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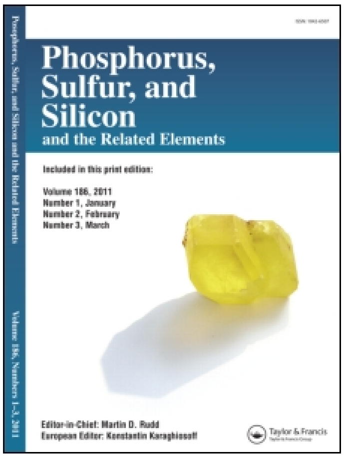

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New Derivatives of Tetrathiafulvalenes (TTF): Towards Organic Metals of Enhanced Dimensionality

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NEW DERIVATIVES OF TETRATHIAFULVALENES (TTF): TOWARDS ORGANIC METALS OF ENHANCED DIMENSIONALITY

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In order to get π-donors prone to develop organic metals of enhanced dimensionality (> 1D), the TTF or TSF derivatives **1-4** bearing two or four 1,4-dithiafulven-6-yl substituents adequately R-substituted have been synthesized. Usual and thin layer cyclic voltammetries evidence their tremendous π-donor ability and also the various stoichiometries of the salts produced upon their oxidation. Among them, X ray structure of $[\mathbf{2}\ (\text{saturated}, R=H)]_1(ClO_4)_1$ exhibits an unusual 2-D network and behaves as a semiconductor of uncommon high conductivity (close to 1 $S.cm^{-1}$ at r.t.). This property is indicative of weak Coulombic repulsions as well as strong interactions between the oxidized donors. By changing the R-substituents of **2** we have recently obtained a $(\mathbf{2})_2(\text{anion})_1$ salt endowed with a 2D character.

Key Words Tetrathiafulvalene (TTF), π-donors, organic metals, Wittig(Horner) reaction, (1,4 -dithiafulvalen-6-yl) TTF, 1 and 2 dimensionality

INTRODUCTION

Cyclovoltammogram of tetrathiafulvalene (TTF) exhibits two reversible oxidation peaks ($Epa_1 = 0.37$ and $Epa_2 = 0.77$ V/SCE, CH_3CN solvent, Bu_4NPF_6 supporting electrolyte) indicative of a good stability of the corresponding cation radical $D^{+\bullet}$ and dication D^{++} which is mainly explained by the presence of 1 or 2 aromatic sextets which are absent in the starting neutral molecule D. Perhaps because they tend to share the benefits of their aromaticity with neutral D,[1] the $D^{+\bullet}$ species first generated when one oxidizes D in the presence of anions Y^-, tend to aggregate, in the solid state, with neutral species D to give rise to "chichkebab" like stacked structures D $D^{+\bullet}DD^{+\bullet}DD^{+\bullet}$... with segregated stacks of donors more or less oxidized and of anions Y^-. One understands that if the distances between two neighbouring molecular

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planes are low enough, one says if the "intrachain contacts" between the donors are strong enough, therefore, an overlap of orbitals will occur along the column, and hence an electron delocalization. The donors will be in a mixed state valence, here 1/2, and such highly 1-D materials will be endowed with anisotropic properties, in particular higher values of the electrical conductivity in the axis of the column as compared to both other perpendicular directions.

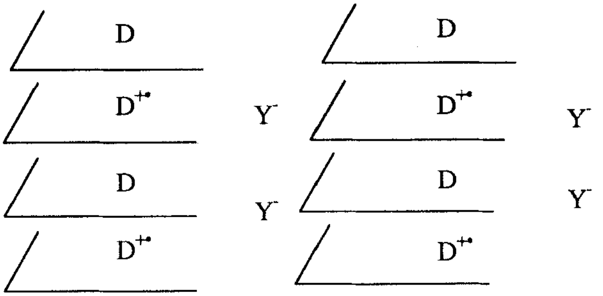

FIGURE 1 1-D Mixed valence salt of D_2Y

However, theory predicts, and experiments confirm, that to much 1-D materials cannot sustain electroconductive properties when you cool them below a given temperature because of the arising of subtle crystalline transitions, the so-called Peierls distorsions, due to electron-phonon coupling. Therefore, the problem is : how to avoid these Peierls distorsions to improve the transport properties of these materials at low temperature and perhaps to reach the superconducting state.

