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Highly extended, planar and sulfur-rich tetrathiafulvalene derivatives: towards an increased dimensionality of organic metals

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Summary — Highly extended π-donors **1–3** have been obtained through twofold or fourfold Wittig olefinations of polyformyl tetrathiafulvalenes with P-ylids bearing the 1,3-dithiol-2-ylidene moiety. Their powerful π-donor properties as well as their ability to generate cation-radical salts of mixed valency have been evaluated by both classical and thin layer cyclic voltammetry. Such extended π-donors prove to be planar in the neutral state, with very short intramolecular S···S distances, as demonstrated by the X-ray diffraction study of the model compound **16b**. Such extended sulfur-rich tetrathiafulvalene derivatives are prone to generate highly dimensional materials as demonstrated in the case of the **3a**.ClO_4 cation-radical salt which presents a unique type of two-dimensional network in the solid-state.

tetrathiafulvalene (TTF) / π-donor molecule / organic metal / Wittig reaction

Résumé — Dérivés du tétrathiafulvalène, à grande extension spatiale et enrichis en atomes de soufre: vers des métaux organiques à dimensionalité accrue. *Les donneurs à systèmes-π très étendus* **1-3** *sont obtenus par double ou quadruple oléfinations de dérivés polyformylés du tétrathiafulvalène, à l'aide d'ylures de phosphore porteurs de groupements 1,3-dithiol-2-ylidène. Leur exceptionnel pouvoir donneur-π, ainsi que leur aptitude à générer des sels de radicaux-cations à valence mixte, ont été évalués aussi bien par voltampérométrie cyclique classique qu'en couche mince. De tels donneurs-π s'avèrent plans à l'état neutre, avec de très faibles distances S···S intramoléculaires, comme le démontre l'étude par diffraction de rayons-X d'un composé modèle. Ces dérivés à grande extension spatiale s'avèrent être de bons candidats pour l'obtention de matériaux à dimensionalité accrue, comme c'est le cas pour le sel de radical-cation* **3a**.ClO_4, *qui présente un réseau bidimensionnel original à l'état solide.*

tétrathiafulvalène (TTF) / donneur-π / métaux organique / réaction de Wittig

The synthesis in the early 70's of the tetrathiafulvalene (bi-[1,3-dithiol-2-ylidene]) (TTF) system as a precursor of organic metallic conductors [1, 2] provided chemists with a unique opportunity to prepare a wide variety of π-donor molecules [3].

Nevertheless, most of the cation-radical salts (CRSs) obtained by electrooxidation of such π-donors undergo a breakdown of their conductivity when the temperature is decreased. It is now well established that, in order to stabilize the metallic state at low temperature, one should increase the dimensionality of the materials. This requirement is satisfied in the case of a set of bis(ethylenedithio)tetrathiafulvalene superconducting CRSs which exhibit numerous S···S intermolecular interactions in the solid state, leading to various types of bidimensional networks within a series of structural polymorphs [4].

For some years we have been interested in the design of new TTF derivatives prone to generate highly dimensional materials [5–8]. In this context we have notably focused on the synthesis of planar, highly extended and sulfur rich TTF derivatives such as **1–3** [5].

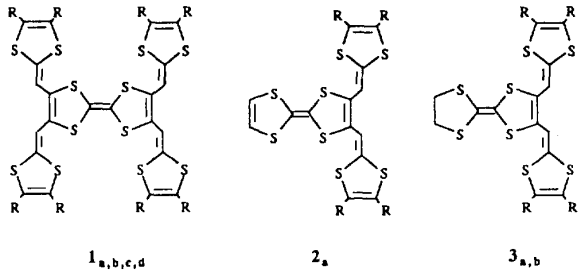

Fig 1

* Correspondance and reprints

This class of compounds is of interest for both electronic and crystallographic reasons: the substitution of the TTF skeleton by two or four π-donating redox functionalities, namely 1,4-dithiafulven-6-yl((1,3-dithiol-2-ylidene)methyl) substituents, should result in (i) an enhancement of the π-donor ability of the molecule and (ii) easier access to highly oxidized states thanks to a lowering of the Coulombic repulsions within the charged species [9]. From a structural point of view, their planar and extended bidimensional T-shape may induce favorable stacking modes associated to efficient overlapping in the solid state. Also, the accumulation of S-atoms in each individual component is expected to promote many intermolecular S···S interactions, hence the enhancement of the dimensionality of the corresponding CRSs.

In the present paper we describe the synthesis of compounds **1–3**, their electrochemical behavior as evaluated by means of classical and thin layer cyclic voltammetry, their electrooxidation, and some characterizations of corresponding organic metals [5].

Results and discussion

Compounds **1–3** may be considered as resulting from the conjugation of two or four dithiafulvenyl substituents through a central TTF unit. Therefore, the straightforward synthetic strategy to reach these polyolefinated compounds lies in twofold or fourfold Wittig reactions between the corresponding polyformyl TTF (or dihydro-TTF) and substituted Akiba's reagents, ie, phosphorus ylids **W** bearing the 1,3-dithiol-2-ylidene moiety [10] (fig 2).

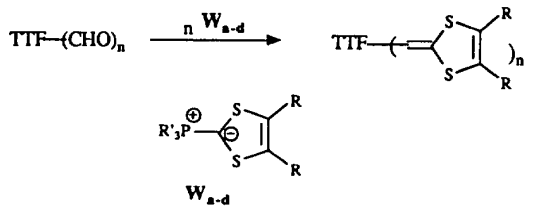

Fig 2

This strategy requires prior grafting of the aldehydic functionality onto the TTF core. Tetraformyltetrathiafulvalene **4** is prepared according to our previously described procedure [11], through the preparation of several 4,5-diformyl-2-oxo- or 2-thioxo-1,3-dithioles **9**, **9′**, possibly mono- or bisacetalized **8**, **10**, resulting from interaction between acetylenedicarbaldehyde mono-di(Et)-acetal [12] and ethylenetrithiocarbonate (fig 3). Note also that this strategy has been generalized to the Se series [13].

