.16 and 7.19 (2s, 2H, S-C-CH=C), 7.47 (d, 2H, CHO-C-CH=CH , $^3\text{J} = 8$ Hz), 7.88 (d, 2H, CHO-C-CH=CH , $^3\text{J} = 8$ Hz), 9.97 (s, 1H, CHO). *IR (KBr)* cm^{-1} : 1695 (C=O). *MS FAB*⁺ *m/e (I%)* : 997 ((M+H)⁺, 16), 930 (100), 668 (62), 624 (55). *Elemental analysis* for $\text{C}_{50}\text{H}_{60}\text{OS}_{10}$ (996.14) calcd. C 60.19, H 6.06, S 32.14; found : C 59.24, H 6.14, S 31.78.

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. = $70\text{-}72^{\circ}\text{C}$. $^1\text{H NMR}$ (C_6D_6 , 340 K) δ : 0.85-1.00 (m, 24H, CH_3), 1.00-1.80 (m, 48H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 2.50-2.90 (m, 16H, CH_2S), 6.42 (s, 4H, H-C=C-H), 7.23 (s, 2H, C-CH=CS_2), 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 $\text{C}_{82}\text{H}_{102}\text{S}_{20}$ (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-triformylbenzene²⁵ (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, CH₃-CH₂-CH₂-CH₂, CH-CH₂), 1.55-1.75 (m, 24H, CH₃-CH₂-CH₂-CH₂), 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 (CH₃-CH₂), 30.1 (CH₃-CH₂-CH₂-CH₂), 31.4 (CH₃-CH₂-CH₂-CH₂), 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 C₁₂₀H₁₅₀S₃₀ (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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