Answer is : by enhancing their dimentionality. Either one must directly prepare 2 or 3-D organized materials or, if one get a columnar material, as shown in Figure 1, in addition to the intrachain contacts between the donors, interchain contacts are required.

Now, let us briefly recall the main trends followed by chemists to achieve that by variations around the TTF core.[2-4]

The first one consisted of replacing S by Se or Te with the idea that the more diffuse orbitals of the chalcogen, the higher the dimensionality of the salts. This track was indeed gratified with the discovery by the franco-danish group of Bechgaard and Jérome of the first organic superconductors based on tetramethyltetraselenafulvalene TMTSeF.[5]

The second trend consists of substituting the H of TTF with chalcogen rich substituents such as bis-ethylenedioxy (BEDO) or bis-ethylenedithio (BEDT). This trend was also gratifified since BEDO-TTF and almost BEDT-TTF are at the basis of a lot of organic superconductors,[6] one of which having the highest Tc achieved so far (12 K).[7]

Another trend, hardly developed to date, consists of replacing the ethylene central bond of TTF or TSeF with more extended conjugating spacers and, in addition, to conjugate more than two 1,3-dithiol-2-ylidene moieties.[8,9]

On these grounds, we have been interested for some years in the synthesis of space extended and S-rich analogs of TTF or TSeF **1-4** (Figure 2) with the aim of stabilizing the metallic state of their charge transfer salts.[10-16]

These compounds can be regarded as derivatives of TTF bearing two or four 1,4-dithiafulven-6-yl groups.

What is the guideline for the design of such target molecules?

- the dithiafulvenyl substituents, which mimic the half moiety of TTF, are held to enhance the π-donor ability of the TXF core (X=S or Se) and, thanks to their S-rich character, should favour the S···S intermolecular interactions in the related salts, thus possibly increasing their dimensionality,
- thanks to their highly delocalized π-systems, a lowering of the coulombic repulsions in the charged species must take place,
- finally, by analogy with previous results by Cava's [8] and Yoshida's [9] groups, these conjugated dithiolylidene moieties are prone to favor multistep oxidation processes and hence, upon oxidation, CT salts of unusual stoichiometries may be expected.

In this communication we successively detail the synthesis of these compounds, the evaluation of their π-donor ability by both classical and thin layer cyclic voltammetry (TLCV), and finally the solid-state properties of one of their related materials.

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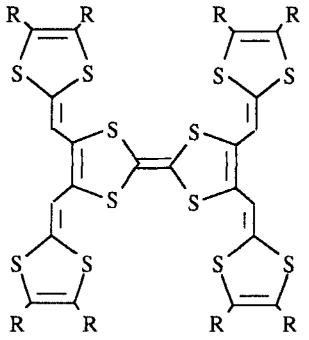

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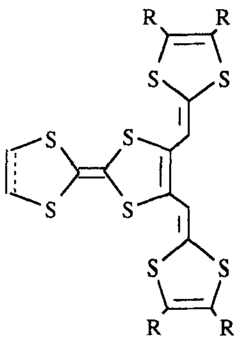

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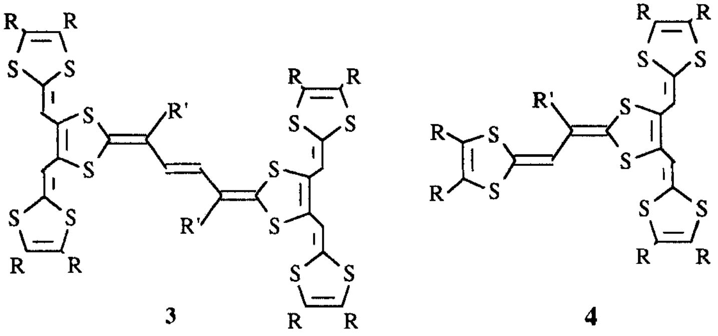