According to their disymmetrical character, the preparation [5] of the diformyl derivatives **5** and **6** first involves a cross-coupling of the mono- **8** or bis-protected **10** dialdehydes with either the non-substituted dithiolethione or ethylenetrithiocarbonate (fig 4). Different combinations have been tried starting from **8**, **8′** or **10**, **10′**, and using various coupling reagents ($Co_2(CO)_8$, $P(OR)_3$, PPh_3). The best yields were obtained using

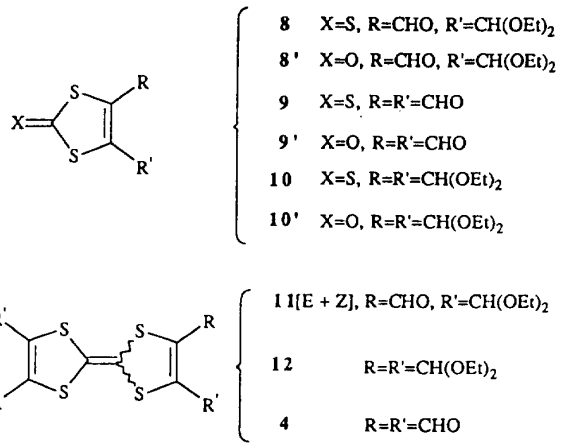

Fig 3

(i) $Co_2(CO)_8$, **8** and 3-thioxo-1,2-dithiole to build the TTF skeleton of **5**, and (ii) $P(OEt)_3$, **10** and ethylenetrithiocarbonate to reach the dihydro-TTF core of **6**.

In order to fully utilize the diformyl thiones **8** or **10** in the formation of the expected cross-coupling products **13** or **14**, a large excess of the readily prepared 2-thioxo-1,3-dithiole and the commercially available (Fluka) ethylenetrithiocarbonate was used.

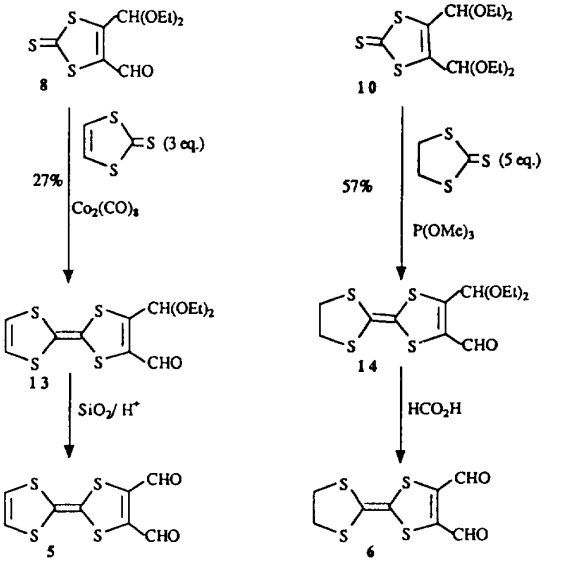

Fig 4

Such a procedure allowed isolation of the ketal aldehyde-TTF **13** in a 27% yield. Classical formolysis having failed in this case, the required final deacetalization could be performed using the wet silica-gel technique to quantitatively afford the diformyl-TTF **5**. In the case of the dihydro-TTF series, the coupling step was performed in a similar way in fairly good yield (57%). The product, isolated by silica-gel chromatography, corresponded in this case to the partially-hydrolyzed compound **14**. This was then quantitatively

formolyzed to afford the diformyl dihydro-TTF **6** as dark blue needles.

A similar strategy has been used in our parallel work with Fabre to reach the selenium or the mixed sulfur-selenium dissymmetrical series, using the corresponding selenated starting materials [14].

The following step to obtain highly extended TTF-derivatives lies in the di- or tetra-Wittig olefinations of polyaldehydes **4–6** using the phosphorous reagents **Wa-d**. Although the corresponding phosphonate anions are known to be more powerful nucleophilic species, phosphorous ylids **Wa-d** (generated from the corresponding phosphonium salts at −78 °C/THF/BuLi), have proven reactive enough to achieve the required polyolefinations of **4–6** (fig 5).

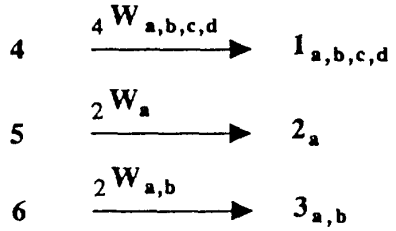

Fig 5

All of these reactions proceed in quite good yields (54–82%) when one considers that in each case a di- or tetraolefination is performed to finally reach the target extended π-systems **1–3** which contain four (compounds **1**) and six sulfur containing heterocycles (compounds **2**, **3**) respectively, instead of only two in the starting polyaldehydes **4–6**. It should be noted that a large variety of R substituents for **W** is accessible, so that one may easily increase either the solubility or the π-donating ability (or both) of the target molecules.

Indeed, the presence of solubilizing substituents on the periphery of these extended π-donors (-SCH_3, -$(CH_2)_4$-, -CO_2CH_3), has allowed fairly easy NMR spectroscopy characterizations ($CDCl_3$ or CS_2 as NMR solvents). On the other hand, the sparingly soluble compounds with R = H have required the use of DMSO-d_6.

Note that Wittig reactions performed on **5** unexpectedly led to poorly stable compounds except in the case of the sparingly soluble derivative **2a**.

From a structural point of view, it is considered that a prerequisite for π-donor molecules to behave as good precursors of conducting CRS lies in their planar character in order to promote proper stacking mode of overlapping in the solid state. Nevertheless, when contemplating molecular models, there was no evidence of planarity in systems such as **1–3**. They revealed strong 1,5-S···S intramolecular interactions which lead to a distortion of the models and force the dithiafulvenyl substituents out of the central TTF plane (see fig 7). Since our attempts at obtaining single crystals of **1** failed, we synthesized the more soluble derivatives **16a,b** and **16'b**, which present the same vicinal bis(dithiafulvenyl) substitution on a 1,3-dithiolylidene moiety. They were prepared as usual through twofold Wittig reactions between **9** or **9'** and **Wa** or **Wb** (fig 6).

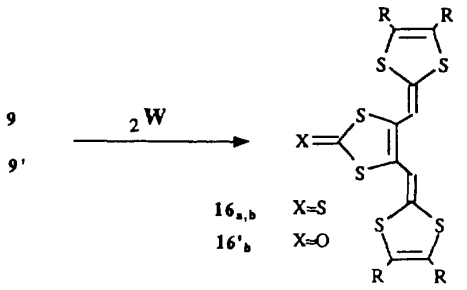

Fig 6

Slow diffusion of *n*-pentane vapors in a methylene chloride solution of **16b** allowed formation of single crystals, the X-ray structure of which (fig 7) unambiguously demonstrates the three sulfur-containing heterocycles to be essentially coplanar (with a dihedral angle of 0.75° between each individual sulfur-containing heterocycle).

Consequently, a very short intramolecular S···S distance (d = 3.065(2) Å, far shorter than the sum of the Van der Waals radii of two S atoms, d = 3.70 Å) is observed between the S-atoms of the central moiety and those of both dithiafulvenyl substituents. We believe that this short intramolecular interaction has to be associated with the in-plane stability attained in such highly delocalized π-systems [15].

The π-donor character of these extended molecules has been evaluated by means of cyclic voltamperometry (CV) [16]. The oxidation potentials of **1–3** are collated in table I. The strong π-donor ability of **1–3** is demonstrated by remarkably low values of oxidation potentials relative to those for other TTF derivatives. This is consistent with the extension of the π-system thanks to the lateral electron-rich dithiole rings which presumably lie in the same plane. These CVs are solvent dependent, revealing (i) in the case of **2** and **3**, two reversible redox processes, almost coalesced in most solvents but fairly well discriminated at slow sweeping rates, and (ii) in the case of **1**, three successive reversible processes.

A typical voltammogram is shown in figure 8 for **1d** which exhibits three reversible oxidation peaks. The tremendous electron-donating character of **1d** is evidenced by the value of the first oxidation potential, close to 0 V/SCE (ie, 0.08 V); the second one at 0.17 V is even smaller than the first oxidation potential of TTF itself.

Another remarkable, albeit expected, feature of these highly extended π-systems is the weak intramolecular Coulombic repulsion in the multicationic states, as shown by the close proximity of the successive oxidation steps relative to TTF and the low oxidation potential value for the third wave in compounds **1**.

Thin-layer cyclic voltammetry (TLCV) [17, 18] has been used to further characterize the electrochemical behavior of **1d**. Indeed, while classical CV works under diffusion control, TLCV does not: all the substance confined within the layer is fully oxidized or reduced at each scan, so that the areas under the peaks are directly proportional to the numbers of electrons exchanged in the redox processes. Thus, comparing the areas under

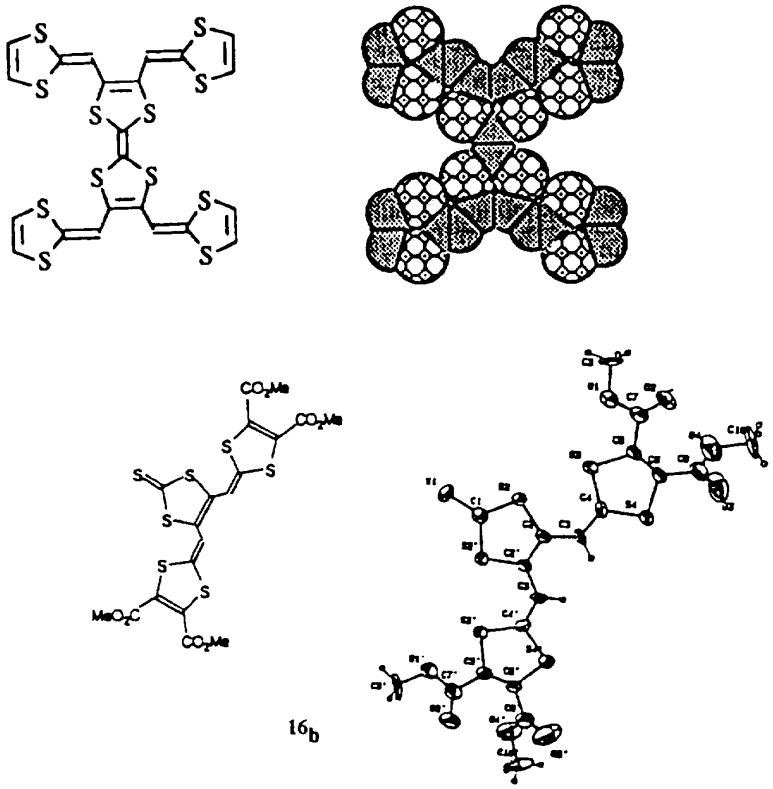

Fig 7. Top: Strong evidence of an intramolecular S···S interaction in compounds **1**. Bottom: Ortep drawing of molecule **16b**. The thermal ellipsoids are drawn at the 50% probability level.
Selected bond lengths (Å) and angles (deg): S1–C1 (1.62(1)); S2–C1 (1.731(6)); S2–C2 (1.748(7)); C2–C'2 (1.39(1)); C2–C3 (1.429(8)); C3–C4 (1.347(9)); C4–S3 (1.748(7)); S3–C5 (1.757(7)); C4–S4 (1.758(7)); S4–C6 (1.730(6); C5–C6 (1.320(9)); S1–C1–S2 (124.3(3)); C1–S2–C2 (99.5(3)); S2–C2–C3 (120.1(4)); S2–C2–C'2 (114.8(2)); C2–C3–C4 (130.2(6)); C3–C4–S3 127.7(5)); C3–C4–S4 (118.8(5)); C4–S3–C5 (95.4(3)); C4–S4–C6 (96.0(3)); S3–C5–C6 (117.4(5)).

Table I. Peak potentials in V/SCE, Pt electrode, 200 $mV \cdot s^{-1}$ if unspecified, 20 °C, Bu_4NClO_4 (0.1 $mol \cdot L^{-1}$).