R = H, Me, CO_2Me, SMe
R-R = $(CH_2\text{-}CH_2)_2$, $(CH{=}CH)_2$, $SCH_2\text{-}CH_2S$

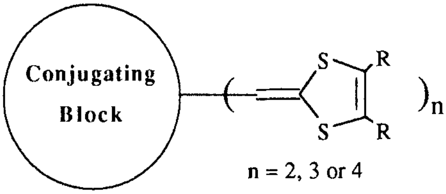
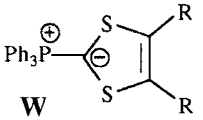


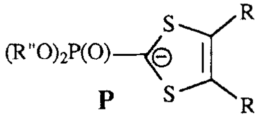
FIGURE 2 Target molecules

RESULTS AND DISCUSSION

All of these compounds can be regarded as resulting from the conjugation of two, three or four dithiafulvenyl substituents across a conjugating spacer (Figure 2). Therefore, all of them can be readily produced thanks to two, three or fourfold Wittig or Wittig-Horner olefinations of the corresponding, di, tri or tetraaldehydes with the Akiba's reagents *i. e* . phosphorous ylids **W** or phosphonate anions **P** bearing the 1,3-dithiol-2-ylidene moiety.[17]



W



P

The common synthetic strategy to reach these polyformyl-TTFs lies in the preliminary interaction between acetylenedicarbaldehyde, or better, the easier to handle corresponding monoketalized form **5**,[18,19] with ethylenetrithiocarbonate (Scheme 1).

Likewise other electrophilic alkynes, the monoacetal of ADCA **5** cycloadds onto ethylenetrithiocarbonate with evolution of ethylene to produce the corresponding difunctionalized dithiolethione **6**.

The latter can alternatively be used as a starting material in the dithiole chemistry [2,3] using standard procedures, *i.e.*

- access to the free dialdehyde **7** by formic acidolysis,
- quantitative ketal conversion to **8** of the free aldehyde functionality of **6**,
- for each of these thiones, quantitative C=S to C=O conversion using the classical mercuric acetate procedure **6',7',8'**.

In order to build the TTF core, the dimerization-desulfurization could be achieved starting from **6** and using $Co_2(CO)_8$ as the coupling reagent, leading to a 50/50 mixture of the [Z]-**9** and [E]-**9** isomers.

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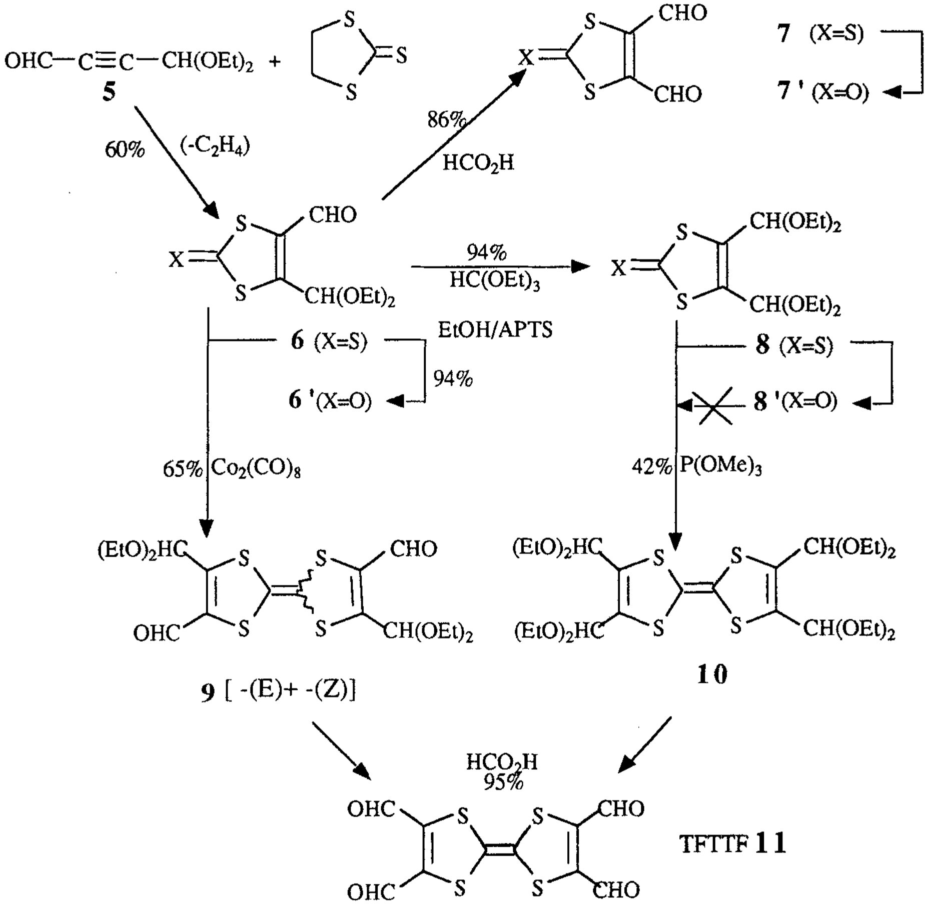

SCHEME 1

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Alternatively this step has been performed using a P(III) reagent ((MeO)$_3$P) but this strategy which requires the use of the previously diketal protected thione **8**, has not allowed any improvement of the dimerization-desulfurization yield.

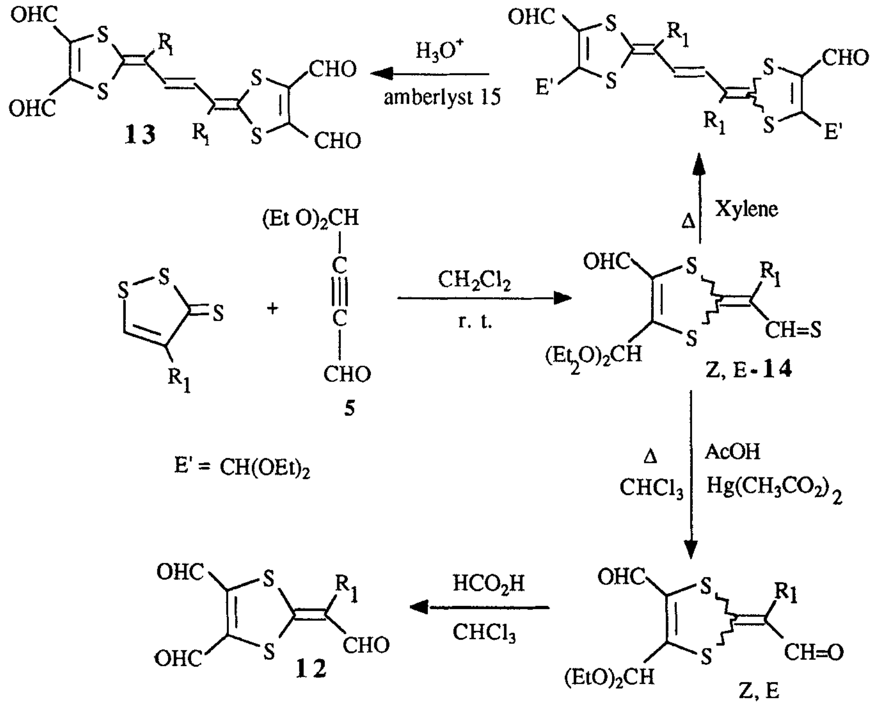
Formolysis of those polyketals-TTF (**9-10**) quantitatively affords the tetraformyl-TTF **11** as dark-blue shiny pellets.