Compound	*Solvent*	Ep_{a1}	Ep_{a2}	Ep_{a3}
TTF	DMF[a]	0.42	0.72	
	TCE[a]	0.40	0.82[e]	
1a	DMF[b]	0.19	0.34	0.50[e]
1b	DMF[b]	0.32	(0.65)[d]	0.81[c,e]
	TCE	0.34	0.65	0.95
1c	TCE	0.09	0.42	0.57
1d	DMF[b]	0.13	0.29	0.48
	TCE	0.08	0.17	0.51
2a	DMF	0.29		
	DMF[f]	0.22	0.30	
3a	DMF	0.29		
	TCE	0.26	0.39[b]	
3b	DMF	0.51	0.58	
	TCE	0.51	0.74	

a) DMF: *N*,*N*-dimethylformamide; TCE: 1,1,2-trichloroethane; b) badly resolved for this sparingly soluble compound, c) exaltation of the oxidation peak, d) badly defined, e) irreversible system, f) sweeping rate 50 $mV \cdot s^{-1}$.

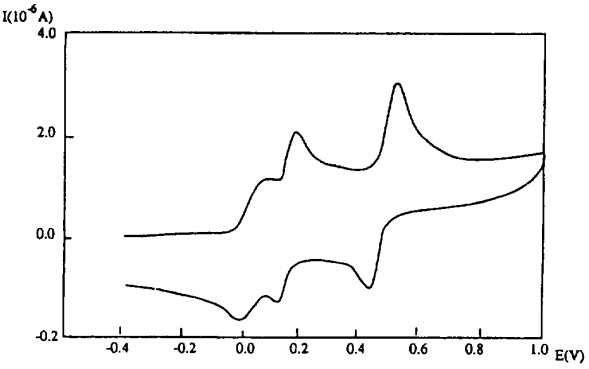

Fig 8. Cyclic voltamperometry of compound **1d** (10^{-3} M) in 1,1,2-trichloroethane, V/SCE, Bu_4NClO_4 (10^{-1} M), 200 $mV \cdot s^{-1}$.

the oxidation peaks in the TLCV of **1d** (fig 9), one observes the third one to be twice as big as the first or second. These results are consistent with three successive oxidation steps involving respectively one, one and two electrons per molecule, allowing obtention of a stable tetracation as low as 0.51 V/SCE.

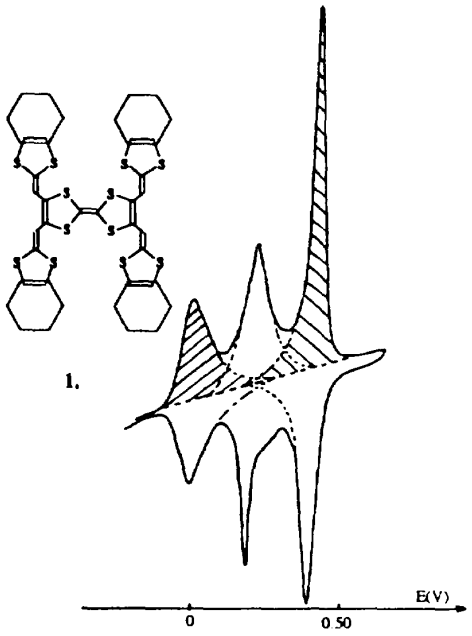

Fig 9. Thin-layer cyclic voltammetry of **1d**, in 1,1,2-trichloroethane, V/SCE, Bu_4NPF_6 (1M), 5 $mV.s^{-1}$.

Compounds **1–3** readily react with tetracyanoquinodimethane (TCNQ), in solution or by grinding of the solids [19]. Thus, with **3a**, a dark blue microcrystalline complex is obtained from a boiling chlorobenzene solution, and analyzed as $(\mathbf{3a})_2(TCNQ)_3$, with a room-temperature compressed pellet conductivity of 1 $S.cm^{-1}$.

CRSs of **1–3** have been generated using the electrocrystallization technique. Here again the usefulness of TLCV must be mentioned. Another facet of this powerful experimental tool has recently been demonstrated [18], ie, its ability to predict stoichiometries in mixed-valence salts obtained by electrocrystallization of a π-donor under given experimental conditions (supporting electrolyte and solvent). Consequently this technique allows straightforward optimization of the experimental conditions for electrooxidation. This is illustrated by TLCV of compound **3a** which has been recorded in the presence of an internal redox standard, namely 2,3-dichloronaphthoquinone (DCNQ) which is known to be reduced by one e^-/molecule (fig 10). Comparing both of the oxidation waves of **3a** with the reduction wave of the standard leads to coulometric determinations of $1e^-$/mol and $0.5e^-$/mol respectively for the two steps.

Therefore, one can predict the stoichiometry of the materials produced at each peak, ie, a 1:1 salt (no mixed valency) at the first peak, and a 1.5 mixed valence salt at the second peak.

Incomplete oxidation of **3a** under galvanostatic conditions at a very low constant intensity (1 $\mu A/cm^2$, Bu_4NClO_4 (0.1 M), 1,1,2-trichloroethane/ethanol (10:1) mixture) allowed production of black needles shown to be $\mathbf{3a}.ClO_4$ by resolution of their structure by X-ray diffraction, a stoichiometry predicted from TLCV data.

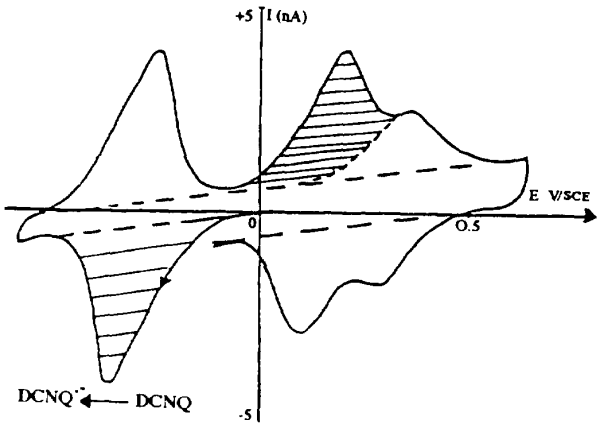

Fig 10. Thin-layer cyclic voltammetry of **3a** (7.02×10^{-4} M) in 1,1,2-trichloroethane, in the presence of 2,3-dichloronaphthoquinone as a standard (9.03×10^{-4} M), V/SCE, Bu_4NPF_6 (1M), 5 $mV.s^{-1}$.

The unique solid state architecture of $\mathbf{3a}.ClO_4$, shown in figure 11, has been recently described and analyzed elsewhere [5d]. The structure is based on the occurrence of connected stacks organized in slabs via intercolumnar S···S contacts. These organic layers are separated by discrete anion sheets. When considering two isolated donor molecules, one observes a head-to-tail alternation both in the stacking (between donors located in the same column) and in the plane of the molecule (between donors located in the same plane); this peculiar feature gives rise to multi S···S intermolecular contacts (3.30 Å $< d <$ 3.67 Å). Besides these interactions, one observes a new type of intermolecular S···S contact between donors located in successive planes but in adjacent columns, through the overlapping of their dithiafulvenyl side arms. In addition to this structural feature, high orbital coefficients have been identified in the HOMO of **3a** at the outer sp^2 carbon atoms of the central TTF unit when compared to TTF itself [5d]. This confers to **3a** an extensively conjugated character prone to generate charge delocalization in the corresponding material. The conjunction of these factors leads to a rare, novel type of two-dimensional network in the organic solid state, which furthermore exhibits a remarkably high room temperature conductivity (0.38 $S.cm^{-1}$, Ea = 170 meV) for such a 1:1 cation-radical salt [5d].

In conclusion, from a synthetic point of view it has been demonstrated that grafting of the synthetically-powerful aldehyde functionality onto a TTF core, allows highly extended analogs to be reached in one step. Therefore, if properly substituted nucleophilic species are reached with these polyformyl-TTF, this strategy should offer a unique opportunity to substitute the TTF core in order to reach other molecular materials such as LB films [20], liquid crystals and dithiolene systems [5e].

Meanwhile, the highly extended analogs of TTF **1–3** have been shown here to constitute a promising new approach towards the enhancement of the dimensionality in cation-radical salts of the TTF family [21].

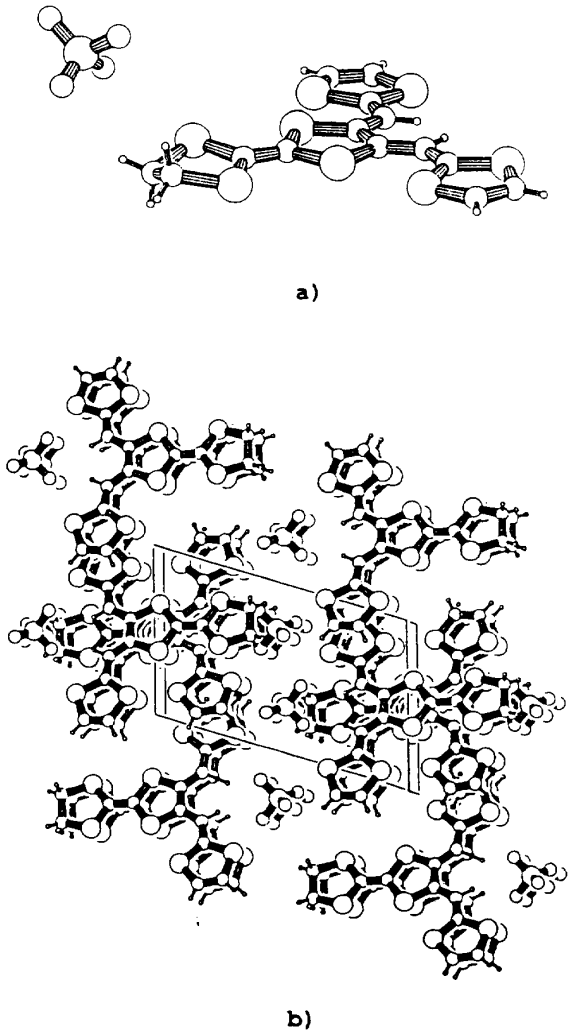

Fig 11. a) Asymmetric unit of **3a**.ClO_4; b) structure of **3a**.ClO_4 viewed approximatively along the [100] direction.

Experimental section

General

^1H spectra have been recorded on either a Varian EM360 or a Jeol GSX270WB spectrometer, operating respectively at 60 and 270 MHz and ^{13}C NMR on the same Jeol apparatus at 67.5 MHz; δ are given in ppm (relative to TMS) and coupling constants in Hz. Mass spectra were recorded under EI or FAB mode either on a Varian MAT 311 in the CRMPO (Rennes, France) or on a VG Autospec (Zaragoza, Spain). Infrared spectra were taken in KBr or Nujol using a Perkin-Elmer 841 spectrometer. Elemental analyses were performed by the Service central d'analyse du CNRS (Vernaison, France). Column chromatography separations and purifications were carried out on Merck silica-gel 60 (0.040–0.063 mm).

Tetraformyl-TTF **4** and precursors **7–12** were synthesized according to the described procedure [11a].

2-Formyl-3-(diethoxymethyl)-TTF **13**

A solution of $Co_2(CO)_8$ in 50 mL toluene (freshly distilled over CaH_2) was slowly added (evolution of CO) under nitrogen to a mixture of thione **8** (3.64 g, 13.8 mmol) and 2-thioxo-1,3-dithiole (5.54 g, 41.4 mmol) dissolved in 20 mL toluene. The temperature was raised to 40 °C for 0.5 h and then to reflux for 5 h. After cooling, the reaction mixture was filtered through a short silica-gel column and eluted with CH_2Cl_2 to remove the black pyrophoric insoluble material. After evaporation of the solvent, cross-coupling and self coupling products were separated by chromatography (CH_2Cl_2 then CH_2Cl_2/Et_2O, 9:1 (v/v)) over a silica-gel pre-packed SiO_2 column (Lobar, Merck). Using this system, the elution order was the following: TTF, **13**, [*E*]-**11** and [*Z*]-**11**. Compound **13**, recrystallized from diisopropyl ether, was obtained as dark red crystals (1.23 g, 27% yield from **8**).

Mp = 76–78 °C.

IR (Nujol): 1 648 (C=O).