Note that all of these results[20] could also be generalized to the Se series by starting from ethylenetriselenocarbonate to finally reach the tetraformyltetraselenafulvalene.[21]

The preparation of the dialdehydes precursors of compounds **2** involves a cross-coupling in the presence of either P(OEt)$_3$ or Co$_2$(CO)$_8$, of the mono- or bis-protected dialdehydes (**6, 8**) with i) ethylenetrithiocarbonate to reach the dihydro-TTF or TSeF series, or ii) various adequately substituted 2-thioxodithioles, the corresponding free aldehydes being then generated by formolysis as usual.[20]

A similar strategy was used in coll. with Fabre to reach the Selenium or the mixed Sulfur-Selenium series, by using the corresponding selenated starting materials.[22]

The tri and tetra aldehydes **12, 13** of the TTF vinylog derivatives were also prepared from monoacetal of ADCA **5** but using 3-thioxo-1,2-dithioles (Scheme 2).[10,23]



SCHEME 2

The thial **14** quantitatively produced is surprisingly stable in the solid state; its structure has been evidenced by X-ray diffraction, showing a very strong intramolecular S···S interaction.[24] The C=S to C=O conversion was achieved with mercuric acetate, and after deprotection with formic acid, the trialdehyde **12** was produced. A similar crystallographic feature as for **14** has been observed in the case of an analog of triformyl compound **12** (strong S···O interaction).[23]

On the other hand, the dimerization-desulfurization of **14** was cleanly performed on simple heating in a xylene solution under nitrogen to finally produce the tetraformyl derivative **13**.

The following step in our strategy to reach highly extended TTF-derivatives lies in the Wittig or Wittig-Horner olefination of these various polyaldehydes using the Akiba's reagents, namely **W** or **P**. Of course, most powerful nucleophilic species are the phosphonate anions **P**, however in many cases, P-ylids **W** are reactive enough to achieve the required polyolefinations of the conjugated polyaldehydes. These reactions (-78°C/THF/BuLi) proceed in quite good yields (50-85%) if one considers that in each case, a di-, tri- or tetraolefination is performed to finally reach the target extended π-systems **1-4** (Schemes 3-5).