^1H NMR ($CDCl_3$): 1.22 (t, $^3J = 6$, 6H, CH_3); 3.69 (q, $^3J = 6$, 4H, OCH_2); 5.72 (s, 1H, OCHO); 6.34 (s, 2H, =CH); 9.92 (s, 1H, CHO).

^{13}C NMR ($CDCl_3$): 14.98 (CH_3); 61.89 (OCH_2); 96.72 (CH); 104.20 and 114.75 (central C=C); 118.87 and 119.36 (*C*=*C*); 135.80 (=*C*CHO); 155.00 (=*C*CH), 180.09 (CHO).

$C_{12}H_{14}O_3S_4$ $M^{+\cdot}$ calc 333.98258; found 333.9812.

Anal calc % C 43.09; H 4.22; O 14.35; S 38.34. Found C 43.25; H 4.13; O 14.66; S 38.01.

2,3-Diformyl-TTF **5**

Sulfuric acid (15%) (2 mL) was added with continuous magnetic stirring to a suspension of silica gel (9 g, silica gel 60, 70–230 mesh from Merck) in methylene chloride (15 mL). The acetal derivative **13** (920 mg, 2.75 mmol) was added and stirring continued for 6 days (TLC control). The solid phase was filtered on a sintered glass funnel, and rinsed with methylene chloride. The solution was then washed with water, dried over $CaCl_2$, and evaporated under reduced pressure. Unreacted starting material was discarded by solubilizing in *n*-pentane. The blue powder thus obtained was then recrystallized from THF to afford **5** (702 mg, 98% yield) as dark blue needles.

Mp = 215–218 °C.

IR (Nujol): 1 650 (C=O).

^1H NMR (DMSO-d_6): 6.80 (s, 2H, CH); 10.38 (s, 2H, CHO).

^{13}C NMR ($CDCl_3$): 98.20 and 118.55 (S_2C=CS_2); 120.23 (*HC*=*CH*); 149.24 (=*C*CHO); 182.14 (CHO).

$C_8H_4O_2S_4$ $M^{+\cdot}$ calc 259.90942; Found 259.9090.

Anal calc % C 36.90; H 1.54; O 12.29; S 49.26. Found C 36.99; H 1.51; O 12.95; S 47.88.

2-Formyl-3-(diethoxymethyl)-6,7-dihydro-TTF **14**

Thioxo compound **10** (3.0 g, 8.9 mmol) and ethylenetrithiocarbonate (Janssen Chimica) (6.0 g, 44.1 mmol) were introduced under nitrogen in a Schlenk tube containing a mixture of freshly distilled toluene (20 mL) and 20 mL triethyl phosphite distilled just before use. The reaction mixture was heated at 80 °C for 4 h, and after cooling the solvent mixture was distilled off under vacuum. The crude oil was then purified by SiO_2 column chromatography (toluene/hexane 6:4 (v/v)), to furnish the partially-hydrolyzed cross-coupling compound **14**. This was recrystallized from an *n*-hexane/CH_2Cl_2 mixture to produce red crystals (1.69 g, 57% yield from **10**).

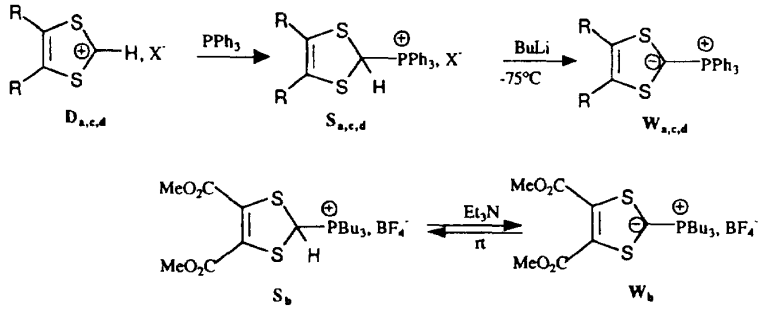

Fig 12

Mp = 112–113.5 °C.

IR (Nujol): 1 650 (C=O).

^{1}H NMR ($CDCl_3$): 1.30 (t, ^3J = 6, 6H, CH_3); 3.57 (s, 4H, SCH_2); 3.76 (q, ^3J = 6, 4H, OCH_2); 5.81 (s, 1H, O-CH-O); 9.99 (s, 1H, CHO).

^{13}C NMR ($CDCl_3$): 14.97 (CH_3); 15.26 (CH_3); 40.44 (SCH_2); 40.51 (SCH_2); 61.84 (OCH_2); 96.71 (CH); 109.47 and 116.10 (central C=C); 135.37 (=*C*CHO), 154.74 (=*C*CH), 180.13 (CHO).

$C_{12}H_{16}O_3S_4$ $M^{+\cdot}$ calc 335.99823; Found 335.9969.

Anal calc % C 42.83; H 4.79; O 14.26; S 38.11. Found C 43.16; H 4.65; O 14.66; S 37.91.

2,3-Diformyl-6,7-dihydro-TTF **6**

A solution of **14** (1.01 g, 3.00 mmol) in 20 mL methylene chloride was treated with 25 mL formic acid. The color of the solution turned blue within a few minutes. The reaction mixture was stirred for 0.5 h, diluted with methylene chloride, washed with Na_2CO_3 (N) and water, and finally dried over $MgSO_4$. The solvent was evaporated in vacuo, and the powder thus obtained was crystallized from toluene to produce **6** as blue needles (661 mg, 92% yield).

Mp = 186–187 °C.

IR (Nujol): 1 650 (C=O).

^{1}H NMR ($CDCl_3$): 3.52 (s, 4H, CH_2); 10.19 (s, 2H, CHO).

^{13}C NMR ($CDCl_3$): 40.77 (CH_2); 105.15 and 120.68 (central C=C); 150.23 (=*C*-CHO); 178.20 (CHO).

$C_8H_6O_2S_4$ $M^{+\cdot}$calc 261.92707; found 261.9248.