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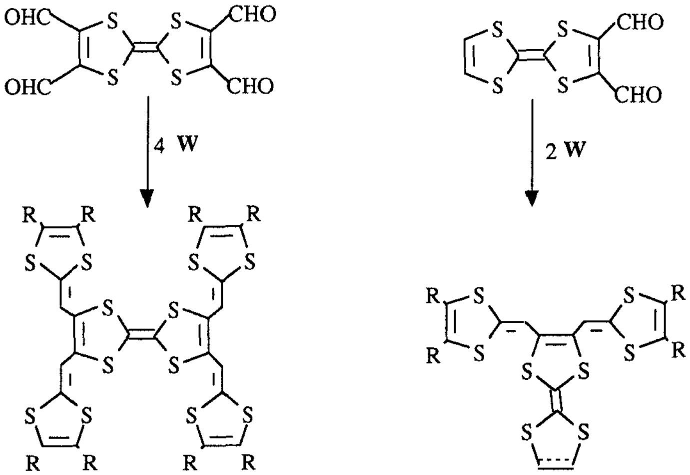
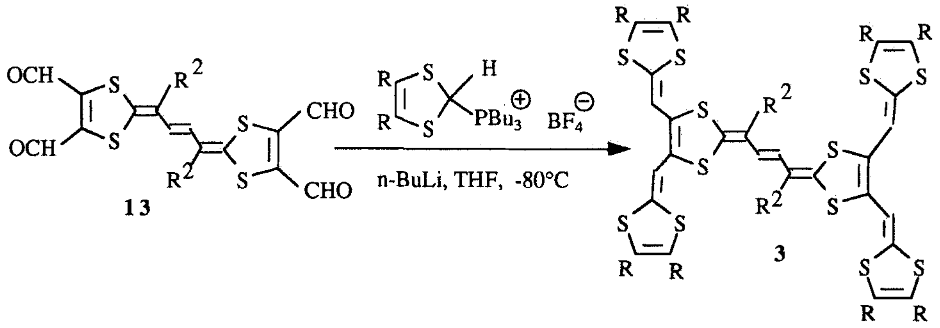
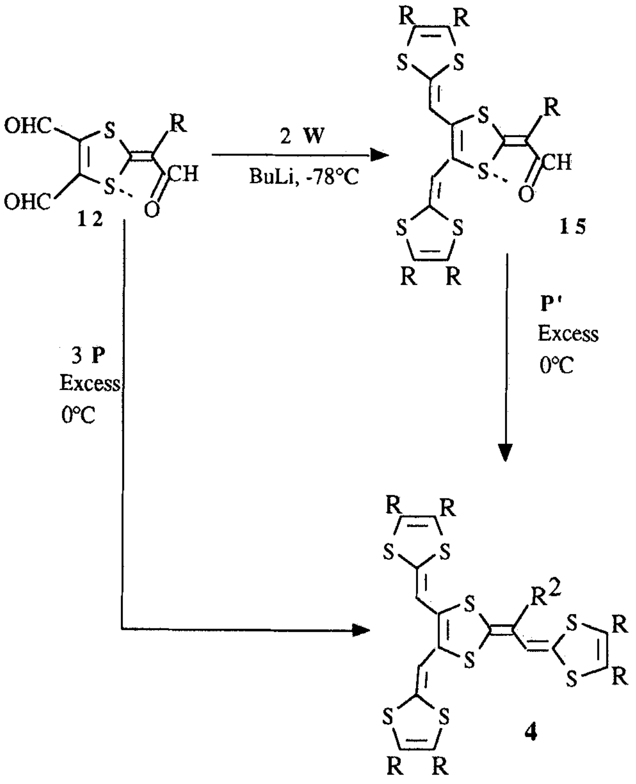


SCHEME 3



SCHEME 4



SCHEME 5

At this stage, one should mention the peculiar behaviour of the trisformyl derivative **12** towards the Wittig-Horner olefination (Scheme 5) : when this compound is

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treated with a large excess of **W**, one observes the formation of the bis-olefination product without any trace of the desired trisolefinated compound. This is interpreted as resulting from a strong lowering of the electrophilicity of the C=O for two reasons : i) a partial S...O bonding interaction, as shown by X-ray structure on a parent ketone,[23] and ii) the introduction of two dithiafulvalenyl substituents with their strong electron releasing effect. These problems could be circumvented by a direct dropping of BuLi (1.6M in hexane) to a 0°C solution of the mixture of the trialdehyde **12** and the adequately substituted phosphonate **P**.[25] The same result has obviously been obtained starting from the previously bisolefinated compound **15** and **P**.

Let us consider the π-donor ability of these systems.

First, from the structural point of view, there was no evidence of planarity in ourextended and S-rich systems when contemplating molecular models. They revealed strong S···S intramolecular interactions which may lead the dithiafulvenyl substituents to lie out of the central TTF plane (Figure 3).