Extended π-systems **1–3**, **16**

Wittig polyolefinations were achieved by reaction between the polyformyl compounds **4–6**, **9** and the phosphorous ylides **Wa,c,d** or **Wb** (fig 12). Ylides **Wa,c,d** were generated at low temperature with *n*-BuLi as a base from the corresponding phosphonium salts **Sa,c,d**, which were prepared in situ by interaction between equimolar amounts of triphenylphoshine and the corresponding 1,3-dithiolium salts **Da,c,d** (method A). In the case of R = CO_2Me, **Sb** was prepared according to the literature [22], and treated at rt with Et_3N to generate **Wb** (method B).

• *Method A (R = H, S-CH_2-CH_2-S, SCH_3, $(CH_2)_4$)*

To allow **Sa,c,d** formation, 2 mmol of **Da,c,d** and an equimolar amount of PPh_3 in 8 mL of freshly distilled acetonitrile were introduced into a three-necked round-bottom flask under nitrogen. After 15 min of stirring at rt, the reaction mixture was diluted with 20 mL dry THF (distilled over Na/benzophenone), cooled to −75 °C, and finally treated dropwise with 1.24 mL (2 mmol) of a 1.6 M *n*-butyllithium solution in *n*-hexane (Janssen Chimica). The yellow solution of **Wa,c,d** was stirred for 10 min, and 0.91 equiv of the polyaldehyde (0.91 mmol for **5**, **6**, **9**, and **9′** and 0.46 mmol for **4**) diluted in dry THF was introduced dropwise, the temperature being kept at −75 °C. At this stage, the color of the solution invariably turned deep red. The reaction mixture was then allowed to warm to rt over a 3 h period, and concentrated in vacuo. The crude material thus obtained was treated with methanol to allow precipitation of the olefination product. This was filtered on a sintered glass funnel and washed with abundant hot methanol, acetonitrile and diethyl ether. Depending on their solubility and stability, the dark red powders or microcrystals were recrystallized (see solvents below) or purified by chromatography over silica gel.

• *Method B (R = CO_2Me)*

A dry THF (40 mL) solution containing the phosphonium salt **Sb** (5 mmol) and a polyformylderivative (**4–6**, **9** or **9′**) (2 mmol and 1 mmol for twofold and fourfold Wittig olefinations respectively), was stirred at rt under nitrogen. The solution was treated dropwise with triethylamine (1 mL), a dark red color appearing immediately. The reaction mixture was stirred at rt for 3 h, and the solvent evaporated in vacuo. The residue was dissolved in methylene chloride, washed with diluted hydrochloric acid, and water and finally dried over Na_2SO_4. Depending on their stability and solubility, the compounds obtained were purified by recrystallization or silica-gel chromatography.

Tetrakis(1,4-dithiafulven-6-yl)-TTF **1**

• **1a** *(R = H)*

Black powder (red in solution), 70% yield (method A).

Mp > 260 °C (decomp).

^{1}H NMR (DMSO-d_6): 6.67 (d, ^3J = 6.5, 4H, S-CH=); 6.68 (s, 4H, C=CH-C); 6.77 (d, ^3J = 6.5, 4H, SCH=).

$C_{22}H_{12}S_{12}$ $M^{+\cdot}$ calc 659,75877; found 659,7 (FAB^+).

• **1b** *($R = CO_2Me$)*

Black powder (red in solution), 54% yield (method B).

Mp = 271 °C (decomp).

IR (Nujol): 1 710 (C=O).

^{1}H NMR ($CDCl_3$): 3.84 (s, 12H, CO_2CH_3); 3.87 (s, 12H, CO_2CH_3); 6.00 (s, 4H, =CH).

Anal calc % C 40.56; H 2.51; O 22.75. Found C 40.95; H 2.49; O 22.56.

• **1c** *($R = SCH_3$)*

Black powder (red in solution), 86% yield (method A).

Mp = 185–190 °C.

^{1}H NMR ($CDCl_3$): 2.41 (s, 12H, SCH_3); 2.44 (s, 12H, SCH_3); 6.06 (s, 4H, =CH).

$C_{30}H_{28}S_{20}$: 1 028 (FAB^+).

• **1d** *(R–R = $(CH_2–CH_2)_2$)*

Recrystallized from THF, brown microcrystals (red in solution), 54% yield (method A).

Mp = 231–234 °C.

^{1}H NMR (CS_2): 1.55 (m, 16H, external CH_2); 2.05 (m, 16H, CH_2-C=), 5.99 (s, 4H, =CH).

^{13}C NMR (CS_2): 23.41 ($CH_2CH_2CH_2CH_2$); 25.68 and 26.15 (=CCH_2-); 104.55 (C=CH-); 109.37 (S_2C=CS_2); 124.92 and 126.62 ($SCCH_2$); 126.39 ($SCCH$=); 138.36 (CH=CS_2).

Anal calc % C 52.01; H 4.14; S 43.85. Found: C 51.87; H 4.22; S 41.96.

2,3-Bis(1,4-dithiafulven-6-yl)-TTF **2** *and 2,3-bis(1,4-dithiafulven-6-yl)-6,7-dihydro-TTF* **3**

• **2a** *(R = H)*

Recrystallized from CS_2, brown microcrystals, 63% yield (method A).

Mp = 223 °C (decomp).

^{1}H NMR (DMSO-d_6): 6.76 (s, 2H, HC = TTF core); 6.75 (d, ^3J = 6.3, 2H); 6.66 (d, ^5J = 1.2, 2H, HCS_2); 6.64 (dd, ^3J = 6.3, ^5J = 1.2, 2H).

$C_{14}H_8S_8$: 432 (EI).

• **3a** *(R = H)*

Recrystallized from CS_2, red-brown crystals, 77% yield (method A).

Mp = 182 °C (decomp).

^{1}H NMR (DMSO-d_6): 3.57 (s, 4H, CH_2); 6.63 (d, ^3J = 7.2, 2H, SCH=); 6.64 (s, 2H, C=CHC); 6.74 (d, ^3J = 7.2, 2H, SCH=).

^{13}C NMR (DMSO-d_6): (CH_2CH_2) masked by DMSO signal: 104.15 (S_2C=CH); 108.94 (CH_2SC=C); 115.27 (CH_2SC=C); 119.45 and 119.59 (SCH=CHS); 124.40 ($SCCH$); 139.01 (S_2C=CH).

$C_{14}H_{10}S_8$ $M^{+\bullet}$ calc 434.761; found 434 (FAB^+).

Anal calc % C 38.68; H 2.32; S 59.00. Found C 38.89; H 2.14; S 59.20.

*(**3a**)$_2$.(TCNQ)$_3$*

Compound **3a** (52 mg, 0.12 mmol) and tetracyanoquinodimethane (TCNQ) (98 mg, 0.48 mmol) were dissolved under nitrogen in respectively 75 mL and 100 mL of hot chlorobenzene. The boiling solutions were then mixed and refluxed for 0.5 h. The mixture was then allowed to cool slowly by standing on a heating plate under nitrogen. The black solid was collected by filtration, and washed with chlorobenzene and acetonitrile till the solution appeared clear. Elemental analyses are in accordance with the following stoichiometry: (**3a**)$_2$.(TCNQ)$_3$.

Mp = 199 °C.

Anal calc % C 51.87; H 2.18; N 11.34; S 34.62. Found C 50.91; H 2.34; N 11.09; S 34.19.

• **3b** *(R = CO_2Me)*

Chromatographed over silica gel (CH_2Cl_2), orange powder, 63% yield (method B).

F = 220–225 °C.

IR (KBr): 1 730 (C=O).

^{1}H NMR ($CDCl_3$): 3.43 (t, 4H, CH_2), 3.78 (s, 12H, OCH_3), 5.47 (s, 2H, =CH)

4,5-Bis(1,4-dithiafulven-6-yl)-1,3-dithiole-2-thiones **16** *and 4,5-bis(1,4-dithiafulven-6-yl)-1,3-dithiol-2-ones* **16′**

• **16a** *(X = S; R = H)*

Crystallized from chlorobenzene, brown powder (orange in solution), 81% yield (method A).

Mp = 199 °C (decomp).

^{1}H NMR (DMSO-d_6): 6.80 (dd, ^3J = 6.5, ^5J = 1.1, 2H, SCH=); 6.91 (d, ^3J = 6.5, 2H, SCH=); 7.00 (d, ^5J = 1.1, 2H, C=CHC).

^{13}C NMR (DMSO-d_6): 102.47 (S_2C=CHC); 119.30 and 120.64 (SCH=CHS); 133.16 ($SCCH$); 142.76 (S_2C=CH); 204.85 (S_2C=S).

$C_{11}H_6S_7$ $M^{+\bullet}$ calc 361.85146; found 361.8521.

• **16b** *(X = S; R = CO_2Me)*

Microcrystalline dark powder (orange in solution), 82% yield (method B).

Mp = 245 °C (decomp).

IR (KBr): 1 734, 1 711 (C=O).

^{1}H NMR ($CDCl_3$): 3.86 (s, 6H, CO_2CH_3); 3.87 (s, 6H, CO_2CH_3), 6.17 (s, 2H, =CH).

^{13}C NMR ($CDCl_3$): 53.54 and 53.64 (CH_3); 103.47 (S_2C=CHC); 130.08 and 132.28 (CCO_2CH_3); 134.27 ($SCCH$); 138.72 (S_2C=CH); 158.99 and 159.62 (C=O); 206.71 (C=S).

$C_{19}H_{14}O_8S_7$ $M^{+\bullet}$ calc 593.87337; found 593.8705.

Anal calc % C 38.37; H 2.37; O 21.52; S 37.74. Found C 37.83; H 2.30; O 22.31; S 37.00.

• **16′a** *(X = O, R = H)*

Brown powder, fairly stable in solution, 63% yield (method A).

Mp = 194 °C.

IR (KBr): 1 660 (C=O).

$C_{11}H_6OS_6$ $M^{+\bullet}$ calc 345.87430; found 345.8757.

• **16′b** *(X = O; R = CO_2Me)*

Chromatographed over silica gel (CH_2Cl_2), orange powder, 78% yield (method B).

Mp = 197 °C.

IR (KBr): 1 710, 1 660 (C=O).

^{1}H NMR ($CDCl_3$): 3.85 (s, 6H, CO_2CH_3); 3.86 (s, 6H, CO_2CH_3), 6.18 (s, 2H, =CH).

^{13}C NMR ($CDCl_3$): 53.49 and 53.58 (CH_3); 104.76 (S_2C=CHC); 130.32 and 131.81 (CCO_2CH_3); 124.28 ($SCCH$); 137.73 (S_2C=CH); 159.22 and 159.60 (C(O)=O); 206.71 (S_2C=O).

$C_{19}H_{14}O_8S_7$ $M^{+\bullet}$ calc 577.89621; found 577.8975.

Crystal structure data for 4,5-bis[(4,5-dimethoxycarbonyl-1,3-dithiol-2-ylidene)methyl]-1,3-dithiole-2-thione **16b**

$C_{19}H_{14}O_8S_7$, *MW* = 594.77, monoclinic space group *C*2/*c*, *a* = 11.398(4), *b* = 17.579(3), *c* = 12.812(6) Å, β = 108.77°, *V* = 2 430.6 Å^3, *Z* = 4, ρ_{calc} = 1.62 g.cm^{-3}, μ(Mo$K\alpha$) = 6.65 cm^{-1}; a red/brown needle shaped crystal (ca 0.24 × 0.06 × 0.03 mm^3), mounted on a glass fiber, was used for data collection on an Enraf-Nonius CAD4 diffractometer at room temperature with monochromatized Mo$K\alpha$ radiation (θ_{max} = 25°). The structure was solved by direct methods. Although the H-atoms were identified on Fourier

difference maps, they were introduced at calculated positions for subsequent refinements. Full-matrix least-squares refinement converged at a final R (wR) value 0.053 (0.051); $w^{-1} = [\sigma^2(F) + 0.04F^2]$ for 967 reflections with $I > 2\sigma(I)$ (GOF = 1.285); lowest and highest peaks on last ΔF maps -0.181 and $+0.198$ e.Å^{-3}.

Supplementary material data for $C_{19}H_{14}O_8S_7$ (compound **16b**) have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° = SUP 90415 and are available on request from the Document Supply Center.

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