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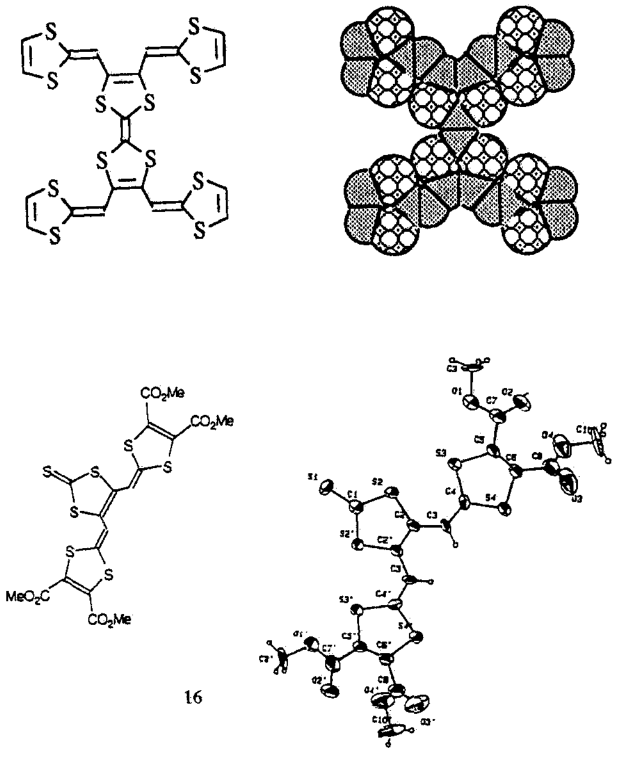

16

FIGURE 3

Although we were not able to isolate single crystals of **1**, we have synthesized the more soluble compound **16**, which presents the same 1,4-dithiafulven-6-yl substitution and therefore which may act as a structural model. X-ray structure solved from single crystals of **16** shows the three heterocycles to be nearly coplanar with strong intramolecular S···S interactions ($d_{S...S}$ =3.06Å, far shorter than the sum of two Sulfur VDW radii (=3.70Å)). This structural feature demonstrates to a large extent the resonance energy reached in these highly delocalized π-systems.

We have studied the π-donor ability of these extended π-donors by usual cyclic voltammetry (CV). A representative example is shown in Figure 3 where compound **1** exhibits three reversible oxidation peaks, and one notes a tremendous electron donating power since the first peak lies near 0 V/SCE (*i.e* 0.08 V), the second one at 0.17 V (even smaller than the first oxidation potential of TTF itself). Note also the weak on-site Coulombic repulsion on these extended π-systems as evidenced from the low value of the third oxidation potential, and the small potential difference between each of the redox couples. Although the shape of the voltammogram is well defined, no coulometric prediction is allowed for each of the redox systems, because of the usual diffusion phenomena inherent in classical CV.

At this stage, in collaboration with Carlier,[26,27] we have decided to use thin layer cyclic voltammetry (TLCV) as a complementary analytical tool. Whereas classical CV works under diffusion control, with TLCV all the substance confined within the layer is fully oxidized or reduced at each scan, so that the area under the peaks are directly proportional to the number of electrons exchanged in the redox process. Therefore, comparing areas under oxidation peaks in the TLCV of **1** (Figure 3), one observes the third one to be twice as big as the first or the second one. These results are consistent with three successive oxidation steps involving respectively one, one and two electrons, allowing to reach a stable tetracation as low as 0.50 V/SCE.

Similar electrochemical results were obtained with compounds **2-4**, all of them exhibiting multiple redox systems (up to four in the case of **3**) with a very strong π-donor ability, and weak coulombic repulsions.

Another important interest of TLCV lies in the ability of this technique to allow the prediction of stoichiometry in mixed-valence salts. As expected, compound **2** exhibits very strong π-donating properties. TLCV has been recorded in the presence of an internal redox standard, namely 2,3-dichloronaphtoquinone (DClNQ) which is known to be reduced with one e^-/molecule. The voltammogram exhibits two peaks which, by comparison with the standard, does correspond to $1e^-$/mol and $0.5e^-$/mol respectively.

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Therefore, one can predict the stoichiometry of the materials produced at each peak, *i.e.* a 1:1 salt (no mixed-valence) at the first peak, and a 3/2 mixed valence salt at the second peak. We have tried to electrooxidize **2** under potentiostatic conditions at the second potential value, but unfortunalety, till now, we have not obtained good quality crystals.

Achieving the oxidation of **2** under galvanostatic conditions at a very low intensity (1μA/cm^2, Bu_4NClO_4 (0.1M), 1,1,2-trichloroethane / ethanol (10/1) mixture), we have obtained a 1:1 CT salt as predicted by TLCV.

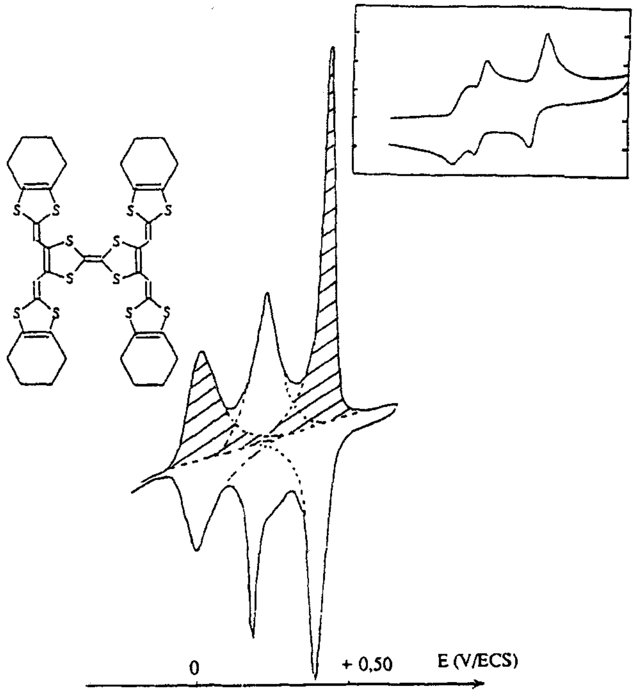

FIGURE 3 : Thin Layer Cyclic Voltammetry of compound **1** (Bu_4NPF_6 1M in 1,1,2-trichloroethane, r.t., 5 mV/sec, E (V/SCE); Insert : Classical CV of **1** (same experimental conditions).

The X-ray structure of the (**2**)(ClO_4) salt is presented in Figure 4;[16] for clarity reasons, only one over two donors has been represented at the four corner positions. An immediate crystallographic feature for this salt lies in the occurence of stacks organized in layers through intercolumnar S···S contacts and separated by anions sheets.

When considering two isolated molecules of donors, one can observe a head to tail alternance either in the stacking (between donors located in the same column) or in the plane of the molecule (between donors located in the same plane), this feature giving rise to multi S····S intermolecular contacts (3.30Å< d <3.67Å). In addition to these interactions, one observes a new type of intermolecular S···S contacts, between donors located in successive planes but in adjacent columns, through the overlapping of the dithiafulvenyl side arms.

Therefore, this material exhibits a new and unprecedented type of bidimensional character.

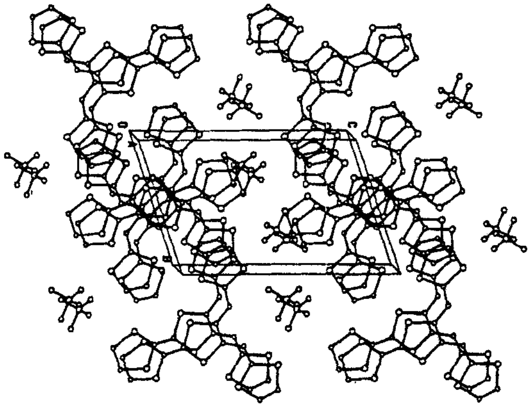

FIGURE 4

It must be noted that this 1:1 salt is a semiconductor with an unusually high value of conductivity (σ=0.38 S.cm^{-1}, Ea=170 meV). In addition to CV data, this is consistent with a weak coulombic repulsion and a strong overlap of the donors thanks to the space extension of the molecule.[16]

Considering these promising results and the unique opportunity TLCV offers to predict stoichiometries of electrogenerated cation-radical salts, we are currently attempting to optimize the design of new S-rich derivatives involving similar electronic and crystallographic features as compound **2**, but able to generate a mixed-valence state in the corresponding materials. And indeed, we have recently obtained an exciting (donor)$_2$(anion)$_1$ salt as shown by preliminary X-Ray data.

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